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Title/Author	**Progress in valorisation of agriculture, aquaculture and shellfish biomass into biochemicals and biomaterials towards sustainable bioeconomy / Wan Mahari, W. A., Waiho, K., Fazhan, H., Necibi, M. C., Hafsa, J., Mrid, R. ben, Fal, S., el Arroussi, H., Peng, W., Tabatabaei, M., Aghbashlo, M., Almomani, F., Lam, S. S., & Sillanpää, M.**
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Atomic Fe Dispersed on N-Doped Carbon Hollow Nanospheres for High-Efficiency Electrocatalytic Oxygen Reduction

Yifan Chen, Zhijuan Li, Yanbo Zhu, Dongmei Sun, Xien Liu, Lin Xu, and Yawen Tang**

Exploration of high-efficiency, economical, and ultrastable electrocatalysts for the oxygen reduction reaction (ORR) to substitute precious Pt is of great significance in electrochemical energy conversion devices. Single-atom catalysts (SACs) have sparked tremendous interest for their maximum atom-utilization efficiency and fascinating properties. Therefore, the development of effective synthetic methodology toward SACs becomes highly imperative yet still remains greatly challenging. Herein, a reliable SiO_2-templated strategy is elaborately designed to synthesize atomically dispersed Fe atoms anchored on N-doped carbon nanospheres (denoted as Fe–N–C HNSs) using the cheap and sustainable biomaterial of histidine (His) as the N and C precursor. By virtue of the numerous atomically dispersed $Fe–N_4$ moieties and unique spherical hollow architecture, the as-fabricated Fe–N–C HNSs exhibit excellent ORR performance in alkaline medium with outstanding activity, high long-term stability, and superior tolerance to methanol crossover, exceeding the commercial Pt/C catalyst and most previously reported non-precious-metal catalysts. This present synthetic strategy will provide new inspiration to the fabrication of various high-efficiency single-atom catalysts for diverse applications.

The ever-increasing energy issues and environmental deterioration have triggered enormous research interests to develop renewable next-generation energy conversion and storage devices, such as fuel cells and metal–air batteries.[1] One of the key factors determining the overall energy-conversion efficiency of these devices greatly lies on the sluggish kinetics of the cathodic oxygen reduction reaction (ORR). Currently, although Pt-based metals have demonstrated prominent electrocatalytic activity toward the ORR, the scarce abundance, prohibitive cost, poor stability, and vulnerability to methanol crossover of Pt severely hamper the large-scale commercialization of these sustainable energy devices.[2] In this regard, it is extremely imperative to explore cost-effective ORR electrocatalysts with competitive or even superior performance to substitute precious Pt.

During the past several years, considerable efforts have been continuously devoted to exploring non-precious-metal-based ORR electrocatalysts, such as perovskites,[3] transition metal (TM)-based oxides,[4] chalcogenides,[5] carbides,[6] nitrides,[7] and heteroatom-doped carbon materials.[8] Among them, nitrogen-coordinated TMs anchored on carbon (TM–N–C) nanomaterials, especially Fe–N–C, have been emerging as a class of appealing alternatives due to their earth abundance, tunable surface chemistry, modified electronic structure, and optimal O_2 adsorption.[9] Generally, to achieve an enhanced ORR performance of Fe–N–C electrocatalysts, at least two crucial aspects should be taken into consideration. One powerful knob is downsizing the metal particles to substantially increase the number of accessible active sites. Due to the maximum atom unitization efficiency, homogeneity of the catalytically active sites, and unsaturated metal coordination, single-atom catalysts provide an ideal platform to afford an outstanding catalytic activity and thus represent a rapidly developing research frontier.[10] On the other hand, nanostructure engineering of the carbon support with optimized geometric features could not only firmly stabilize the highly energetic single atoms through a metal-support interaction to mitigate aggregation, but also effectively facilitate the transport of ORR-relevant species during the electrocatalytic process. Among a variety of carbon nanostructures, hollow carbon nanospheres with thin wall generally possess rigid framework and high surface-to-volume ratios, thus offering shortened pathway for mass diffusion and more exposure of the active sites. Furthermore, the 3D spherical structure could significantly prevent aggregation of active sites, exhibiting sufficient electrochemical stability.[11] Taken together, it is reasonable to postulate that atomically dispersed Fe single atoms anchored on N-doped C hollow nanospheres could be a promising candidate as a robust ORR catalyst. However, fabrication of such architecture through a feasible approach still remains a grand challenge.

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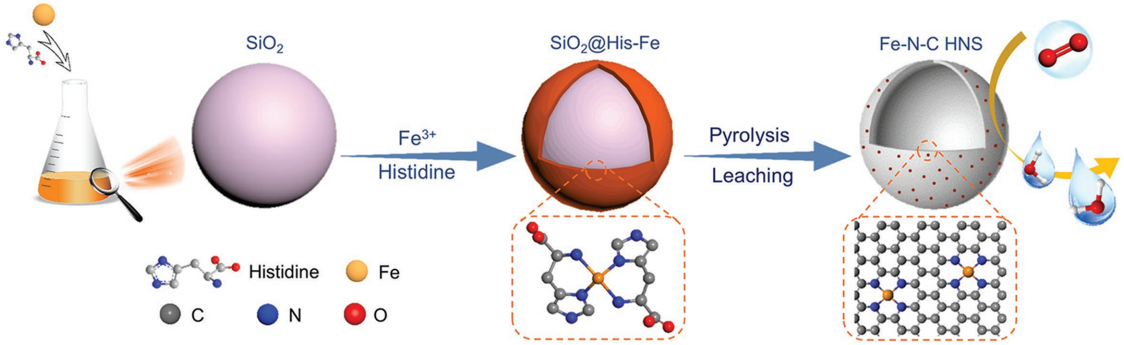

Figure 1. Schematic illustration of the synthetic process of Fe–N–C HNS.

Herein, we elaborately designed an efficient SiO_2-templated strategy to fabricate atomically dispersed Fe atoms anchored on N-doped carbon nanospheres (denoted as Fe–N–C HNSs hereafter) using a biomaterial of histidine (His) as the N and C precursor. The judicious selection of His molecules was mainly on account of their natural abundance, environmental benignity and high content of heteroatoms. Profiting from the numerous atomically dispersed Fe–N_4 moieties and unique spherical hollow architecture with high conductivity and large surface area, the as-fabricated Fe–N–C HNSs exhibited excellent ORR performance in alkaline medium with outstanding activity, high long-term stability, and superior tolerance to methanol crossover, surpassing commercial Pt/C catalyst and most of reported non-precious-metal catalysts. This present synthetic strategy could inspire the future design of high-efficiency single-atom catalysts in terms of feasibility and versatility.

As schematically illustrated in **Figure 1**, the overall synthesis of Fe–N–C HNSs essentially involves the following steps: (1) uniform coating SiO_2 template with Fe^{3+} and His, (2) pyrolysis of the resultant Fe^{3+}-His coated SiO_2 (SiO_2@Fe-His) nanospheres at high temperature, (3) chemical etching inactive and unstable species by hydrofluoric acid (HF). Specifically, uniform SiO_2 nanospheres with an average diameter of 150 nm (Figure S1, Supporting Information) were presynthesized to serve as the hard template. After surface modification with negative charges, Fe^{3+} ions could be readily adsorbed on the surface of the modified SiO_2 nanospheres through electrostatic attractions. Subsequently, the His molecules, which contain an amine functional group, a carboxylic acid group and an imidazole group, could strongly bind with the Fe^{3+} ions via coordination interactions, forming SiO_2@Fe-His nanospheres (Figure S2, Supporting Information). After pyrolysis at 800 °C under an inert atmosphere, the coated Fe^{3+}-His layers on the resultant SiO_2@Fe-His nanospheres carbonized into N-doped carbon and the coordinated Fe^{3+} ions were transformed into metallic, carbide, or oxide species simultaneously. Eventually, the annealed product was leached in HF solution to remove the SiO_2 template and undesirable and electrochemically inactive species, resulting in the formation of isolated single Fe atoms immobilized on N-doped carbon hollow nanospheres.

Scanning electron microscopy (SEM) images (**Figure 2**a,b) demonstrate that the formed Fe–N–C HNSs exhibit the spherical structure, which perfectly retains the original morphology and size of the SiO_2 templates. Moreover, these hollow nanospheres are highly interconnected, forming rich cavities and robust 3D framework structures. Such unique 3D hollow innerconnected archetecture is believed to facilitate the effective mass diffusion during the electrocatalytic process.[11d,12] Notably, the spherical structure of Fe–N–C HNSs can be well preserved after the etching of the SiO_2 template, manifesting their excellent structural robustness. Typical transmission electron microscopy (TEM) images (Figure 2c,d) reveal the wall thickness of the hollow nanospheres as thin as around 2.6 nm. Note that no visible nanoparticles or clusters can be observed from the TEM images, implying that Fe atoms might exist in an atomically dispersed form. The ring-like selected area electron diffraction (SAED, Figure S3, Supporting Information) pattern discloses the poor crystallinity of the fabricated Fe–N–C HNSs. To corroborate the formation of Fe single atoms, aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) with subangstrom resolution measurements (Figure 2e) were performed. A number of well-dispersed bright dots marked with red cycles are corresponding to heavier Fe atoms. The small size (≈0.2 nm) of these bright dots further verifies the presence of isolated Fe atoms, instead of Fe clusters or other nanoparticles (Figure S4, Supporting Information). Moreover, the element mapping images (Figure 2f) reveal the uniform distribution of Fe and N over the entire carbon architecture. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis indicates that the weight fraction of Fe in the formed Fe–N–C HNSs is 1.4 wt%.

In order to decipher the local and electronic structure of Fe–N–C HNSs, extended X-ray absorption fine structure (EXAFS) investigations were conducted. Bulk Fe foil and Fe_2O_3 sample were also measured as reference samples. As shown in **Figure 3**a, the absorption edge of the Fe–N–C HNSs in the X-ray absorption near-edge structure (XANES) spectra shifts to the higher energy region in comparison with the reference Fe foil but lower energy region in comparison with the reference Fe_2O_3, manifesting that the valence state of Fe atom in the Fe–N–C HNS sample is situated between metallic Fe(0) and Fe^{3+}. Notably, an inconspicuous pre-edge peak around 7115 eV in the Fe–N–C HNSs sample (marked by an asterisk), which originates from the 1s → $4p_z$ transition along with simultaneous charge transfer of ligand-to-metal, suggesting that Fe single atoms are confined in square-planar Fe–N_4 moieties with a porphyrin-like structure.[13] More quantitative structural information of Fe has been documented by Fourier-transformed

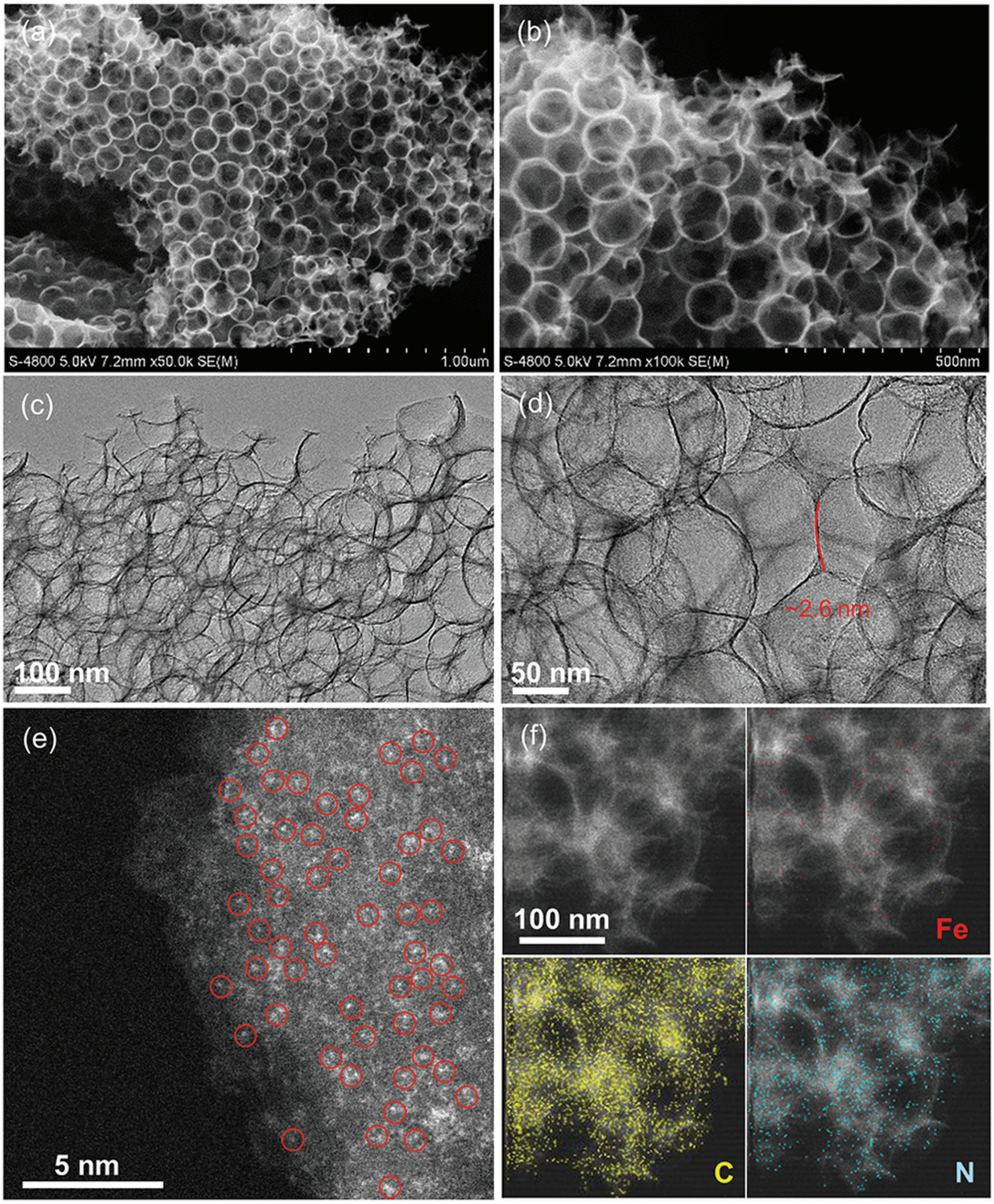

Figure 2. Morphological characterization of the synthesized Fe–N–C HNSs: a,b) SEM images, c,d) TEM images, e) aberration-corrected HAADF-STEM image, and f) corresponding element mappings.

EXAFS. As presented in Figure 3b, the predominant peak located at 1.59 Å is assigned to the backscattering of Fe–N coordination in the first shell, which ascertains the presence of Fe–N_x coordination in the Fe–N–C HNSs.[14] Additionally, no appreciable Fe–Fe coordination peak (around at 2.2 Å) can be detected, further indicating that no Fe–Fe bond is formed and the Fe sites exist as an atomically dispersed form.[10b] This observation is in good accordance with the aforementioned HAADF-STEM result. The EXAFS results are further fitted to explore the coordination configuration around the Fe center. The fitted curve (Figure S5, Supporting Information) keeps almost identical with the experimental data. According to the fitting parameters (Table S1, Supporting Information), the isolated Fe atom is coordinated by four N atoms with an average bond length of 2.09 Å. The proposed model of the Fe–N_4 planar architecture is schematically shown in the inset of Figure 3b.

To investigate the surface composition and electronic structure of the Fe–N–C HNSs, X-ray photoelectron spectroscopic

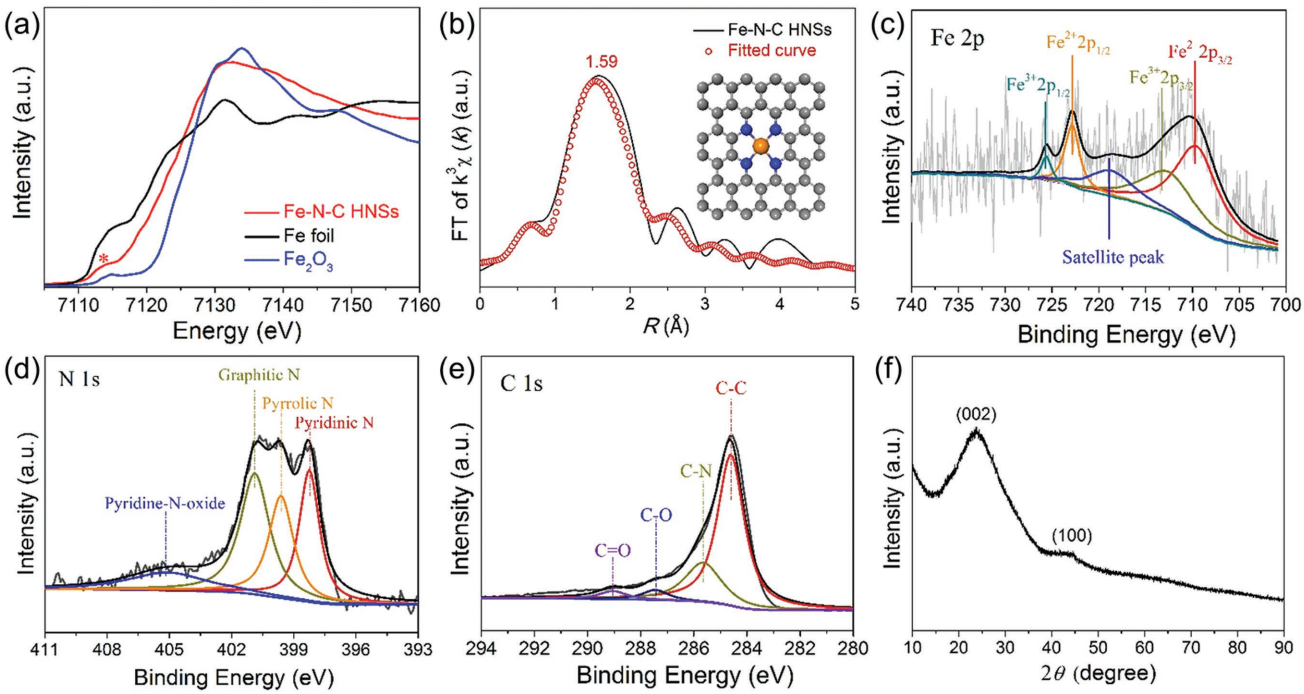

Figure 3. Compositional analyses of the prepared Fe–N–C HNSs. a) Normalized XANES spectra at Fe K-edge, b) Fourier-transformed EXAFS spectra, c–e) high-resolution Fe 2p, N 1s, and C 1s XPS spectra, respectively, and f) XRD pattern.

(XPS) measurements were performed. The typical XPS survey spectrum (Figure S6, Supporting Information) indicates the coexistence of Fe (0.5 at%), N (8 at%), and C (91.5 at%) in the Fe–N–C HNSs. The high-resolution Fe 2p spectrum (Figure 3c) shows two pairs of peaks for Fe^{2+} (709.8 and 722.8 eV) and Fe^{3+} (713.3 and 725.6 eV). Additionally, the peak around 710.3 eV can be assigned to Fe–N_x species, again proving the formation of Fe–N_4 configuration.[11a,15] The high-resolution N 1s spectrum (Figure 3d) could be well deconvoluted into four peaks located at 405.2, 400.9, 399.6, and 398.2 eV, which are assigned to oxidized N, graphitic N, pyrrolic N, and pyridinic N (or Fe–N), respectively. It has been well-established that the pyridinic N plays a vital role in the formation of Fe–N–C active sites with modified local electronic structure and the graphitic-N species facilitate the occurrence of 4-electron transfer pathway during the ORR.[16] Therefore, the high content of both pyridinic N and graphitic N in the Fe–N–C HNSs not only provides plentiful sites to anchor single Fe atoms, but also conduces to boost the ORR activity. The high-resolution C 1s spectrum (Figure 3e) exhibits four peaks at 289.1, 287.4, 285.7, and 284.6 eV, which can be assigned to C=O, C—O, C—N, and C—C group, respectively. Carbon-oxygen species are regarded as defects which facilitate ORR in alkaline media.[17] Profiting from the high electrical conductivity, the sp^2 C is also believed to be favorable for ORR.[11e]

The X-ray diffraction (XRD) pattern (Figure 3f) of the Fe–N–C HNSs exhibits two broad peaks at 25.7° and 44°, which may be assigned to the (002) and (100) planes of graphitic carbon respectively. Notably, no diffraction peak ascribed to metallic Fe or other Fe-based species can be detected, being indicative of the atomically dispersed Fe single atoms in the Fe–N–C HNSs. The N_2 adsorption–desorption isotherms (Figure S7a, Supporting Information) of the Fe–N–C HNSs exhibit a type-IV curve with a distinct hysteretic loop, indicating the existence of mesopores. The pore size distribution curve (Figure S7b, Supporting Information) reveals the presence of bimodal mesopores (3.7 and 44 nm) in the Fe–N–C HNSs, which greatly enlarge the electrolyte/catalyst contact area and promotes the O_2 diffusion during the ORR. The Brunauer–Emmett–Teller (BET) surface area of the Fe–N–C HNSs is measured to be 388.3 m^2 g^{-1}.

The atomically dispersed Fe sites and robust 3D hollow spherical architecture of the fabricated Fe–N–C HNSs render them promising for electrocatalytic ORR. The ORR activity of the Fe–N–C HNSs was investigated in a three-electrode system by linear sweep voltammetry (LSV) on a rotating disk electrode (RDE) in O_2-saturated 0.1 M KOH electrolyte. As well known, the annealing temperature exerts a sensitive influence on the ORR performance for carbon-based electrocatalysts, and the ORR activities of the Fe–N–C HNSs samples synthesized under different temperatures (700, 800, 900, and 1000 °C) were investigated. As shown in Figure S8 (Supporting Information), the Fe–N–C HNSs prepared at 800 °C possess the highest ORR activity with the most positive onset potential (E_{onset}) and half-wave potential ($E_{1/2}$) among all catalysts. This phenomenon maybe caused by the fact that lower annealing temperature (700 °C) is not sufficient to produce highly graphitic carbons, while higher pyrolysis temperature (900 and 1000 °C) may induce the destruction of the graphic structure, as revealed by the Raman spectra in Figure S9 in the Supporting Information.[18] Accordingly, 800 °C is considered as an optimal pyrolysis temperature to achieve the highest ORR activity and the Fe–N–C HNSs discussed below are synthesized at 800 °C. Aside from commercial Pt/C catalyst,

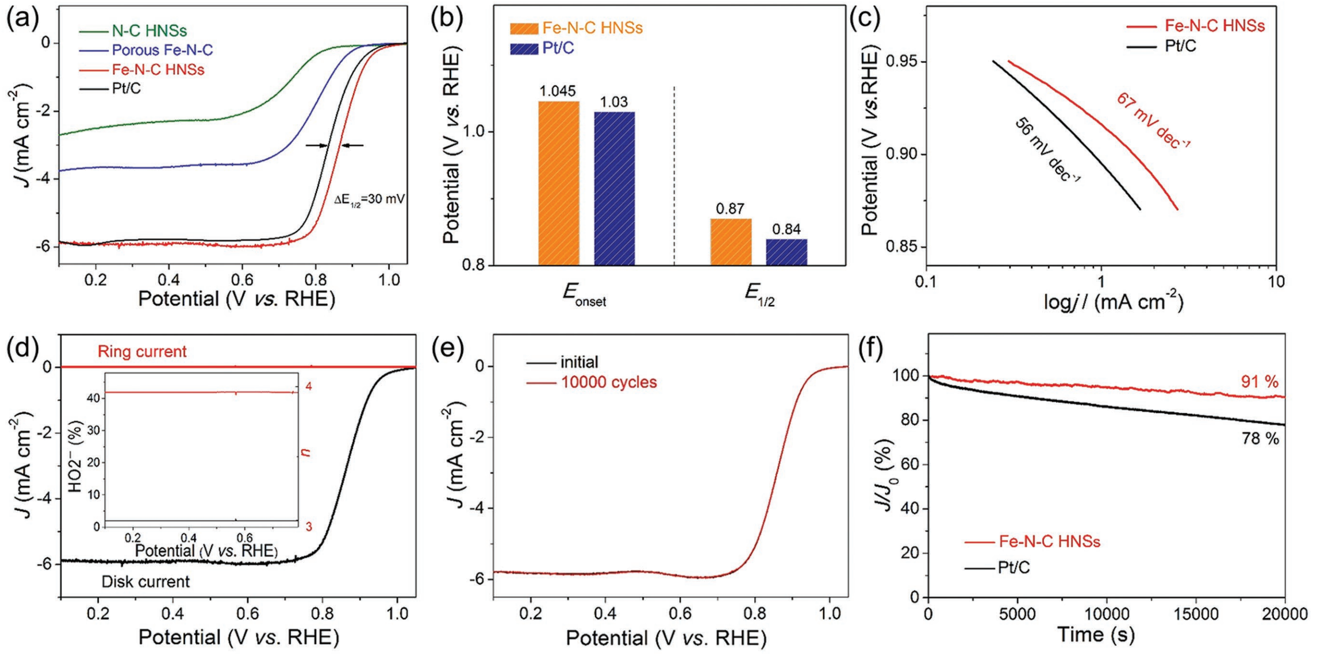

Figure 4. Evaluation of ORR performance of different catalysts. a) LSV curves of Fe–N–C HNSs, N–C HNSs, porous Fe–N–C, and Pt/C recorded in O_2-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm, b) E_{onset} and $E_{1/2}$ of Fe–N–C HNSs and Pt/C, c) Tafel plots of Fe–N–C HNSs and Pt/C, d) RRDE test of the Fe–N–C HNSs; the inset shows the HO_2^- yield and n, e) ORR polarization curves of the Fe–N–C HNSs before and after 10 000 cycles, f) relative current-density–time curves of Fe–N–C HNSs and Pt/C at 0.7 V.

N-doped carbon hollow nanospheres without Fe (N–C HNSs, Figure S10, Supporting Information) and Fe–N–C sample synthesized without the involvement of SiO_2 template (porous Fe–N–C, Figure S11, Supporting Information) were also prepared as reference samples in order to demonstrate the importance of metal center and the structural advantage of hollow spherical structure.

Figure 4a displays the typical LSV curves of the four catalysts recorded in O_2-saturated 0.1 M KOH solution with a scan rate of 5 mV s^{-1} and a rotating rate of 1600 rpm. Impressively, the Fe–N–C HNSs sample affords the highest activity with the most positive E_{onset} and $E_{1/2}$ among all catalysts. In contrast, as evidenced by the more negative LSV curves and greatly reduced diffusion-limited current densities, the N-C HNSs and porous Fe–N–C exhibit rather inferior ORR activities, signifying that metal centers and hollow spherical structure make decisive contributions to the boosted ORR activity. As illustrated in Figure 4b, the E_{onset} and $E_{1/2}$ of Fe–N–C HNSs are measured to be 1.046 and 0.87 V, respectively, which surpass the values of Pt/C ($E_{onset} = 1.03$ V and $E_{1/2} = 0.84$ V). To the best of our knowledge, the ORR performance of the obtained Fe–N–C HNSs in alkaline electrolyte exceeds most of the previously reported Fe-based ORR electrocatalysts (Table S2 Supporting Information). The exceptional ORR activity of the Fe–N–C HNSs can be further verified by the similar Tafel slope (Figure 4c) of 67 mV dec^{-1} compared with that of Pt/C (56 mV dec^{-1}). Rotating ring-disk electrode (RRDE) measurement was performed to identify the ORR pathway of the Fe–N–C HNSs. As illustrated in Figure 4d, the ring current ascribed to the H_2O_2 oxidation is significatly lower than the disk current assigned to oxygen reduction, manifesting the predominant product of OH^-. The H_2O_2 yield detected on Fe–N–C HNSs is quite low (<2%) and the electron transfer number (n) is calculated to be around 4 (inset in Figure 4d), suggesting an efficient four-electron transfer process. In addition, the fabricated Fe–N–C HNSs also exhibit outstanding long-term durability after the accelerated durability test (ADT). As displayed in Figure 4e, a negligible decay in $E_{1/2}$ of Fe–N–C HNSs is observed even after 10 000 continuous cycles. Besides, TEM image (Figure S12, Supporting Information) reveals that the hollow spherical structure of the Fe–N–C HNSs can be well preserved after the ADT test, underlining the superior structural robustness. Whereas, the $E_{1/2}$ of commercial Pt/C displays an obviously negative shift of ≈11 mV under the same condition (Figure S13, Supporting Information). Chronoamperometric (CA) tests performed in O_2-saturated 0.1 M KOH solution at 0.7 V further verify the excellent stability of the Fe–N–C HNSs (Figure 4f). After running for 20 000 s, the Fe–N–C HNSs exhibit a 91% retention of the initial current density, while only 78% retention can be found on the commercial Pt/C.

To further testify the role of Fe active sites in the ORR, thiocyanide (SCN^-) ions are employed to poison the Fe–N–C HNSs since SCN^- ion has a strong affinity to Fe and thus severely poison $Fe–N_4$ active sites.[10b,19] As shown in **Figure 5**a, the ORR activity of Fe–N–C HNSs is significantly deteriorated in the presence of potassium thiocyanate (KSCN), as documented by the much more negative $E_{1/2}$ and largely decreased diffusion-limiting current density. Notably, after being rinsed several times with water to get rid of SCN^- ions and remeasured in fresh O_2-saturated 0.1 M KOH electrolyte, the ORR activity of the Fe–N–C HNSs could recover well and almost reach to the original activity. These observations strongly elucidate

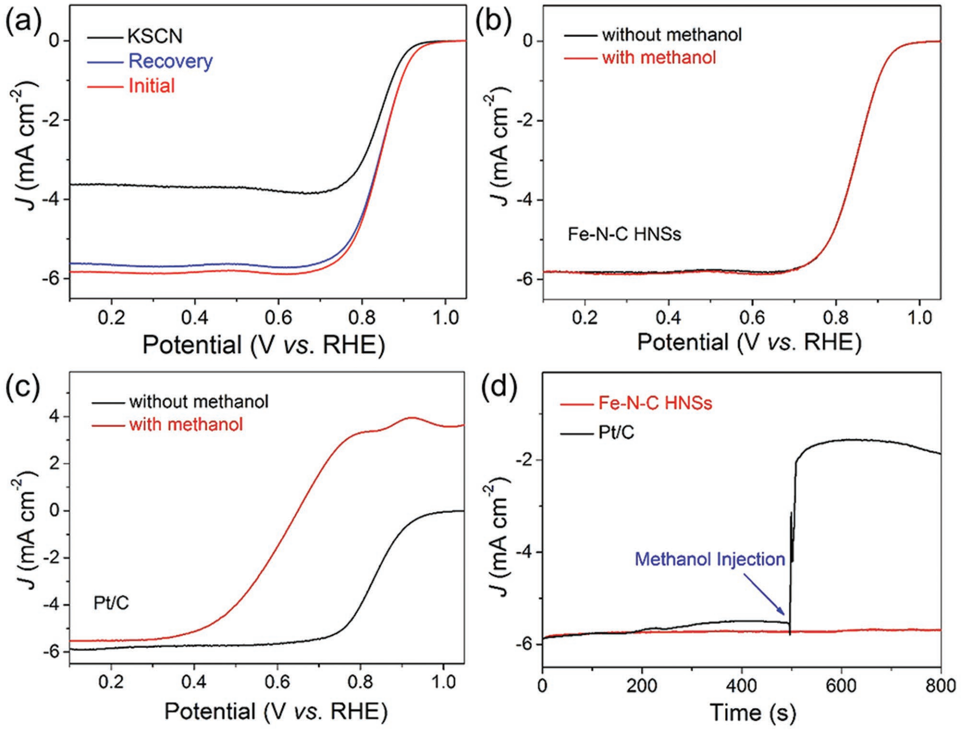

Figure 5. a) LSV curves of Fe–N–C HNSs in O_2-saturated 0.1 M KOH with and without KSCN, respectively. b,c) LSV curves of Fe–N–C HNSs and Pt/C in O_2-saturated 0.1 M KOH with and without methanol, respectively. d) current-density–time curves of Fe–N–C HNSs and Pt/C at 0.7 V in 0.1 M KOH with an addition of methanol.

that the atomically dispersed Fe sites represent the origin of the excellent ORR activity of Fe–N–C HNSs. The resistance to methanol crossover of a catalyst is also essential for practical applications. From Figure S14a (Supporting Information) and Figure 5b, one can clearly see that there is no appreciable variation in both CV and LSV curve of the Fe–N–C HNSs after the addition of methanol into the electrolyte. Whereas, for the Pt/C, upon the introduction of methanol, the typical inverse peak ascribed to methanol oxidation appears in CV (Figure S14b, Supporting Information) and the LSV plot negatively shifts dramatically (Figure 5c). CA measurements further confirm the above results. As shown in Figure 5d, the Fe–N–C HNSs could maintain a quite stable current density after the methanol injection, while a sharp jump of current density caused by the methanol oxidation occurs on the commercial Pt/C catalyst. All these results firmly indicate that the prpared Fe–N–C HNSs exhibit outstanding tolerance to methanol and high selectivty toward the ORR.

The superb ORR performance of the fabricated Fe–N–C HNSs could be rationally ascribed to the unique architectural and favorable compositional advantages. Specifically: (1) the hollow carbon nanospheres with thin wall and open framework could effectively expose the active sites and thus fully utilize the active components. Furthermore, the interconnected spherical architecture could also afford a facilitated pathway for mass transportation during the ORR process.[11a,e] In addition, the bimodal mesopores within the carbon nanospheres could remarkably enlarge the electrolyte/catalyst contact area and promote the O_2 diffusion. (2) The high degree of graphitization of the Fe–N–C HNSs can be expected to enhance the electrical conductivity, and then facilitate electron transfer.[20] (3) The strong affinity between atomic Fe sites and carbon support induced by the high-temperature pyrolysis not only guarantees the homogeneous distribution of active sites, but also contributes to the excellent stability. (4) The high fraction of pyridinic-N and graphitic-N in carbon matrix not only facilitates the adsorption of O_2 due to the N doping-induced alternation of C electronic structure, but also promotes the electrical conductivity and hydrophilicity.[15a,21] All above profitable features render the Fe–N–C HNSs a promising ORR electrocatalyst with reinforced activity and durability.

In conclusion, we have demonstrated a feasible SiO_2-templated approach to prepare Fe single atoms dispersed on N-doped carbon hollow nanospheres for high-efficiency ORR in alkaline medium. Aberration-corrected TEM and EXAFS measurements strongly manifest the existence of Fe single atoms with Fe–N_4 configuration. Benefiting from the architectural merits and homogeneity of atomic active sites, the resultant Fe–N–C HNSs catalyst exhibits excellent ORR performance with impressive E_{onset} and $E_{1/2}$, high long-term stability, and superior tolerance to methanol crossover, outperforming commercial Pt/C catalyst, and most of state-of-the-art non-precious-metal catalysts. The present study not only develops a cost-effective and high-performance ORR electrocatalyst to substitute Pt, but also offers a reliable and versatile strategy to fabricate other single-atom catalysts for diverse applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Fe–N–C, hollow carbon nanospheres, non-precious metals, oxygen reduction reaction, single-atom catalysts

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A sustainable route from biomass cotton to construct lightweight and high-performance microwave absorber

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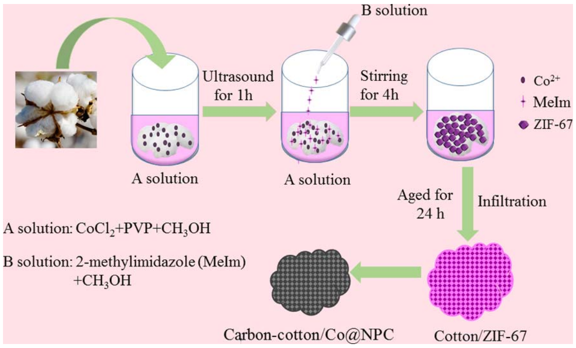
HIGHLIGHTS

- Using cotton as precursor to make sustainable lightweight microwave absorber.
- Carbon-cotton was decorated by a flexible impregnation and annealing method.
- Investigated the effect of temperature on the EMA properties of the media.
- The RL value can reach −51.2 dB with bandwidth of 4.4 GHz at only 1.65 mm.

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, carbon materials derived from natural biomaterials have been drawn considerable attention because the biomaterials are vastly available, accessible and renewable. Hereinto, it is fascinating that employing cotton as carbonaceous precursors to fabricate novel sustainable lightweight microwave absorber due to its unique hierarchical macro-/microporous architecture. In current study, we adopt a sustainable route from biomass cotton to construct cotton/zeolitic imidazolate framework (ZIF-67) and subsequent sintering to fabricate carbon-cotton/Co@nanoporous carbon (NPC) products. The as-prepared composites showed definitely superior microwave absorption performance than the pristine carbon-cotton and Co@NPC. It is confirmed that a better impedance matching is the key factor to realize excellent absorption. When the sample filling ratio is as low as 25 wt% in paraffin matrix, the maximum reflection loss can achieve −60.0 dB at 8.48 GHz. Furthermore, via adjusting the thickness to only 1.65 mm, the optimal reflection loss can obtain −51.2 dB at 13.92 GHz with a broad bandwidth of 4.4 GHz. In addition, the annealing temperature for the composites was also investigated, which had significant influence on tuning absorption properties. Prospectively, our present work may provide a new guideline to design carbon composites from earth-abundant recyclable biomass materials as sustainable, lightweight and high-performance absorber.

1. Introduction

In order to solve the increasingly severe electromagnetic (EM) wave pollutions resulted from the extensive usage of electronic equipment and wireless communications, a great deal of researches have been dedicated to the high-performance EM wave absorber [1–3]. As

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exploration in the past decades, carbon-based materials acted as a sort of compelling absorbing material have drawn representative attention due to their lower density and great electrical conductivity. For example, Wang et al. synthesized Fe_3O_4/graphene and Ni/graphene composites by atomic layer deposition method, and showed enhanced microwave absorbing properties because of remarkable conduction loss from graphene [4]. Also, Wang's group illustrated that the composites of Fe_3O_4 nanocrystals with multiwall carbon nanotube are availably forming conductive network and promoting dielectric loss ability [5]. Furthermore, Shen and his coworkers plated metal Co into nitrogen-doped ordered mesoporous carbon to achieve favorable impedance matching in Ku-band [6]. Additionally, our group has already done some related works about carbonaceous composites [7–9]. From these researches, we can conclude that carbon composition played a vital role in these composites, unfortunately, the carbon resources are too expensive for us to realize industrialization. Delightedly, in virtue of the renewable and ubiquitous biomass materials to construct carbon-based composites is an attractive strategy to make up the issue.

Recently, various of natural biomaterials such as bagasse [10], wood [11], cotton [12,13], egg [14], walnut shells [15], seaweed [16], broad beans shells [17] and okara [18] have been served as templates or carbon precursors to prepare advanced biomorphic functional materials for different fields [13,19]. Typically, using cotton as template or carbon source can not only inherit hierarchical porous structure of raw materials, but also hold the unique fiber-shape. For instance, Yan's group designed mesoporous and tubular Co_3O_4 with high specific surface area employing cotton as sacrificial template [20]. Chung et al. managed to fabricate the flexible carbon-cotton cathode to improve the dynamic and static stabilities of lithium-sulfur batteries by using the natural hierarchical macro-/microporous architecture of cotton [12]. For microwave absorption, SiC microtubules prepared by the cotton as carbon source and template gained a reflection loss below −10 dB (90% absorption) at different frequencies [21]. Those reports give us much inspiration that selecting cotton acted as precursor to obtain sustainable and lightweight carbon-based composites. On one hand, it is environmentally friendly, renewable, affordable and mass-produced. On the other hand, the carbon-cotton possesses loose and porous structure as well as fiber-shape, which would be beneficial for the scattering intensity of EM wave. However, according to impedance matching theory, the impedance matching value (Z) should be as possible as close to 1, that is, the complex permittivity (ε_r) needs to approach complex permeability (μ_r). Thus, single carbon materials usually cannot meet the demand of broad bandwidth. Generally, directly compounding traditional magnetic metal or alloys, or ferrites with carbon materials would be detrimental to its intrinsic lightweight advantage. Therefore, it is imperative to seek a way to resolve the contradiction [22–24].

More recently, the absorber derived from the directly thermal pyrolysis of metal organic frameworks (MOFs) has been considered as a potential candidate for high-performance EM wave absorption, because these materials possess inherent complementary dielectric and magnetic loss abilities. For example, Qiang et al. prepared Fe/C nanocubes by situ pyrolysis of prussian blue, and achieved the maximum absorption peak value of -20.3 dB at thickness of 2 mm under the filler content of 40 wt% [25]. Lü's group reported the synthetic of porous Co/C nanocomposites via calcining zeolitic imidazolate framework-67 (ZIF-67) and demonstrated superior EM wave absorption properties with RL of −35.3 dB at the thickness of 2 mm when the samples was dispersed in the paraffin with mass percentage of 60 wt% [26]. Although these kinds of absorber have exhibited good EM wave absorption achievement, the filler content was usually higher than 30 wt% [27]. For further improving the comprehensive properties of the absorber made from the single MOF materials, various strategies were adopted. Especially, incorporating other functional categories (such as Fe_3O_4, TiO_2, RGO, CNTs, Ferrite, CuO et al.) with MOF has been considered as an effective approach [28–33]. For example, Yin et al. employed the pretreated multiwalled carbon nanotubes (MWCNTs) as templates for growth of ZIF-67. The Co-C/MWCNTs composite, obtained by subsequent heat treatment process, showed superior EM wave absorption properties, which was attributed to the formation of conductive network [31]. Wang's group prepared ferrite/Co/porous carbon composite by the calcination of $Ba_{0.85}Sm_{0.15}Co_2Fe_{16}O_{27}$@ZIF-67 precursor. The enhanced EM wave absorption performance were achieved due to the synergistic effect of dielectric loss and magnetic loss [32]. Although a great progress has been made, these composites usually need complicated functional process and expensive ingredients, which restrain their commercial application. In addition, when we explore the ideal absorber, energy consumption, yield of sample as well as poisonous substances should be taken into consideration in the synthesis route. Based on the above analysis, we used cotton as substrate to deposit ZIF-67 particles for developing carbon-cotton/Co@NPC absorber. As we know, ZIF-67 is one of the most important members among metal organic frameworks (MOFs) with lots of merits such as large specific surface, microporous structure and distinct morphologies. The Co@NPC derived from ZIF-67 not only inherits its aformentioned advantages, but also produces magnetic metal Co. Thus, anchoring Co@NPC on carbon-cotton could maintain light feature as well as effective magnetic loss [33]. Furthermore, the prepare process is sustainable and high-produce.

In detail, we fabricated the carbon-cotton/Co@NPC composites by designing cotton/ZIF-67 precursor and subsequent calcination. The composites showed enhanced absorbing properties compared with pure carbon-cotton and Co@NPC, which could achieve the optimal value of −51.2 dB with the broad bandwidth of 4.4 GHz at thickness of only 1.65 mm. As a result, the carbon-cotton/Co@NPC composites have great potential to be ideal microwave absorber towards "broad, strong, light, thin and high-yield".

2. Experimental

2.1. Pretreatment of cottons

First, pristine cottons were activated based on the report [34]. Typically, 0.18 g of cotton fabrics were impregnated in a mixture solution (60 mL) containing H_2O_2 (2 mol/L), sodium silicate (Na_2SiO_3, 4 g/L) and sodium hydroxide (NaOH, 10 g/L). The immersion was treated at 90 °C for 1 h. Then, the activated cottons were rinsed with hot water and cold water several times to rule out possible impurities and finally dried in a vacuum at 60 °C for one night.

2.2. Preparation of ZIF-67/cotton composites

Firstly, the activated cottons were dipped in the mixture solution including cobalt chloride ($CoCl_2{\cdot}6H_2O$, 2 mmol), polyvinylpyrrolidone (PVP, 600 mg) and methanol (CH_3OH, 40 mL), and sonicated for 1 h. Then, the methanolic solution (40 mL) of 2-methylimidazole ($C_5H_8N_2$, 2.63 g) was introduced dropwise into the above solution under magnetic stirring for 4 h. Finally, the resultant solution was aged at ambient temperature for 24 h. The purplish red cottons were collected by vacuum filtration, and washed several times with ethanol, and dried under vacuum conditions at 60 °C for 12 h.

2.3. Preparation of carbon-cotton/Co@NPC composites

The as-prepared cotton/ZIF-67 composites were directly annealed in N_2 atmosphere at 600 °C, 700 °C and 800 °C for 2 h with a heating rate of 1 °C min^{-1}. The obtained products were denoted as S600, S700, and S800. For comparison, the pure carbon-cotton was prepared by calcining raw cotton at 700 °C, named as C700. And Co@NPC was also obtained by annealing ZIF-67 at 700 °C.

2.4. Characterizations

The crystal structure was measured by X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer using Cu Kα radiation (λ = 0.154718 nm with 40 kV scanning voltage, 40 mA scanning current.). The morphologies of the samples were observed by scanning electron microscope (SEM, Hitachi S4800 type). Chemical composition of samples was revealed by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 Versa Probe. The Brunauer–Emmet–Teller (BET) specific surface areas and the pore size distribution of the samples were determined by a high speed automated area and pore size analyzer (ASAP 2010). The content of Co was calculated by Thermogravimetry (TG) curve measured by an NETZSCH STA 449F3 thermal gravimetric analyzer under air from 23 to 800 °C. Magnetic properties of the composites were measured by a vibrating sample magnetometer (Lakeshore 7404) at room temperature. The electromagnetic parameters of the samples in the frequency range of 2–18 GHz were tested by Agilent PNA N5244A vector network analyzer according to the coaxial-line method. The measured samples were prepared by homogeneously mixing paraffin wax (75 wt%) with products (25 wt%) and then pressing into toroidal-shaped samples (Φ_{out}: 7.0 mm, Φ_{in}: 3.04 mm).

3. Results and discussion

Due to the strong binding ability with Co^{2+} of carboxyl groups than hydroxyl groups, the raw cotton needs to be activated by H_2O_2 solution [35]. And the formation process of carbon-cotton/Co@NPC composites is displayed in Fig. 1. First, the activated cotton was infused in a solution and sonicated for 1 h so as to the Co^{2+} could be adsorbed adequately on the surface of cotton through ion exchange and complexation. Then, B solution was slowly dropped into the above solution with magnetic stirring for 4 h. After ageing 24 h in ambient temperature, ZIF-67 would uniformly load on the surface of cotton. At the last, the cotton/ZIF-67 precursors were annealed at high temperature under N_2 atmosphere to obtain carbon-cotton/Co@NPC.

Fig. 2a shows the XRD patterns of pristine carbon-cotton, Co@NPC derived from ZIF-67 and carbon-cotton/Co@NPC composites with different annealing temperature. The C700 sample exhibits two broad diffraction peaks ((0 0 2), (1 0 0)) at 26.5° and 44°, which can be ascribed to amorphous nature of pure carbon-cotton [36]. For the Co@NPC sample, aside from the carbon peak at $2\theta = 26.5°$, other peaks corresponding to (1 1 1), (2 0 0) and (2 2 0) crystal planes could be indexed to the metal Co (JCPDS No.: 01-1259) [37]. The carbon-cotton/Co@NPC composites consisted of amorphous carbon and metal cobalt phase. In addition, it is clearly seen from the XRD patterns of composites that the increasing heat treatment temperature leads to an enhancement of graphited peaks at 26.5°. Meanwhile, the crystalline degree of Co strengthens with increasing temperature according to gradually enhanced peaks. In order to clarify the state of carbon atom, Raman spectrum was carried out. As observed in Fig. 2b, all samples display two strong peaks at 1341 cm^{-1} and 1581 cm^{-1}, attributing to the typical D- and G- band of carbon materials, respectively. It is well known that D-band means disorder or amorphous carbon and G-band represents graphitization carbon. The intensity ratio of D- and G-band (I_D/I_G) usually stands for the graphitization degree of sample. The ratio of C700, S600, S700, and S800 are 0.81, 0.79, 0.84, and 0.96, respectively. One can find that the values of carbon-cotton/Co@NPC samples obtained at different temperature rise with increasing temperature, demonstrating the removal of defects in carbon component at elevated temperature. In addition, Although the C700 and S700 samples was obtained at the same calcining temperature, the I_D/I_G ratio S700 is higher than that of C700, which are accounted for the catalysis effect of transition metal (Co). The improvement of graphitization degree facilitates the raise of complex permittivity for the composites because of better conductivity of carbon. The phenomenon is resulted of higher carbonization temperature and in agreement with XRD results. In addition, the close ratio of C700 and S700 illustrated similar graphitization degree.

The morphologies of C700 and S700 were characterized by field-emission SEM. It can be clearly seen in Fig. 3a that the pure carbon-cotton exhibits a relatively smooth surface and thick diameter with ca. 6.5 μm. When the cotton-carbon was coated by Co@NPC, there are a mass of nanoparticles arose on the cotton-carbon surface in Fig. 3b. From improved resolution of Fig. 3c, we can confirm the nanoparticles present regular dodecahedron shape inherited from ZIF-67. The elemental mapping from Fig. 3c and d demonstrates the presence of C, Co, and distribute uniformly in S700. Moreover, the EDS data of S700 in Fig. 3f further affirms the point.

The composition and element state of S700 were revealed by XPS. As shown in Fig. 4a, it is assured that C and Co are in the composites, consisting with EDS results. The appearance of O could be ascribed to the oxidation of Co on the composite surface without carbon shell protective. The concrete chemical valence about Co element was shown in the Fig. 4b. The signals located at 778.3 eV and 793.5 eV can be assigned to $2p_{3/2}$ and $2p_{1/2}$ of metal Co. [38] Whereas the peaks at 780.7 eV and 796.5 eV are corresponded to $2p_{3/2}$ and $2p_{1/2}$ of Co^{2+}. Other small peaks are satellite peaks [39].

To better quantify Co in S700, TG measurement was done under air.

Fig. 1. Schematic illustration of the synthesis process of carbon-cotton/Co@NPC composites.

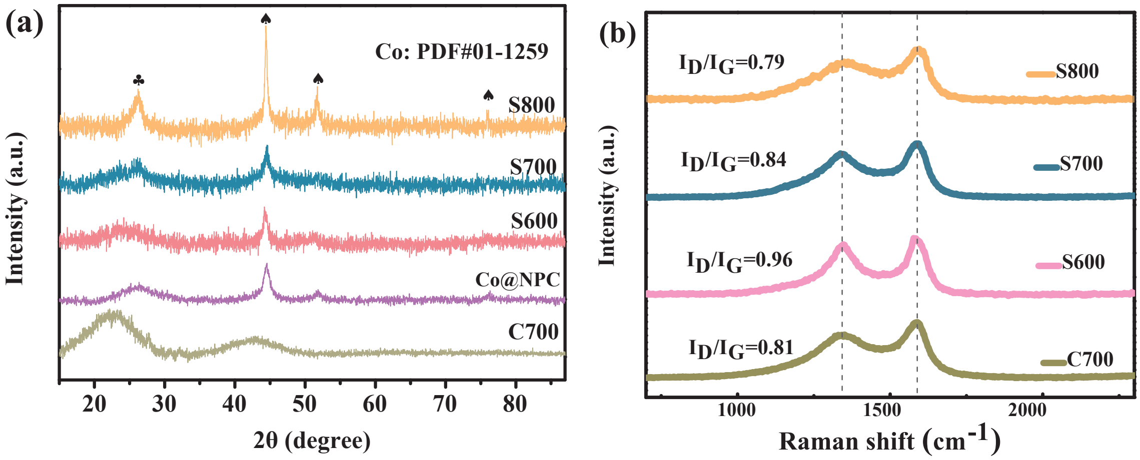

Fig. 2. The (a) XRD patterns and (b) Raman spectra of the obtained samples.

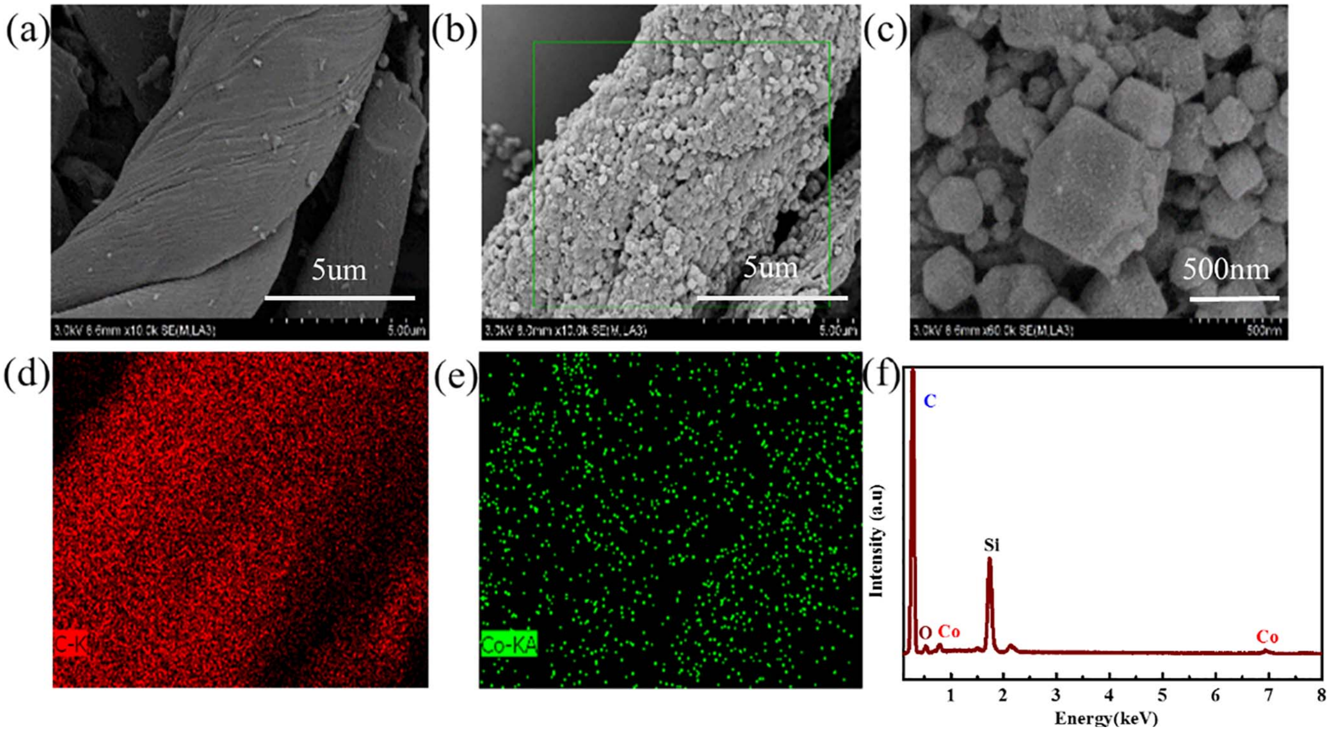

Fig. 3. SEM images of (a) C700 and (b) S700, (c) amplified image of S700, (d, e) elemental mapping of selected area in (b), (f) EDS data in selected area of (b) for S700.

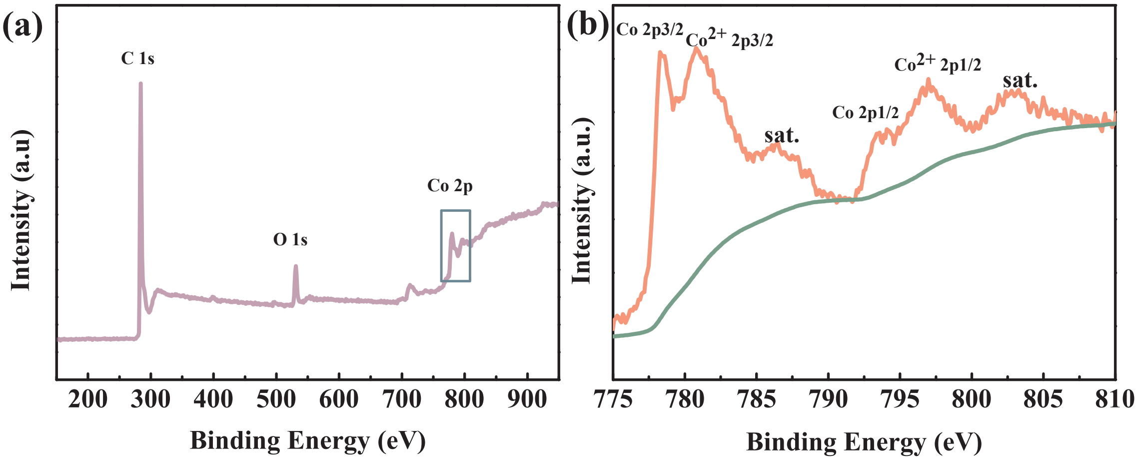

Fig. 4. (a) The XPS spectra of S700 and (b) high-resolution Co 2p spectra.

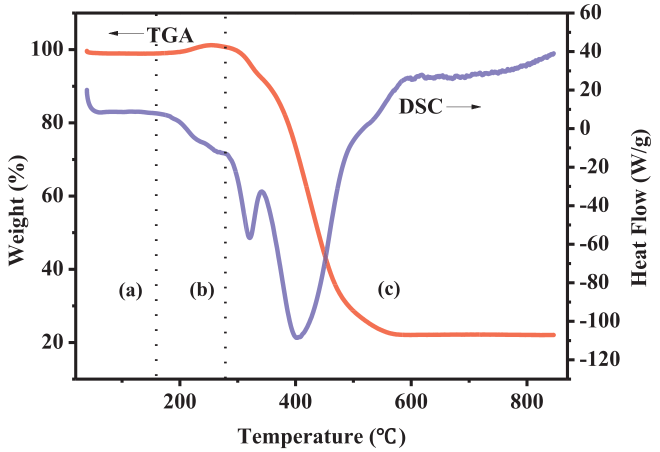

Fig. 5. TG and DSC curves of S700.

As shown in Fig. 5, the TG curve of S700 can be divided into three steps within the measured temperature. In step (1), a slight weight loss of 1.01% at 165 °C attributes to the adsorbed water evaporation. The weight increase of 2.1% from 165 to 270 °C (step (2)) can be associated with the oxidation of Co along with a small exothermic peak in the DSC curve [40]. In step (3), the TG curve shows a drastic decrease tendency until placid at 570 °C as a result of carbon-cotton burning. After that, no obvious weight loss was observed, indicating the carbon species has been completely burned out and only left Co_3O_4 residue. On the basis of following equation:

$$\text{Co (wt\%)} = \frac{\text{Residue (wt\%)}}{M_{Co_3O_4}} \times 3M_{Co}$$

The actual mass fraction of Co in S700 is ca. 15%, and the carbon content is ca. 85%.

Brunauer-Emmett-Teller (BET) test was utilized to identify the pore structure of the composites. As shown in Fig. 6a, S700 demonstrates a representative type IV isotherm with a distinct hysteresis loop at the P/P_0 range of 0.4–1.0, manifesting the presence of mesoporous [41]. Moreover, the result of Barrett-Joyner-Halenda (BJH) indicates that the average pore diameter of S-700 mainly focuses at 5 nm (Fig. 6b). The porous structure not only makes composites possess large specific surface area ($S_{BET} = 380.33\ cm^2/g$) and total pore volume ($V_{pore} = 0.34\ cm^3/g$), but also extends the transmission path of electromagnetic wave and facilitates the EM wave absorption.

The magnetic hysteresis loop of the composites with different heating temperature is displayed in Fig. 6c and d. It can be observed that the coercivity force (H_c) for S600, S700 and S800 are almost the same. While the magnetization shows a gradually increasing trend of 10.39, 14.00 and 23.5 emu/g, respectively. This can be interpreted by the strength of crystallinity and growth of grain for metal Co [29]. As a result, the metal Co with soft magnetic property could induce certain magnetic loss in gigahertz frequency region.

It is well known that EM absorption property is the most significant standard to evaluate the microwave absorber. Commonly, the excellent microwave absorption materials are required to have a RL value lower than −10 dB within a wide frequency bandwidth under low thickness. According to the transmission line theory, the RL value can be calculated through measured relative complex permittivity and permeability based on the following formulas [31]:

$$Z_{in} = Z_0\sqrt{\mu_r/\varepsilon_r}\,tanh\,[j(2\pi\pi f/c)]\sqrt{\mu_r\varepsilon_r} \quad (1)$$

$$RL(dB) = 20\log|(Z_{in}-Z_0)/(Z + in + Z_0)| \quad (2)$$

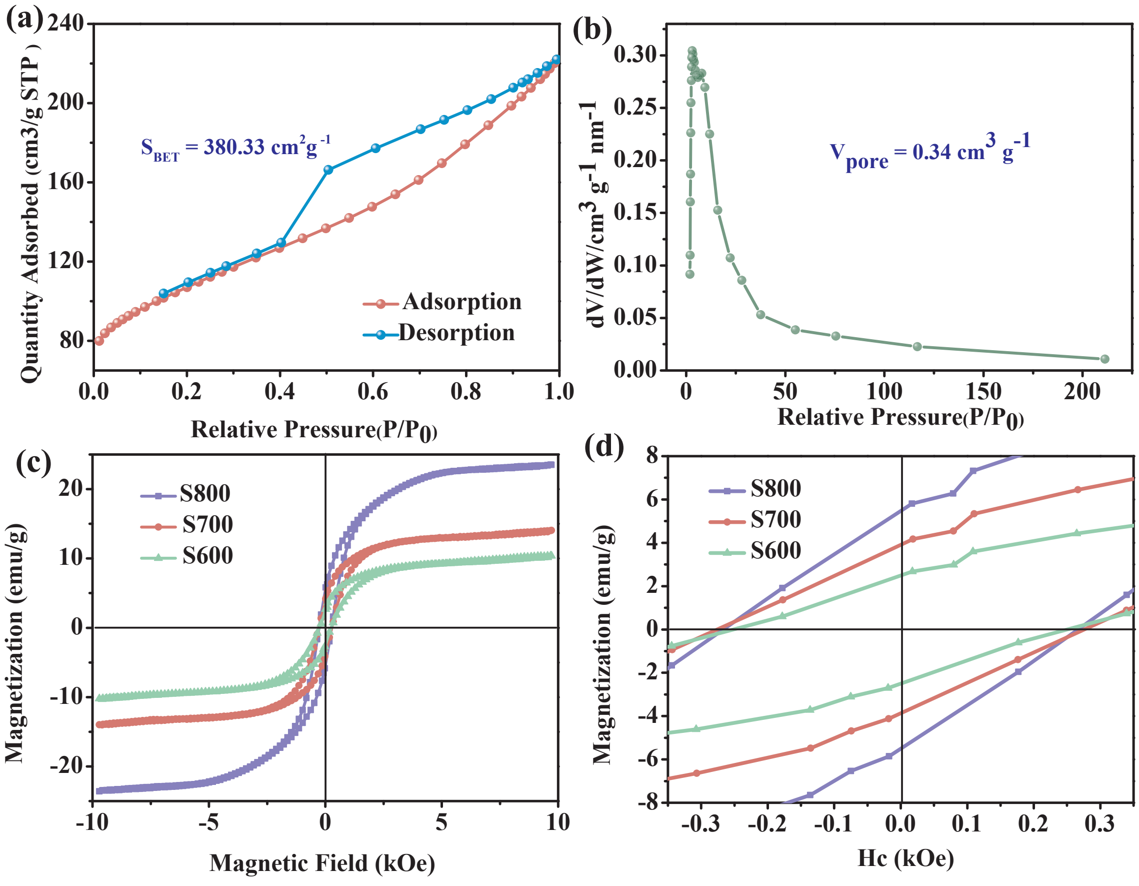

Fig. 6. (a) N_2 adsorption–desorption isotherm and (b) pore size distribution of S700, (c) and (d) Hysteresis loop of S600, S700 and S800 measured at room temperature.

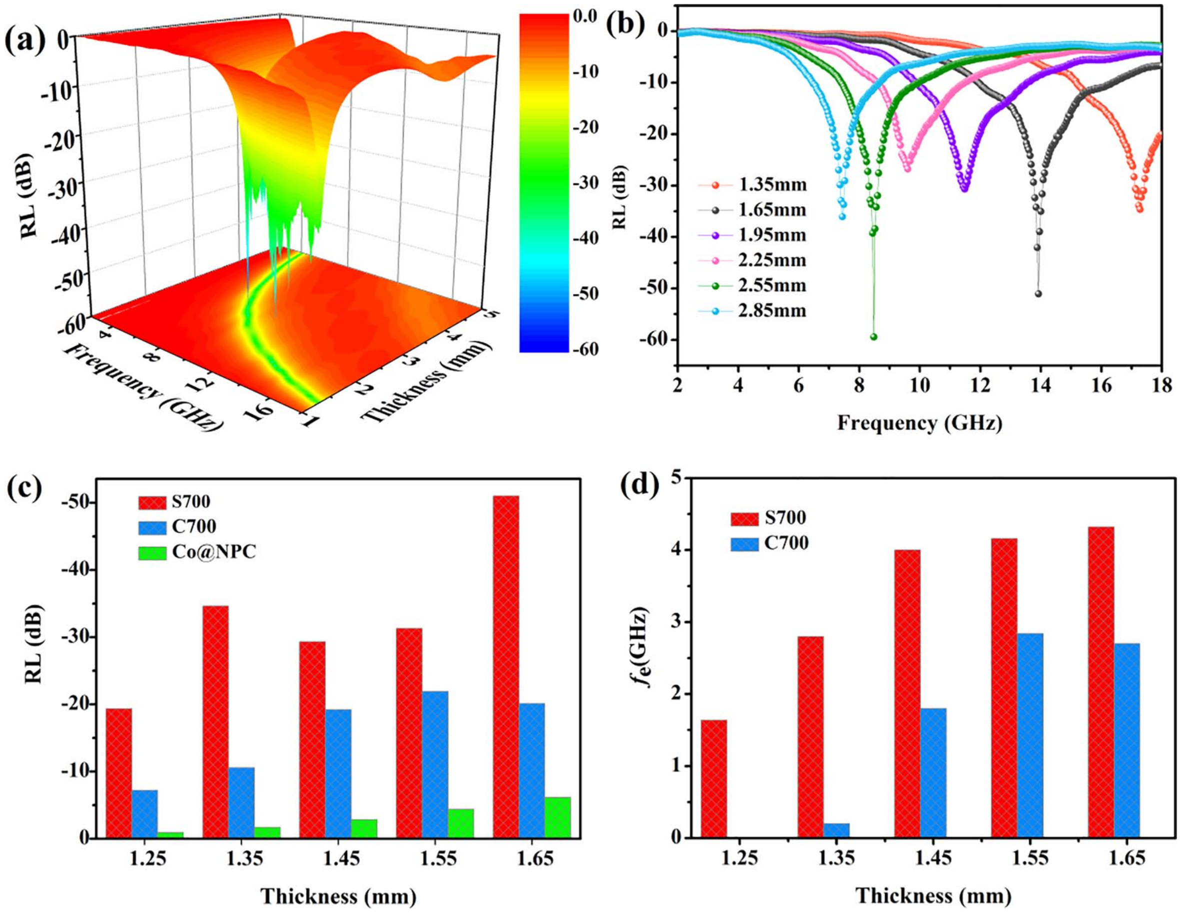

Fig. 7. Color map of the reflection loss (a) and the RL values versus different thickness (b) of S700, RL peak values of S700, C700 and Co@NPC (c), effective frequency bandwidth of S700, C700 (d).

where Z_{in} represents the input characteristic impedance, Z_0 is the impedance of air, and c means the velocity of EM wave in free space. The microwave absorption performance of S700 is shown in Fig. 7a and b. It can be observed that S700 exhibits superior absorption properties, which can achieve −51.2 dB at only thickness of 1.65 mm with a broad bandwidth of 4.4 GHz. Furthermore, when the thickness is 2.55 mm, S700 can reach as high as −60.0 dB. Strikingly, the effective frequency bandwidth exceeding −20 dB can even reach 10.5 GHz (7.5–18 GHz) by adjusting thickness of 1.0–3.0 mm. For purpose of comparison, the RL values and effective frequency bandwidths (f_e) of S700, C700 and Co@NPC with thickness less than 1.65 mm are also performed in Fig. 7c and d. Although C700 and Co@NPC present some absorption performance, those RL intensity and effective bandwidth under the same thickness are still undesirable. While compositing carbon-cotton with Co@NPC, the compounds present clearly enhanced microwave absorbing properties than singleness, so which are promising to be used as a microwave absorber. From Fig. S1a and b, it is clearly seen that the microwave absorption performance of S600 and S800 is fairly poor when compared with the S700. Consequently, the most suitable annealed temperature is 700 °C in this experiment. Meanwhile, the effect of filler content on EM wave absorption was also investigated. Figs. S2 and S3 demonstrate the EM parameters vs frequency for S700 with different mass percentage of 15 wt%, 20 wt%, 30 wt% and 35 wt%, and corresponding RL peaks, respectively. It can be observed that the maximum RL values of these S700-wax composites are both lower than −20 dB, which indicates the moderate filler content of S700 is 25 wt%. Table S1 summaries the EM wave absorption achievements of various MOF-derived materials and similar absorber. By virtue of lower filler content (25 wt%), thin thickness (1.65 mm), and strong reflection attenuation (−60.0 dB) as well as broad effective frequency bandwidth (4.4 GHz), the carbon-cotton/Co@NPC can be taken as a satisfying candidate for the fabrication of lightweight and high performance microwave absorbing media.

To understand readily the improved absorbing performance for S700, dependence of the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) on frequency were explored, which were measured from loading 25 wt% samples with paraffin matrix in the range of 2–18 GHz. In general, the values of ε' and μ' stand for the storage capability of the electric and magnetic energy, and the imaginary parts (ε'' and μ'') symbolize the loss capability of the electric and magnetic energy [42]. Fig. 8 shows dependence of complex permeability and permittivity on the frequency for all samples. As shown in Fig. 8a and b, it is found that S600 has the lowest ε' and ε'' values and there is no obvious fluctuation for the two curves, which are about 3.2 and 0.6, respectively. Such low complex permittivity indicates great wave-transparent capability but poor dissipated behavior, thus, almost no microwave can be wiped out for S600. This can be ascribed to very weak graphitization degree under calcination of 600 °C. It is considered that, at this condition, the carbon decomposed from cotton cannot form valid graphitization and the most are amorphous carbon. Also, the Co@NPC presents poor electric storage capacity and dissipated ability in terms of the low ε' and ε'' values, this cannot still attenuate microwave efficiently. Interestingly, the ε' and ε'' values of S800 are the highest and in the range of 27.6–17.4 and 13.6–6.5, respectively. Although it has the strongest dielectric loss property according to high ε'' values, the excessive attenuated ability would lead to a mass of microwave reflected from the absorber surface due to impedance mismatching. There are less microwave entering into material also gives rise to inferior microwave absorbing properties. It can be presumed that, under annealing at high temperature of 800 °C, the carbon constituent from

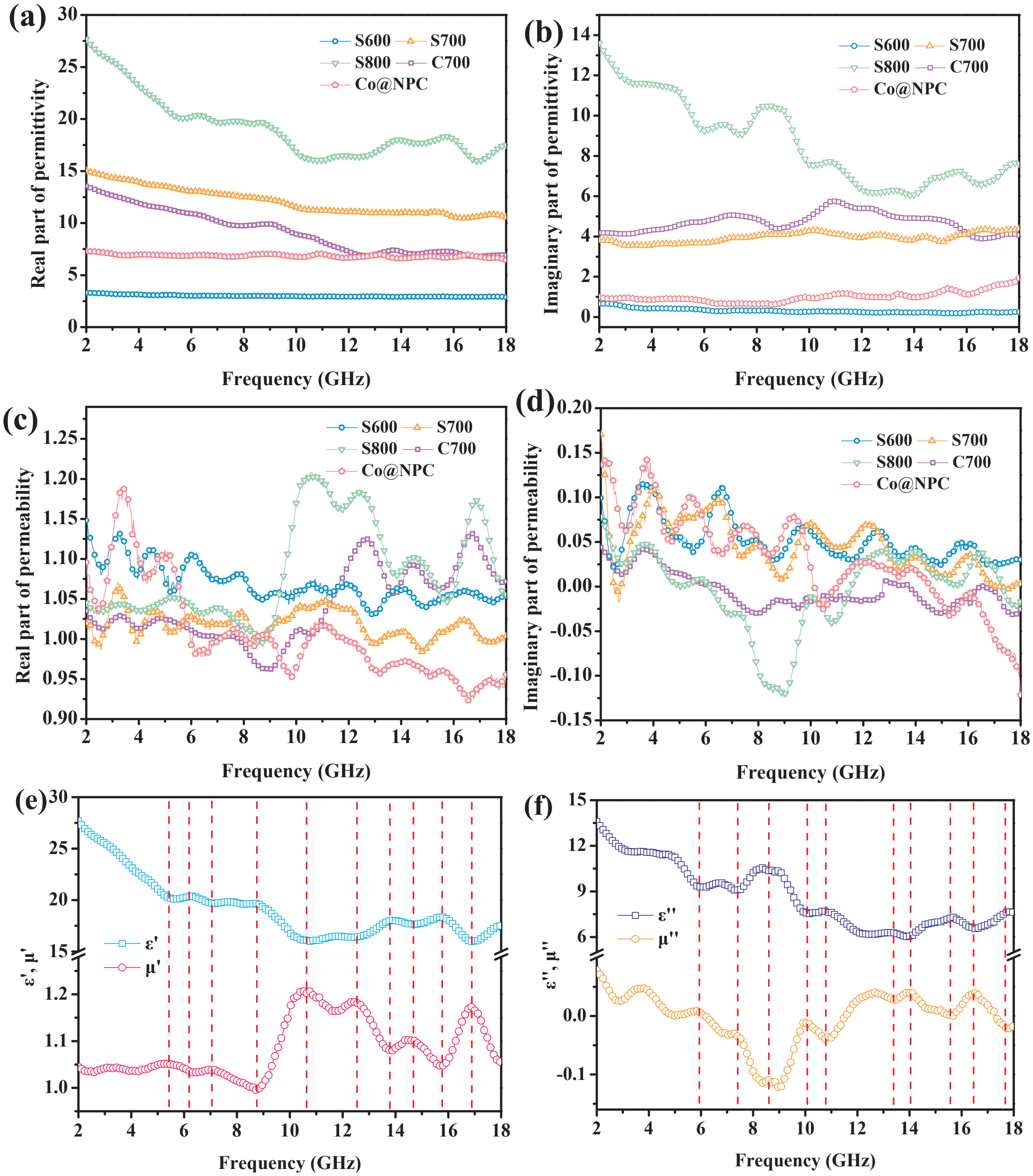

Fig. 8. Frequency dependence of (a) real part of permittivity, (b) imaginary part of permittivity, (c) real part of permeability and (d) imaginary part of permeability of all samples; correspondence between (e) ε' and μ', (f) ε'' and μ'' for S800.

carbon-cotton and Co@NPC could get graphitization adequately, thereby, which would form conductive current with assistance of metal Co along the composites network at the alternated magnetic field. For S700, its ε' and ε'' values are both moderate and between 15.0 and 10.5 and 4.3–3.6, respectively, indicating not only well impedance matching behavior but also excellent dielectric attenuated capability. As compared to C-700, S700 shows slight increase for ε' values but little decrease for ε'' values, which may be put down to the introduction of metal Co. The multiple interfaces of Co/Carbon could contribute to the storage ability of electric energy that leads to the increase of ε'. According to the Debye and free electrons theory that ε'' can be associated with the equations [43,44]:

$$\varepsilon'' = \frac{\delta}{2\pi\varepsilon_0 f} \tag{3}$$

$$\varepsilon'' = \frac{2\pi f\tau(\varepsilon_s - \varepsilon_\infty)}{1 + j(2\pi f)^2\tau^2} \tag{4}$$

From ε'' curve of S700, there is no obvious polarization presence. As a result, conductive loss is the main loss manner. On the prior Raman results, the poor graphitization could be responsible for the lower ε'' values. With regard to the complex permeability for all composites (Fig. 8c and d), they are relatively small because of weak magnetism and low filling loading ratio. For the complex permeability of the composites, all samples present much fluctuation on the curves. By carefully observing electromagnetic parameters of S800, it is discovered that there are exact connections between μ' and ε' curves because of

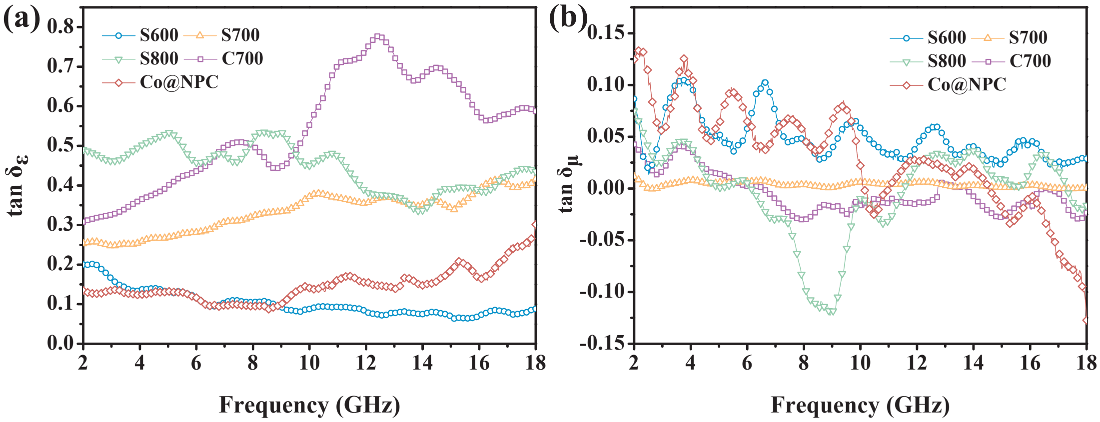

Fig. 9. (a) The dielectric loss tangent ($\tan \delta\varepsilon = \varepsilon''/\varepsilon'$) and (b) magnetic loss tangent ($\tan \delta_\mu = \mu''/\mu'$) of all samples.

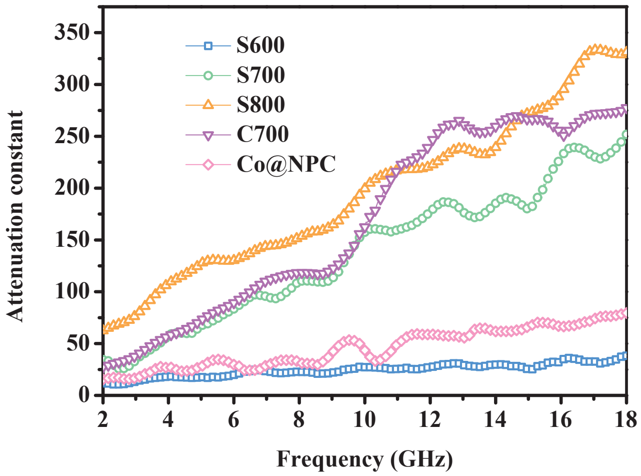

Fig. 10. Attenuation constant versus frequency of all samples.

precise correspondence for peak in μ' to valley in ε' at the same position as well as μ'' to ε'' (Fig. 8e and f). We have reason believe that the complex permeability would be responded to the dielectric transformation, which may be resulted from electromagnetic coupling effect. The result is similar with the previous reports [45,46]. For μ'', other peaks without impacting by dielectric parts could be related with multiple resonance behavior of metal Co [40]. Comparing with C700, S700 reveals obvious magnetic loss benefiting microwave dissipated.

In order to find out the dissipated mode, the dielectric loss tangent (δ_ε) and magnetic loss tangent (δ_μ) of all samples are given in Fig. 9. Clearly, S600 and Co@NPC have minor dielectric loss factors ranged from 0.06 to 0.2 and 0.09–0.25 but relatively high magnetic loss factors. S800 (0.53–0.34) and C700 (0.3–0.77) display decent dielectric loss, which is higher than that of S700 (0.25–0.41). It is noteworthy that the high dielectric loss factors usually greater than 0.5 would be harmful to the impedance matching characteristic of the absorber. Comparing with the magnetic loss values, clearly, the dielectric loss is the main microwave attenuation for the composites. Besides, S700 presents superior magnetic loss than C700.

Furthermore, the attenuation competences of materials, relating to the RL value closely, can be evaluated by the attenuation constant (α), which can be written as: [28]

$$\alpha = \frac{\sqrt{2}\pi f}{c \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}}} \tag{5}$$

As seen in the Fig. 10, the Co@NPC and S600 have a low α value, which was result from the poor dielectric properties and weak magnetic loss. It is clearly observed that the C700, S700 and S800 exhibit the strong attenuation EM wave capacities and the maximum α value could reach 276, 252 and 334, respectively.

Apart from the attenuation constant, the impedance match is another key factor to impact the intensity and f_e of RL peak. It is widely accepted the impedance matching behavior is the necessary prerequisite to determine whether an absorber is outstanding or not, so we should make the complex ε_r closer to the complex permeability μ_r as much as possible. Thus, most of microwave could be allowed into absorber and realize subsequent dissipation. On the ground of impedance matching equations [6,7]:

$$Z = Z_{\text{in}}/Z_0 \tag{6}$$

$$Z_1 = (\mu_r/\varepsilon_r)^{1/2} Z_0 \tag{7}$$

The Z values of all samples are simulated as displayed in Fig. 11a–e. It is found that S700 possess more regions that ranged from 0.9 to 1.1 than other four samples. Therefore, the excellent microwave absorbing properties of S700 could be attributed to the favorable impedance matching. To help understand the point, taken impedance matching of 1.65 mm as illustration (Fig. 11f), we can found that S700 has more values near 1 than other samples, meanwhile, it performs the best microwave absorption properties with the maximum RL value of −51.2 dB and effective bandwidth of 4.4 GHz. By comparison, the Z values at same thickness for other samples are further away from 1 leading to inferior microwave absorption properties. As a consequence, it can draw a conclusion that more values close to 1 could bring about the better microwave absorbing properties.

4. Conclusions

To sum up, we have elaborately designed the carbon-cotton/Co@NPC as outstanding microwave absorber and further researched the influence of annealing temperature. The results state that composites decomposed at proper temperature shows better microwave absorbing properties than pure carbon-cotton. Simultaneously, the enhanced impedance matching characteristic plays a significant role for better microwave absorption properties of S700. It can obtain the maximum RL value of −51.2 dB with effective bandwidth of 4.4 GHz at 1.65 mm. We hope this work may shed light on designing outstanding microwave absorber by recyclable cotton.

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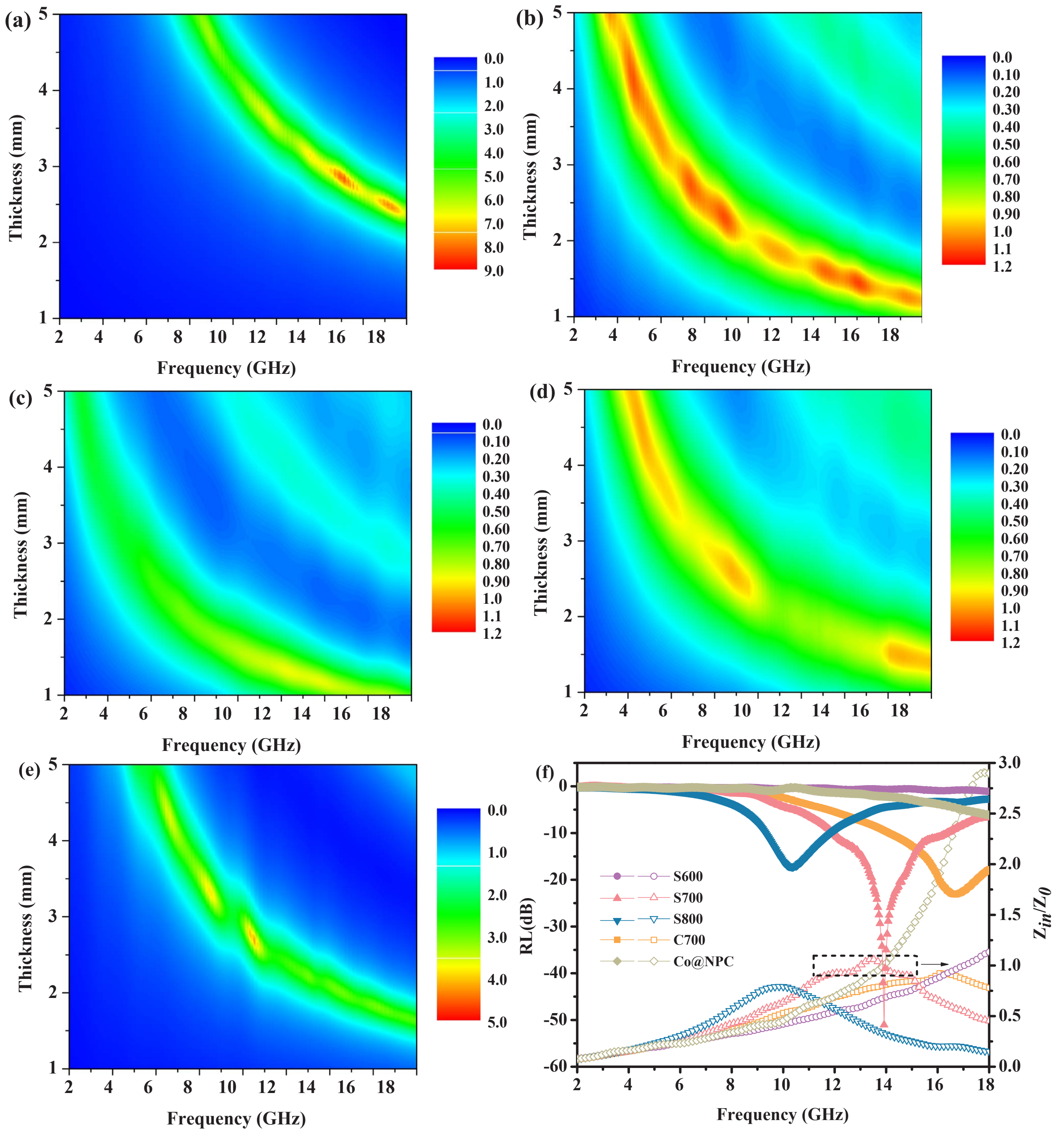

Fig. 11. 3D representation of Z values of (a) S600, (b) S700, (c) S800 and (d) C700, (e) Co@NPC; (f) $|Z_{in}/Z_0|$ values of all samples at thickness of 1.65 mm and corresponding RL values.

are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2018.01.151.

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Review

Bioconversion of agro-industry sourced biowaste into biomaterials via microbial factories — A viable domain of circular economy[☆]

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Low-carbon economy

ABSTRACT

Global increase in demand for food supply has resulted in surplus generation of wastes. What was once considered wastes, has now become a resource. Studies were carried out on the conversion of biowastes into wealth using methods such as extraction, incineration and microbial intervention. Agro-industry biowastes are promising sources of carbon for microbial fermentation to be transformed into value-added products. In the era of circular economy, the goal is to establish an economic system which aims to eliminate waste and ensure continual use of resources in a close-loop cycle. Biowaste collection is technically and economically practicable, hence it serves as a renewable carbon feedstock. Biowastes are commonly biotransformed into value-added materials such as bioethanol, bioplastics, biofuels, biohydrogen, biobutanol and biogas. This review reveals the recent developments on microbial transformation of biowastes into biotechnologically important products. This approach addresses measures taken globally to valorize waste to achieve low carbon economy. The sustainable use of these renewable resources is a positive approach towards waste management and promoting circular economy.

1. Introduction

Food is vital for the survival of humanity and its consumption increases in tandem with population. Over the past decades, WHO & FAO (2003) reported the global per capita food consumption increased steadily from 1960s (2358 kcal/capita/day) to 1990s (2803 kcal/capita/day) with an increment of 100–200 kcal/capita/day each decade. Moreover, to feed the ever-growing population, agro-industries need to work harder to ensure the food supply is sufficient. According to FAOSTAT (2017) and FAOSTAT (2020) the global food supply increased steadily from 1961 to 2017 at 2196 kcal/capita/day to 2917 kcal/capita/day, respectively. However, the population in 1961 and present has increased by 141.77% (FAOSTAT, 2019). The approach in generation of food then and now is different due to the massive increase in human population in the past six decades. To make ends meet Crist et al. (2017) reported that the method of approach was intensification but this method of approach clearly neglects the effects it has on the environment such as increase in agricultural waste production. The Food and Agriculture Organization (2013) reported that in a food supply chain the upstream wastage volume amounted 54% of total food wastage volumes and contributed approximately 34% of total carbon footprint. Waste produced at an alarming rate need to be emphasized urgently for a sustainable production and consumption to maintain the balance of Earth systems (Mihai and Ingrao, 2016). Food wastage and waste has become a global issue and is highlighted in SDG 12 (Responsible consumption and production) under target 12.3 (*By, 2030, halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses*) and target 12.5 (*By,*

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2030, substantially reduce waste generation through prevention, reduction, recycling and reuse). To realize both targets, there is a need for circulating the waste lost and re-utilizing it through recycling and reusing.

Agro-industrial wastes are wastes such as agricultural field and process residues and industrial residues (Sadh et al., 2018). These are known as biowaste and they are fed by industrial and agricultural sectors with no sustainable ways of putting them to good use (Mihai and Ingrao, 2016). Biowaste contributes to a huge fraction of municipal solid waste stream especially in developing countries (Mihai and Ingrao, 2016). These biowastes can be used for the production of carbon based products in the place of fossil sources with the impressive reduction of carbon dioxide releases into the atmosphere (Fava et al., 2015). However, biowaste were usually sent to landfills as a disposal method (Fava et al., 2015) as it is a cheaper option. Traditional methods for biowaste recovery such as composting and animal feed were used (Mihai and Ingrao, 2016) but despite the traditional approach only 25% (i.e. 30 million tons per year) of the total biowastes (118−138 million tons per year) were recycled (Razza et al., 2018). The remaining ended up landfilled producing greenhouse gases at an unthinkable rate (Siebert, 2015). Fig. 1 shows the waste disposal and treatment methods practiced globally.

The current socioeconomic system rides on the linear economy which prompts industries to make and consumer to use and dispose (Michelini et al., 2017). However, we are quickly reaching a point where the linear model is no longer suitable due to increasing global population and the availability of potentially useful industrial wastes (Lacy and Rutqvist, 2015). The world is pushing the land, forests and water past their regenerative capabilities (Lacy and Rutqvist, 2015) and damage have to be minimized before it is too late. For a developing or developed country economic development and environmental sustainability are both essential to ensure a sustainable place for the future generations. China being one of the world's largest manufacturer and exporter has taken the first step into implementing the circular economy model to harmonize economic development and environmental conservation (Ellen MacArthur Foundation, 2018). The circular economy is a systemic approach that promotes regenerative and restorative by intention and aims to decouple growth from the consumption of non-renewable resources (Lacy and Rutqvist, 2015; Ellen MacArthur Foundation, 2017, 2018).

Microbial-derived organic compounds such as surfactant, enzymes and polymers are valuable resources. However, biosynthesizing these products are quite costly compared to the fossil-derived counterpart. For example, the production of polyhydroxyalkanoate (PHA) is expensive due to costs of raw materials and downstream process (Tripathi et al., 2019). The carbon sources are needed in continuous supply if the biotechnological products were to be mass produced. Studies done by Riedel et al. (2015), Yustinah et al. (2019) and Yatim et al. (2017) had proved that wastes from food and agricultural industries can be used as carbon feedstock for PHA production and Tripathi et al. (2019) concluded that agricultural waste gave better yields compared to other expensive carbon sources.

Previously published reviews on circular economy models focuses on the laws and legislations enacted (Nelles et al., 2019), embracing the 3R (reduce, reuse, recycle) principles (Liu et al., 2017), putting the circular economy concept to practice (Pesce et al., 2020) and approaches on utilization of the wastes for second generation production (Girotto et al., 2015). Our review highlights recent efforts on valorization of biowastes by microbial biotransformation into biotechnologically important organic compounds such as surfactant, enzymes and biopolymer among the others as a promising platform in closing the loop in a circular economy model especially concerning agriculture and food industries. Besides, the circular economy concept and implementation as well as and the policies on recycling or reusing biowastes in countries will be reviewed as this is one of the important efforts towards achieving low carbon economy. The outlook includes recommendation for future research on filling the existing knowledge gaps in microbial utilization of biowastes for sustainable use of these resources as an approach towards waste management and promoting circular economy.

2. Biowaste

Agricultural residues are generated from the growing and

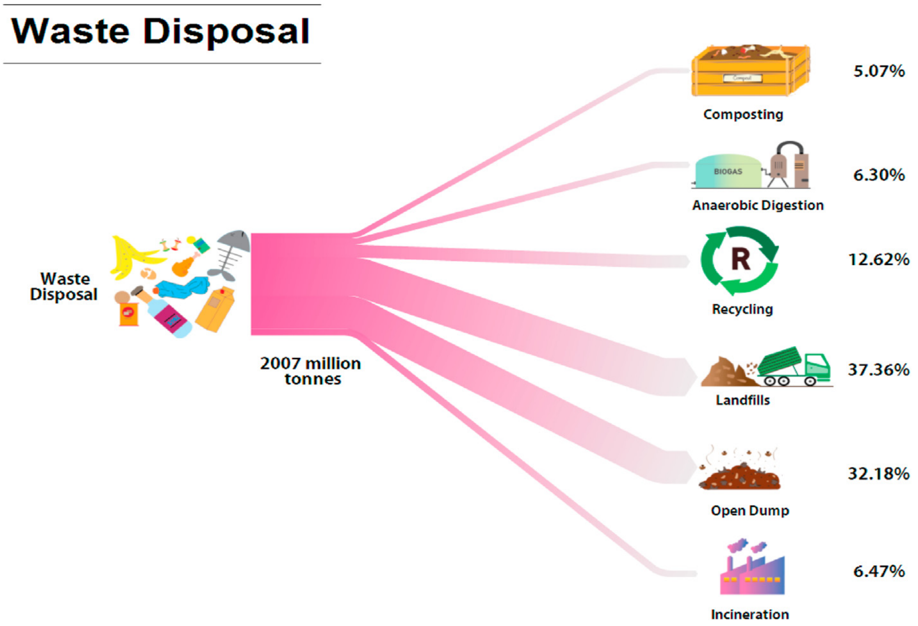

Fig. 1. Percentage of waste disposal and treatment methods practiced globally [Illustration adapted and modified from Kaza et al. (2018)].

processing of raw products such as vegetables, poultry, meat, fruits, crops and dairy products (Obi et al., 2016). According to Sadh and coworkers (2018) the food processing industries produces large amount of organic waste and related effluents annually. There are two types of food wastage: food loss and food waste. There is no common definition of food waste and food loss as it reflects on the perspective of the stakeholders on food waste and food loss (FAO, 2019). However, FAO (2019) conceptually defined food loss as the loss of food in the entire supply chain excluding the point where there is interaction with the retail, food service providers and consumers. Food waste was conceptually defined as the loss of food due to the purchasing decisions by consumers, or decisions by retailers and food service providers that affects the consumers' behavior (FAO, 2019).

According to Östergren et al. (2014), food waste was defined as "*any food, and inedible parts of food, removed from the food supply chain to be recovered or disposed (including composted, crops ploughed in/not harvested, anaerobic digestion, bio-energy production, co-generation, incineration, disposal to sewer, landfill or discarded to sea)*". The discharge of food material occurs from the start to the end of the food supply chain (Girotto et al., 2015). The agricultural sector produces waste from farming and husbandry while the food processing and manufacturing sector produces food loss and food waste due to damage during transport, inappropriate storage and contamination (Girotto et al., 2015). Annually one-third of the food produced is wasted through the supply chain stirring up social, environmental and economic problems (Girotto et al., 2015; Xu et al., 2018). These wastes are normally landfilled (Ayodele et al., 2020). However, landfilling leads to release of landfill gas (LFG) such as carbon dioxide and methane when microorganisms degrade biowaste (Powell et al., 2015; Zuberi and Ali, 2015; Faubert et al., 2019). According to Sun et al. (2016), the recovery of methane is possible using a landfill bioreactor. The carbon dioxide emission was subjected to international carbon market mechanisms implemented under the 1997 Kyoto Protocol (Schneider and Theuer, 2018). Countries like Canada, Britain, United States and Australia has put a price on carbon per ton which were $15, $25, $5-$15 and $10, respectively (Ayodele et al., 2020).

2.1. Oil palm and its waste

Elaeis guineensis, the oil palm tree that originated from Africa is one of the agricultural crops that thrive in tropical hot climates (Awalludin et al., 2015; Loh, 2017). Malaysia is one of the world largest producer of palm oil (Hazman et al., 2018). In 2019, there are a total of 5.9 million hectares of oil palm planted in Malaysia and produced a total of 19.86 and 1.09 million tons of palm oil and palm kernel oil, respectively (MPOB, 2020). The oils were exported to India, China, European Union, Pakistan, Turkey and Philippines (MPOB, 2020). In 2015, Malaysia contributed 20 million tons of edible palm oil equivalent to one-fourth of global total production of the commodity (Owolabi et al., 2017). The magnificent production of palm oil ultimately leads to large amount of oil palm-derived waste. The wastes consist of palm oil mill effluent (POME) (Chan and Chong, 2019), empty fruit bunches (EFB) (Rubinsin et al., 2019; Yustinah et al., 2019), mesocarp fibre (MF) (Awalludin et al., 2015), palm kernel shell (PKS) (Loh, 2017), oil palm fronds (OPF) (Tan et al., 2016), and oil palm trunks (OPT) (Kunasundari et al., 2017).

POME is one of the major industrial wastewater generated in the palm oil processing mill (Chan and Chong, 2019). Raw POME is a thick, brownish liquid effluent (Zainal et al., 2017) discharged at a temperature of 80–90 °C (Alhaji et al., 2016). The POME produced is triple the amount of crude palm oil (CPO) produced (Chan and Chong, 2019). Raw untreated POME has high biological (BOD) and chemical oxygen demand (COD) which causes rapid deoxygenation to the water body when released (Kamyab et al., 2018; (Lee et al., 2019). Other than wastewater, the palm oil production line also produces massive amounts of lignocellulosic waste. OPF is the largest Malaysian biomass source at a staggering amount of 48 million tons per year (Zain et al., 2018). EFB is obtained after the fresh fruit bunches are harvested for their fruits. EFB compose the largest fraction from palm oil mills waste (Krishnan et al., 2017) second to OPF. Malaysia generates approximately 15 million tons of EFB yearly (Koguleshun et al., 2015). MF is one of the many lignocellulosic wastes produced in an oil palm plantation (Yahayu et al., 2018). It is obtained after palm oil was extracted through pressing (Yahayu et al., 2018). Besides that, PKS is another lignocellulosic wastes produced in an oil palm plantation (Lin et al., 2016). It is a layer of endocarp that surrounds the kernels and seeds, produced when the nuts are crushed to extract the kernels (Nizamuddin et al., 2016). On average, the oil palm tree (OPT) will be felled every 20–25 years as the oil productivity decreases (Noparat et al., 2017; Gomes et al., 2018; Poh et al., 2020). Approximately 74.48 tons of OPT will be produced in 1 ha of oil palm planted area (Loh, 2017).

2.2. Paddy and its wastes

Rice (*Oryza sativa*) residing at the bottom of the food pyramid is the chief staple of the human diet. It provides the necessary nutrient and energy for humans to carry out daily routines. It contributes approximately 21% of global human per capita food energy and 15% per capita protein (Kumar et al., 2016). According to statistics, in 2018/2019 China is currently at the top producing 148.5 million metric tons (MMT) followed by India and Indonesia (116.42 MMT and 36.7 MMT, respectively) (Shahbandeh, 2020a). The waste that is produced after harvesting rice husk and rice straw. One kilogram of harvested paddy produces rice husk comprising 20–30% of the paddy weight (Pode, 2016). Rice straw accounts for between 0.41 and 3.96 kg (Pode, 2016; Azat et al., 2019).

2.3. Corn and its wastes

Corn (*Zea mays*) or better known as maize is widely cultivated in the United States producing 345.89 MMT in 2019/2020 followed by China and Brazil at 260.77 MMT and 101 MMT, respectively (Shahbandeh, 2020b). Corn is one of the major cereal crops used to manufacture human food, animal feed and products such as corn starch, adhesives, cereals and sweetener (Ruan et al., 2019). Since the 1970s, United States has reign over the exports of corn at approximately 40% of the global market share (Hutchins, 2018). The massive cultivation and exports led to the generation of corn waste. During the harvesting and processing, corn stover, corn cob, corn germ, condensed distillers solubles, corn distillers dried grains with solubles and wastewater are generated in huge amounts (Ruan et al., 2019). Corn stover and corn cob are the most abundant lignocellulosic biomass in the corn plantation.

3. Bioconversion of biowastes into biomaterial by microorganisms

Biowastes has been piling up in landfills or being discarded into the water bodies at astounding amounts every year. However, with the advances of technologies complementing the waste-to-energy strategy, energy recovery from solid wastes has become a tempting option for an effective waste management solution globally (Manna et al., 2018). There are several energy recovery approaches such as mass incineration (Yap and Nixon, 2015), pyrolysis (Lam et al., 2016; Mahari et al., 2018), gasification process (Akhtar et al., 2018), greenhouse gas (GHG) recovery (Zuberi and Ali, 2015) and composting (Smith and Aber, 2018) can convert waste to electricity, heat or fuels from biowastes.

There are numerous studies done using the waste-to-energy (WTE) strategy. This concept enables the world to look at wastes as a source of renewable energy. With the resources pricing fluctuating, wastes can be utilized to reimagine the production line. By embracing the WTE strategy, microorganisms can be used as a waste management tool. The end product produced by the microorganisms can be tailored to suit the demand. Studies had been done on the utilization of biowaste by microorganisms to produce biotechnologically important products. This approach not only gives the biowaste a second chance in life but also solves one of the toughest challenges in bacterial fermentation which is the need of continuous supply of inexpensive carbon feedstock. Therefore, this section reviews on four different biotechnological important products that can be produced by utilizing biowaste as feedstock.

3.1. *Biopolymer*

One of the most common types of bacterial biopolymer according to Mohamed et al, (2017) is PHA. PHA is a family of naturally occurring biopolymers synthesized by microorganisms (Tan et al., 2014). PHA biosynthesis is kickstarted by limiting factors (nitrogen, phosphorus, sulfate and oxygen) and excess carbon and stored in the cytoplasm of the bacteria in the form of intracellular granule (Urtuvia et al., 2014). PHAs are natural polyesters of 3-, 4-, 5-, and 6-hydroxyalkanoic acids (Raza et al., 2018). More than 150 monomers of hydroxyacids have been reported to be produced. According to a review done by Meng et al. (2014), PHA has been classified into groups namely homopolymers (consists of one monomer), random copolymers (consists of two or more monomers) and block copolymers (at least two homopolymers). Among the PHA-producing microbes, *Cupravidus necator*, *Bacilllus* sp. and *Pseudomonas* sp. has been widely studied (Sagong et al., 2018). PHA biosysthesis involves utilization of carbon sources converting into precursor molecules and polymerized by PHA synthase (Bhubalan et al., 2011). Sagong et al. (2018) reported acetyl-CoA is an important key precursor for the synthesis of short-chain-length (SCL-) and medium-chain-length (MCL-) PHAs. The most common types of PHAs studied are poly(3-hydroxybutyrate) [P(3HB], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(3HB-*co*-3HV)], poly(3-hydroxybutyrate-*co*-4-hydroxyvalerate) [P(3HB-*co*-4HV)] poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [P(3HB-*co*-3HHx)] and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) [(P(3HB-*co*-4HB)]

PHAs are known to possess properties such as insoluble in water (Amelia et al., 2019), non-toxic (Alves et al., 2017), biodegradable (Isola et al., 2017), biocompatible (Yeo et al., 2018) and thermoplastic (Raza et al., 2018) which makes PHA versatile second to synthetic plastics. PHA has very wide application which includes agricultural (Amelia et al., 2019), medical implantation (Vigneswari and Amirul, 2017), drug delivery and tissue engineering (Elmowafy et al., 2019) and food packaging (Bakar and Othman, 2019). However, one of the major challenges of PHA is the large-scale production cost which is dependent on three crucial factors, which include the cost of carbon feedstocks (up to 50% of process costs), cost of downstream processing cost and process development (Riedel et al., 2015). Utilization of inexpensive carbon feedstock like agro-industrial wastes, facilitates cost reduction and benefits large-scale PHA production (Riedel et al., 2015). As reported by Tripathi et al. (2019) the cost can be reduced by opting agro-based waste as carbon source. The varying carbon sources used for PHA production can be found in Table 1.

It is a common practice to use pure substrates for PHA production as high yields can be achieved at a constant rate. These cultivation systems employ pure bacterial cultures or single strain cultivation. Among the main challenges of using wastes as carbon substrates is the availability, composition and production yield. These shortcomings are the focal points on which researchers are working at improving by developing more robust strains or cultivation system which involves lesser aseptic techniques. Through genetic engineering, strain which are contamination resistant could be developed to withstand the impurities found in biowastes. On the other hand, a study reported that bacteria from seawater have been used to produce PHA using seawater as growth media in the presences of different carbon substrates (Yatim et al., 2017). Halophiles are promising PHA producers as they can thrive in seawater-based medium which eliminates the contamination by non-halophiles which in return eliminates the sterilization step.

3.2. *Surfactant*

Surfactants (SURface ACTive AgeNTS) are amphiphilic molecules with hydrophobic and hydrophilic moieties which allows reduction of the surface tension of an aqueous medium (Chong and Li, 2017; Tripathi et al., 2019; Jahan et al., 2020). This allows two immiscible media to form an emulsion layer. It is widely used in households, healthcare industry and agriculture (Varjani and Upasani, 2017). The demand for surfactant is ever growing (Gudiña et al., 2016). It is

Table 1
Production of PHA by various bacteria using different types of biowastes.

Bacteria	Carbon source	PHA type	Reference
Bacillus megaterium UMTKB-1	Glycerol	P(3HB)	Yatim et al. (2017)
	Sweetwater	P(3HB)	
	Sugarcane molasses	P(3HB)	
Haloferax mediterranei DSM1411	Whey	P(3HB-*co*-4HV)	Koller (2015)
Bacillus cereus *suaeda* B-001	Glucose	P(3HB)	Yustinah et al. (2019)
	Oil palm empty fruit bunch	P(3HB)	
Haloferax mediterranei ATCC 33500	Cheese whey	P(3HB-*co*-3HV)	Pais et al. (2015)
Cupravidus necator Re2058/pCB113	Sludge palm oil	P(3HB-*co*-3HHx)	Thinagaran and Sudesh (2017)
C. necator Re2058/pCB113	Animal fat	P(3HB-*co*-3HHx)	Riedel et al. (2015)
Cupravidus necator H16	Animal fat	P(3HB)	
	Tallow	P(3HB)	
Bacillus subtilis RS1	Pre-treated sugarcane molasses	P(3HB)	Rathika et al. (2018)
H. mediterranei DSM 1411	Olive mill wastewater	P(3HB-*co*-3HV)	Alsafadi and Al-Mashaqbeh (2017)
Halomonas halophila CCM 3662	Spent coffee grounds	P(3HB)	Kovalcik et al. (2018)
Pseudomonas aeruginosa STN-10	Frying oil	P(3HB) & P(3HB-*co*-3HV)	Tufail et al. (2017)
Bacillus spp. BM 37	Corn cob hydrolysate	P(3HB)	(Stoica et al. (2018))
Pichia kudriavzevii VIT-NN02	Banana peel	P(3HB-*co*-3HV)	Ojha and Das (2020)

estimated that the total worldwide annual production of surfactant is over 15 million tons and it is expected to hit approximately 24 million tons annually by 2020 (Gudiña et al., 2016). Currently, most surfactant are man-made deriving from petroleum due to low cost production (Chong and Li, 2017). However, synthetic surfactants may pose a threat to the environment due to its non-biodegradability (Chong and Li, 2017). With the advances in biotechnology, surfactant from microorganisms are gaining attention from researchers world over (Roy, 2018).

3.2.1. Biosurfactant

Biosurfactants are amphiphilic (both hydrophobic and hydrophilic) compounds biosynthesized by a wide range of microbes including bacteria, yeast and fungi (Roy, 2018). Biosurfactants possess several advantages over synthetic surfactants which include low toxicity, biodegradability, stable in extreme pH, temperature and salinity (Akbari et al., 2018). Synthetic surfactants elicit pollutants by-products that are harmful to the environment. Therefore, it has become imperative to look for an environmentally friendly alternative without compromising on the performance. Biosurfactants have garnered much attention in the recent times, as an alternative eco-friendly, biodegradable, biocompatible, low-toxicity and stable material, with potential application in many industries such as food and beverages, pharmaceuticals and cosmetics (Vijayakumar and Saravanan, 2015). Moreover, biosurfactant has been used for microbial enhanced oil recovery for enhanced oil recovery projects due to its functional properties. Biosurfactant are classified into five types which are glycolipids, lipopeptides, phospholipids, fatty acids and polymeric biosurfactants (Geetha et al., 2018). Studies have proved that the best-known microorganisms for biosurfactant production are *Bacillus* sp., *Pseudomonas* sp., *Rhodococcus* sp., *Candida* sp. and *Acinetobacter* sp. (Geetha et al., 2018). The most widely studied bacterium is *Pseudomonas aeruginosa* which is a consistent producer of rhamnolipids (Martínez-Toledo et al., 2018). However, the production of biosurfactant is comparatively low in the global market. One of the main cost escalating factors of biosurfactant production is the feedstock for the microorganisms as the downstream process. The feedstock cost is estimated to be 50% of the total production cost. Researchers had turned to low-cost or cost-free feedstocks such as agricultural by-products for biosurfactant production (Silva et al., 2017). The cheapest and most widely available biosurfactant in the market, sophorolipid is priced at $34/kg active matter compared to synthetic surfactants sold up to $4/kg (Dolman et al., 2019). Table 2 shows recent studies on the production of biosurfactant using biowaste as feedstock.

The overall production cost of biosurfactants can be reduced by regulating both upstream and downstream processes when wastes are being used as carbon feedstocks. Since biosurfactants are produced extracellularly, the important part of the bacterial culture is the supernatant. Instead of inoculating microbes into the medium, they can be introduced using the 'tea bag' concept where it eliminates the need for separation step. The microbes can be immobilized on activated carbon or beads and placed in 'tea bag' for continuous production of biosurfactant. Biosurfactant producers can be isolated directly from the waste or waste treatment plant. These microbes are believed to have acclimatized to the conditions of its surrounding. Conversely, the wastes can be used as the growth medium and the feedstock simultaneously which eliminates the need of a separate growth medium. However, a proper separation process of wastes from the biosurfactant-enriched medium is required to ensure the purity of biosurfactant is not affected. For example, isolation of the biosurfactant rich supernatant can be done by placing the microbes and waste in the same entity with pores just enough for water molecules to pass through. During the extraction, the microbes and waste free media can be filtered to remove excess particles (suspended solids).

3.3. Enzymes

Enzymes are found in every living system. Enzymes act as catalyst that increases the rate of chemical reactions in the living system. Enzymes are able to increase rates of chemical reactions without getting consumed and altering the chemical equilibrium between reactants and the products (Cooper, 2019). Without enzymes, the chemical reactions in the living systems would take a very long time to complete since the enzymes hastens the reactions by a millionfold. Therefore, enzymes are highly valued especially in the industrial sectors. Enzymes produced by microorganisms are more stable and active compared to plants and animals which make them excellent for industrial and medicinal purposes (Bharathiraja et al., 2017). Production of enzymes involves high cost which urged researchers to look for alternative ways such as solid state fermentation as compared to the liquid fermentation (Mojumdar and Deka, 2019). Moreover, contents of synthetic media for enzyme production are expensive and it may very well be

Table 2
Biosurfactant production via microbial fermentation using various types of biowaste as feedstock.

Bacteria	Feedstock	Surfactant	References
Pseudomonas aeruginosa UMTKB-5	Sweetwater	Rhamnolipid	Azemi et al. (2016)
Pseudomonas cepacia CCT6659	Canola waste frying oil	Rhamnolipid	Silva et al. (2017)
Bacillus subtilis ATCC 6633	Glycerol	Surfactin	Cruz et al. (2018)
Bacillus amyloliquefaciens RHNK22	Rice bran husk Banana leaf Coconut oil cake Sunflower oil cake Sugarcane leaf Cheese whey	Iturin	(Kumar et al., 2017)
Aneurinibacillus migulanus NCTC TSA 7092	Molasses and tuna by-product	Rhamnolipid	Sellami et al. (2016)
Pseudomonas aeruginosa PAO1	Palm fatty acid distillate	Rhamnolipid	Radzuan et al. (2017)
Bacillus subtilis DDU20161	Potato peels and potato pulp	Surfactin	Vishal et al. (2019)
Pseudomonas azotoformans AJ15	Potato peels and sugarcane bagasse	Rhamnolipid	Das & Kumar (2018)
Achromobacter sp. BP(1)5	Rice straw hydrolysate Corn cobs hydrolysate	Rhamnolipid	Ni'matuzahroh et al. (2020)
Bacillus safensis J2	Sugarcane bagasse	Surfactin	Das & Kumar (2019)
Pseudomonas aeruginosa	Waste canola oil	Rhamnolipid	Pérez-Armendáriz et al. (2019)
Pseudomonas aeruginosa #112	Corn steep liquor, sugarcane molasses and oil mill waste	Rhamnolipid	Gudiña et al. (2016)
Pseudomonas aeruginosa DR1	Mango kernel oil and glucose	Rhamnolipid	Reddy et al. (2016)

replaced by agro-industrial waste in future.

Lignocellulosic waste are the most abundant on Earth because 181.5 billion tons were generated annually (Dahmen et al., 2018). These lignocellulosic wastes can be degraded into fermentable sugars that can be used to produce bioethanol (Rubinsin et al., 2019). The degradation and production are achieved by lignocellulolytic enzymes produced by microorganisms. Table 3 shows the enzymes produced by microorganisms in the bioconversion of lignocellulosic wastes. The enzymatic degradation of lignocellulosic biomass is carried out by three main groups of enzymes: cellulase, hemicellulase, and ligninase. Cellulases are used in the bioconversion of agricultural wastes as initial processing steps of the lignocellulosic waste bioconversion. These are class of enzymes that degrade the main cell wall polysaccharide into smaller fermentable sugars such as maltose and glucose. Fungal cellulases and hemicellulases from *Trichoderma* sp., *Aspergillus* sp., and *Penicillium* sp. are the most widely used cellulases in the industry due to high enzyme activity (Andersen et al., 2016; Cologna et al., 2017). Among the bacterial cellulases *Clostridium* sp., *Zymomonas mobilis*, *Streptomyces* sp. and *Bacillus* sp. are the most commonly used bacterial strains (Saini et al., 2015; Bardhan et al., 2019; Thapa et al., 2019). Enzyme cost contribute largely to the production cost of bioethanol and on site production of cellulase are recently getting attention instead of purchased enzymes (Hong et al., 2013). Hemicelluloses, one of the most abundant polysaccharides and a heterogenous copolymer of cellulose, comprises 15–19% of dry weight of cell wall polysaccharides of fruits and vegetables and 17–38% of crop straw composition (Saini et al., 2014; Toushik et al., 2017; Wang et al., 2020).

In order to achieve a sustainable bioconversion, a sufficient amount of yield and revenues but cost-efficient biomass-to-product process is crucial, such as in the production of ethanol. Optimization of the step-by-step process is needed to meet the techno-economic feasibility. Enzyme cost plays a major contribution in the distribution cost during production and the use of on-site or near-site enzyme production has significantly reduced the enzyme cost by 30–70% due to simpler processes and logistics (Hong et al., 2013). For example, in 2018, a team from the University of Salerno, Italy performed a techno-economic analysis of lignocellulosic biorefineries by means of process simulations, cost and profitability analysis. Their work suggests an improvement of the sustainability of lignocellulosic wastes in biorefineries by utilizing the added value of co-produced chemicals such as xylitol or furfural. The sustainability of lignocellulosic bioconversion was determined based on the payback selling price of ethanol from purchased enzymes, on-site produced enzymes, xylitol co-production and furfural co-production. The economic analysis revealed that co-production of xylitol appeared to be more convenient due to higher revenues and lower thermal conversion (Giuliano et al., 2018).

Microbial enzymes production has come a long way since the derivatization of enzymes from animals and plants. Besides the feedstock, the cost incurred for the pretreatment of feedstock and purification of enzymes could not be neglected. This becomes more evident when wastes are used as carbon feedstocks. For example, the pre-treatments (chemical, physical and biological) are needed to depolymerize the cellulose and hemicellulose of the lignin complex of the waste. The variation of lignocellulosic wastes also poses a problem to biorefineries as the industries must match effective enzymes for particular lignocellulosic feedstocks which the quality varies by species and even batches. This is a research focus that needs work where there is a possible need for a universal enzyme. Future studies on genetic engineering of microbes to obtain a universal enzyme cocktail that is robust enough to attack any lignocellulose is highly sought after. Studies suggest that extremophiles are a potential source of enzymes with extreme stability under inhabitable conditions. This approach, for the time being, allows the extremophiles to thrive in the pretreaments where it can attack the lignocellulose simultaneously.

3.4. Other organic compounds

Lignocellulosic agricultural wastes are a popular choice of biowastes to be converted into a variety of organic compound. These renewable resources are processed in biorefineries and are converted to compounds that have a wide range of applications in food and chemical industries. Table 4 shows a list of compounds that are commonly produced from lignocellulosic materials from hydrolysis or conversion processes.

Celluloses and hemicelluloses are biodegraded into C5 (xylose, arabinose) and C6 (glucose, mannose, galactose) sugars through enzymatic hydrolysis by the microorganisms. Food and dietary uses are among the popular applications of these monosaccharides. In biorefineries, however, these monosaccharides do not become the end products, but are just intermediates in the over-all process. They are further converted into compounds that have high industry demands, such as alcohols, through microbial fermentation. These hexoses and pentoses are converted into furans, namely 5-hydroxymethylfurfural (HMF) and furfural or 2-furaldehyde (2F). A product of the Maillard reaction, HMF was shown to have antioxidative properties through free-radical scavenging, suppression of mast cell activation, and *in vitro* antiproliferative activity against melanoma cells (Turkut et al., 2018; Uchida et al., 2020). These furans are also the ideal and cheap bio-based materials in polymerization and composites, and may also be converted to a biofuel in the form 5-methoxyfurfural (Zuo et al., 2018; Asad et al., 2020).

The three hydroxycinnamyl alcohol products of lignin degradation, namely p-coumaryl, coniferyl, and sinapyl, that are all potential raw materials for valorization. Levulinic acid, a derivative of these phenolic compounds, is a precursor for many high-value and essential products such as biofuels, cosmetics, plastics, and chemical commodities (Adeleye et al., 2019). Levulinic acid was on the United States Department of Energy list of 12 most promising chemicals from biomass. For the bio-based solution to progress, the biorefinery sector should produce the needed materials at a low cost (Bomgardner, 2015). In Indonesia, a techno-economic assessment of levulinic acid production from *Sorghum bicolor* (sorghum, great millet) revealed that a minimum production capacity of 7.7 ton per day would achieve an internal rate of return and payback period values of 19.61% and 3.93 years, respectively (Gozan et al., 2018). For food safety, levulinic acid with sodium dodecyl sulfate shows bactericidal activities, which allows it to be a promising sanitizing agent in the food production sector. This tandem treatment effectively inactivates *Listeria monocytogenes*, *Salmonella typhimurium*, and Shiga toxin-producing *Escherichia coli* (STEC) in biofilms on the surface of stainless steel coupons (Chen et al., 2015). Xylitol may be produced efficiently by fungal lignocellulases from hemicellulosic biomasses (Baptista et al., 2018). In addition, this sugar alcohol is also anticariogenic since it limits the adherence of *Streptococcus mutans* and inhibits plaque formation (Gul et al., 2017).

Microbial derived organic compounds from lignocellulosic wastes hold promises to industries as they offer sustainable sources of high valued products. However, the drawback is the costs incurred while processing complex mixtures, the perishable character of the lignocellulosic wastes and the extraction approaches. Studies are geared towards identifying efficient and systematic processes which addresses microbial productivity in complex media as well as recovery of sensitive and selective organic compounds. The established conventional techniques (e.g., Soxhlet

Table 3
Enzymes produced by microorganisms in the bioconversion of lignocellulosic wastes.

Type of microorganism	Name of microorganism	Feedstock	Enzyme *(enzyme activity)*	Remarks	References
Fungi	*Pleurotus ostreatus*	Sugarcane bagasse and wheat bran	L, MP, LP, FPC, AV, CMC, X, BG, BX *(ligninolytic, cellulolytic, hemicellulolytic)*	Highest activities occurred in yeast mixtures as source of lignocellulolytic enzymes	Rodrigues et al. (2019)
	Coriolus versicolor	Sweet sorghum bagasse	L, MP, LP, PPO, AAO, FPC, AV, CMC, X, BG, BX *(ligninolytic, cellulolytic, hemicellulolytic)*	Glucose yield in hydrolysis = 402.9 ± 14.1 mg/g feedstock	Mishra and Jana (2019)
	Irpex lacteus	Corn stover	LP, MP, DDP, CBH, EG, BG, X, BX, AF, AXE *(ligninolytic, cellulolytic, hemicellulolytic)*	Degradation rate = 74.9% lignin, 86.3% cellulose, and 83.5% hemicellulose in 9 days	Qin et al. (2018)
	Trichoderma reesei NRRL 3652	Rice husk, Soybean hulls, Sugarcane bagasse, Powder toothpick yerba mate	FPC, CMC, X *(cellulolytic, hemicellulolytic)*	Hydrolytic efficiency of about 0.16 g/g	Astolfi et al. (2019)
	Trichoderma reesei QM9414ΔP70	Cellulose and xylan	FPC, CMC, EG, X *(cellulolytic, hemicellulolytic)*	The cellulase and hemicellulase activities in ΔP70 exhibited 65–150% and 6% higher than the parental strain QM9414Δmus53, respectively.	Qian et al. (2019)
	Aspergillus oryzae NRRL695	Soybean husk, Flour mill waste	AM *(amylolytic)*	Optimized conditions yielded amylase activity of about 47,000 U/g dry substrate	Melnichuk et al. (2020)
	Aspergillus niger	Sugarcane bagasse and wheat bran	L, MP, LP, FPC, AV, CMC, X, BG, BX *(ligninolytic, cellulolytic, hemicellulolytic)*	Highest activities occurred in yeast mixtures as source of lignocellulolytic enzymes	Rodrigues et al. (2019)
	Saccharomyces cerevisiae	Corn stalk	ED, EX, BG, X *(cellulolytic, hemicellulolytic)*	Conversion rate of 27.4% and reduced hydrolysis cost	Zhao et al. (2019)
	Streptomyces fulvissimus CKS7	Corn stover, Horsetail waste, Yellow gentian waste, Cotton fabric, Corona treated cotton fabric	CMC, AV, AM, X, pectinase *(cellulolytic, hemcellulolytic, amylolytic)*	Hydrolytic efficiency of 1.81–2.55 mg/mL	Mihajlovski et al. (2020)
	Wikerhamomyces chambardii	Corn straw	CMC *(cellulolytic)*	Ethanol yield is 26.13 ± 6.27 g/L	Adelabu et al. (2019)
	Candida shehatae	Sugarcane bagasse and Rice straw	xylose reductase and xylitol dehydrogenase *(fermenting)*	74.5–78.4% ethanol yield in continuous batch and 96.01–98.0% yield in recycled batch	Meethit et al. (2016)
Bacteria	*Anoxybacillus beppuensis* JF84	Sugarcane bagasse, dairy whey, Wheat straw	AM *(amylolytic)*	Most suitable substrate is sugarcane bagasse for amylase production (0.135 U/mL)	Jabeen et al. (2019)
	Recombinant *Zymomonas mobilis* (pGEX-4T-3 BI 120−2)	Cellulose and Beechwood xylan	CMC, X *(cellulolytic, hemicellulolytic)*	Ethanol yield is about 2.65 g/L	Todhanakasem et al. (2019)
	Bacillus amyloliquefaciens	Wheat bran, Rice bran, potato peel	AM *(amylolytic)*	Enzyme activity of 0.9–1.2 U/μg	Mojumdar and Deka (2019)
	Bacillus coagulans	Beechwood hydrolysate	lactate dehydrogenase *(fermenting*	Conversion rate of about 85.4 ± 4.7%	Glaser and Venus (2018)
	Bacillus lichenforms AT70	Raw corn granules	AM *(amylolytic)*	Optimal activity at 14–20% of raw corn starch	Afrisham et al. (2016)
	Bacillus subtilis B2	Groundnut oil cake, Coconut oil cake, Wheat bran	AM *(amylolytic)*	Highest amylase production (300.51 ± 1.7 U/mL) for groundnut oil cake as substrate	Elumalai et al. (2019)
	Bacillus subtilis J12	Corn cob, Napier grass	CMC, X *(cellulolytic, hemicellulolytic)*	Hydrolytic efficacy: Corn cob – 13.2% and Napier grass – 9.6%	Kuancha et al. (2017)
	Recombinant Escherichia coli FBR5	Corn stover hydrolysate	PD, AD *(fermenting)*	Ethanol yield is 28.9 ± 0.2 g/L	Saha et al. (2015)
	Rhodococcus opacus PD630	Corn stover	L *(ligninolytic)*	Fatty acid methyl ester yield and oleaginicity of about 1.28 g/mL	Le et al. (2017)
	Clostridium thermocellum DSM1313	Rice husk, Banana pseudostem, Sugarcane bagasse	FPC, CMC, AV, AD *(cellulolytic, fermenting)*	Ethanol yield is about 1–1.2 g/L	Nisha et al. (2017)
	Clostridium acetobutyliticum ATCC 824	Sugarcane bagasse	CMC, AV, EG, BG, X, AF *(cellulolytic, hemicellulolytic)*	Butanol yield is 7.68; Acetone-butanol-ethanol yield is 12.12 g/L	Li et al. (2017)
	Cellvibrio japonicus	Corn xylan and Beech xylan	BG, EG, X, BX, AF, AXE *(cellulolytic, hemicellulolytic)*	Rhamnolipid yield of 4.9 mg/L from Beech xylan	Horlamus et al. (2019)
	Lactobacillus plantarum strains	Palm kernel cake	FPC, CMC, AV, BG, X, β-mannanase, proteases *(cellulolytic, hemicellulolytic, proteolytic)*	High extracellular hydrolytic enzyme activities	Lee et al. (2019)
	Lactobacillus plantarum RI11	Rice straw, Molasses, Palm kernel cake, Soybean pulp	EG, EX, BG, β-mannanase *(cellulolytic, hemicellulolytic)*	Enzyme activity of about 11.70 μg/min/mg (EG), 9.99 μg/min/mg (EX), 10.43 nmol/min/mg (BG), and 8.03 μg/min/mg (mannanase)	Zabidi et al. (2020)

Legend: L-laccase, MP – Manganese peroxidase, LP – lignin peroxidase, DDP – dye decolorizing peroxidase, PPO – polyphenol oxidase, AAO – aryl alcohol oxidase, FPC – filter paper cellulase, CMC - carboxymethylcellulase, AV - avicelase, ED – endocellulase, EX – exocellulase, CBH – cellobiohydrolase, AM – amylase, EG – endoglucanase, BG – β-glucosidase, BX – β-xylosidase, X – xylanase, AF – arabinofuranosidase, AXE – acetylxylan esterase.

Table 4
Compounds that are commonly produced from lignocellulosic materials.

Microorganism	Feedstock	Compounds produced	Industrial uses of product	References
Scheffersomyces stipitis, Lactobacillus casei, Aspergillus niger A42	Wheat bran	glucose	Thickener, sweetener, humectant	Germec et al. (2019)
S. stipitis, L. casei, A. niger A42	Wheat bran	xylose	Sweetener, Raw material for surfactants, diagnostic agent for malabsorption	Germec et al. (2019)
Trichoderma reesei ATCC 26921	Pinewood	mannose	Dietary supplement, raw material for drug synthesis and animal feeds	Borand et al. (2020)
S. stipitis, L. casei, A. niger A42	Wheat bran	arabinose	Sweetener, functional additive in medical and pharmaceutical industries	Germec et al. (2019)
T. reesei ATCC 26921	Pinewood	galactose	Sweetener, used in flavoring, occasional ingredient in vaccine production	Borand et al. (2020)
Saccharomyces cerevisiae PE-2ΔGRE3 and CA11	Corn cob	furfural/HMF	Precursor molecule for polymers and adhesives	Cunha et al. (2019)
Methylocystis bryophila, Methylocella tundrae, Methyloferula stellate	Coconut coir	methanol	Fuel, solvent, ethanol denaturant, antifreeze compound	Patel et al. (2019)
Scheffersomyces stipitis	Wheat bran	ethanol	Fuel, solvent for organic synthesis, preservative for biological samples, disinfectant	Germec et al. (2019)
Corynebacterium glutamicum Cg-ax3	Sorghum stover	xylitol	Sugar substitute, dental care ingredient, prebiotic	Dhar et al. (2016)
Saccharomyces cerevisiae, Clostridium beijerinckii	Rice straw	butanol	Fuel, solvent, precursor compound in organic synthesis	Wu et al. (2020)
Enterobacter aerogenes EMY-22_M1Gb	Sugarcane bagasse	butanediol	Precursor for synthesis of polymer materials, drugs, pesticides and cosmetic products, starting material for conversion reactions	Kim et al. (2020)
Lactobacillus casei	Wheat bran	lactic acid	Its esters are emulsifying agents in bakeries, ingredient in topical ointments and skin care, monomer for biodegradable thermoplastic	Germec et al. (2019)
Microbial consortium TC-5	Wheat straw, Rye Straw	methane	Natural gas, fuel, reinforcing agent for tire rubber, Hydrogen source	Kong et al. (2018)
Rhodococcus jostii RHA1 ΔpcaHG	Empty fruit bunch	phenolic compounds	Fragrance and flavoring in food industry, antimicrobial in pharmaceutical industries	Ramachandran et al. (2020)
Lactobacilli sp.	Wheat straw	levulinic acid	Precursor molecule for plasticizer, animal feed, antifreeze compound, resins and coating, textile	Gubelt et al. (2020)

extraction, maceration and hydrodistillation) suffer from low extraction rates, selectivity and high-energy costs related to solvent evaporation for recovery and recycling. A more designed strategy would be to develop catalyst based extraction system targeted to specific organic compounds. Pre-treatment of lignocellulosic wastes has been well established in order to increase its bioavailability and biotransformation. The valorization of lignocellulosic wastes and establishment of consolidated process of pre-treatment, enzymatic digestibility and fermentation ensures successful utilization of these abundant and renewable resources.

4. Circular economy

The current socioeconomic system is based on the linear economy where manufacturers produces and consumers use and dispose ('take, make and dispose' model) (Michelini et al., 2017; Garcés-Ayerbe et al., 2019). This traditional linear model assumes that there are limitless supply of natural resources and unlimited capacity of the environment to absorb waste and pollution (Garcés-Ayerbe et al., 2019). When the global demand increases, the demand for resources increases exponentially which causes overuse and removal of natural resources from the environment leading to higher priced resources ultimately causing inflation and volatility in markets (Ellen MacArthur Foundation, 2015). Without a doubt the wastes produced from the processing to the consumer will increase by several folds and end up being landfilled. Therefore, the linear economy is no longer suitable as our environment is reaching its limit to cope with our waste disposal.

To this date, there are different versions of definition of circular economy (CE) but most of it revolves around the efficient use of wastes, wastes minimization and sustainable development. Virlanuta et al. (2020) defined the CE as a major concern at the global level and can be defined as a sustainable approach for the current economic model with a clear goal which is efficient use of resources via waste minimization and recycling of waste back into production processes. Morseletto (2020) defined CE as an economic model targeted at the efficient use of resources through waste minimization, long-term value retention, reduction of primary resources, and closed loops of products, product parts, and materials within the boundaries of environmental protection and socioeconomic benefits. Ellen MacArthur Foundation (2017) defined CE as a circular economy is based on the principles of designing out waste and pollution, keeping products and materials in use, and regenerating natural systems. Therefore, this review defines CE as a sustainable economic model by keeping the wastes in use as long as possible, so waste generation is minimized and in turn ensuring minimal fluctuation in resource commodity pricing providing a stable platform for manufacturers, retailers and consumers.

Based on the Ellen MacArthur Foundation (2015), CE rests on three principles: (1) preserve and enhance natural capital by controlling finite stocks and balancing renewable resource flows, (2) optimize the yield of resources by circulating products, components and materials at the highest level of use at all times, and (3) promote system efficiency by identifying and designing negative externalities. These principles of CE include the 3R and 6R (reuse, recycle, redesign, remanufacture, reduce, recover) (Winans et al., 2017).

Every country has their own legislative framework that suit to their infrastructure, population and economy. Transitioning from a linear to circular economy is not an overnight achievement. Therefore, each country has their unique policies and legislations as shown in Table 5. According to Table 5, most of the early stages of CE-related legislations are based on recycling, reusing and reducing of wastes. However, most policymakers had turned to CE due to the economic constraints and absence of raw materials (Nelles et al., 2019). As shown in Table 5, the countries are putting effort in transitioning into the circular economy by enacting and implementing new policies and regulations.

Table 5
The CE related legislations implemented by several countries.

Countries	Policies/Acts/Laws/Regulations	Year	Description	References
Canada	Waste Diversion Act	2002	Promote reduction, reuse and recycling of waste and to provide for the development, implementation and operation of waste diversion programs	Waste Diversion Act (2002)
	Resource Recovery and Circular Economy Act (RRCEA)	2016	Reduce waste generation and increase resource recoverability by implementing recycling and reusing of packaging materials and promote public education and awareness with respect to resource recovery and waste reduction.	Resource Recovery and Circular Economy Act (2016)
China	Administrative Measures for the Recovery of Renewable Resources	2007	The purpose of these Measures is to promote the recovery of renewable resources, regulate the development of the industry of recovery of renewable resources, save resources and protect the environment.	Administrative Measures for the Recovery of Renewable Resources (2007)
	National 12th Five Year Plan for Environmental Protection	2011	Aims to reduce total discharge of major pollutants by raising the standard of pollutant emission. Promotes cleaner production in production industries and establish resource reuse system covering the whole society.	National 12th Five-Year Plan for Environmental Protection (2011)
	13th Five Year Plan for Economic and Social Development of The People's Republic of China: Chapter 43 Section 5	2016	Aims to implement a plan for guiding circular development, encourage the circular use of resources and accelerate efforts to recycle resources from refuse.	13th Five Year Plan for Economic and Social Development of The People's Republic of China (2016)
	Circular Economy Development Strategy and Action Plan	2013	Aims to accelerate the transformation of economic development, build a resource-saving and eco-friendly society and achieve sustainable development.	Circular Economy Development Strategy and Action Plan (2013)
	Energy Development Strategy Action Plan (2014—2020)	2014	Aims to achieve energy conservation, domestic energy security and push forward low-carbon strategies. The action plan also covers fossil fuel and renewable energy, rural energy access, technology and innovation, and energy market measures.	Energy Development Strategy Action Plan 2014-2020 (2014)
Germany	Closed Substance Cycle Waste Management Act	1994	Promote closed substance cycle waste management to conserve natural resources and to ensure environmentally compatible disposal of waste.	Closed Substance Cycle Waste Management Act (1994)
	End-of-life Vehicle Act	2002	Successor to End-of-life Vehicle Ordinance. Promotes the environmentally sound disposal (reuse, recycling and recovery) of the end-of-life vehicles.	(End-of-life Vehicle Act (2002))
	Battery Act	2009	Aims to increase the percentage of batteries and accumulators that are returned due to the valuable materials and environmental and health hazards contained. This act extends responsibility of the manufacturers of batteries and accumulators to cover the entire life cycle of the equipment.	(Battery Act (2009))
	Act on Reorganising the Law on Closed Cycle Management and Waste	2012	Aims to promote circular economy to conserve natural resources and to ensure the protection of human health and the environment in the generation and management of waste	Act on Reorganising the Law on Closed Cycle Management and Waste (2012)
	Electrical and Electronic Equipment Act	2015	Aims to protect the environment and health and conserve natural resources. This Act assumes the producers to bear full responsibility over the entire life cycle of their products. This Act also regulates the placing on the market, the taking back and recycling as well as the environmentally acceptable disposal of electrical and electronic equipment.	(ElektroG (2015))
European Union	EU Circular Economy Package (CEP).	2020	Aims at increasing recycling rates (65% municipal wastes) and reducing the waste sent to landfill in order to create a cleaner waste industry and reduce carbon emissions	The Waste (Circular Economy) (Amendment) Regulations (2020))
Malaysia	Environmental Quality Act (Section 21,30A & 51)	1974	Aims to monitor the emission, discharge or deposit of environmentally hazardous substances by reducing, recycled, recovered or regulated.	Environmental Quality Act 1974 (2006)
	Solid Waste and Public Cleansing Management Act (Section 101)	2007	Aims to promote the usage of eco-friendly material, reduce the generation of solid waste, promote recycling, reducing and reusing of controlled solid waste.	Solid Waste and Public Cleaning Regulation (2007)
Korea	Act on the Promotion of Saving and Recycling of Resources	2002	Aims to contribute to the preservation of the environment and sound development of the national economy by regulating the use of recycled resources by controlling the generation of wastes and facilitating recycling.	Act on the Promotion of Saving and Recycling of Resources (2002)
	Construction Waste Recycling Promotion Act	2003	Aims to promote the efficient use of national resources by facilitating the proper environment-friendly disposal and recycling of construction waste generated during construction works, etc. to contribute to the development of the national economy and advancement of public interests.	Construction Waste Recycling Promotion Act (2003)

(*continued on next page*)

Table 5 (*continued*)

Countries	Policies/Acts/Laws/Regulations	Year	Description	References
	Act on Promotion of Purchase of Green Products	2011	Aims to prevent waste of resources and environmental pollution and contribute to the sustainable development of the national economy by encouraging purchase of green products.	Act on Promotion of Purchase of Green Products (2011)
	Act on Resource Circulation of Electrical and Electronic Equipment and Vehicles	2007	Aims to establish a resource recycling system for the efficient use of resources and contribute to environmental conservation and the sound growth of the national economy by placing restrictions on the use of hazardous substances, encouraging manufacturers to produce products readily recyclable, and facilitating the optimum recycling of wastes thereof to ensure that recycling of electrical and electronic equipment, as well as vehicles, can be promoted appropriately	Act on Resource Circulation of Electrical and Electronic Equipment and Vehicles (2007)
	Framework Act on Resource Circulation	2016	Aims to transform the economic structure into a more sustainable and efficient resource-circulating one at a fundamental level by encouraging reusing and recycling wastes rather than disposing into landfills or incinerators.	Ministry of Environment & Korea Environment Institute (2016)
Singapore	Resource Sustainability Act	2019	Aims to implement a framework where parties that profit from distributing products bear the responsibility of their entire life cycle, encourage packaging producers to reduce, reuse or recycle packaging and to enable proper segregation and treatment of food waste.	Resource Sustainability Act (2019)
Iceland	National Plan Waste Management 2013–2024	2013	Aims to reduce the amount of waste and improve the utilization of resources	National Plan Waste Management (2013-2024) (2013)

The bioeconomy is based on an idea of implementing biological principles and processes in all economy sectors and replacing the fossil-based raw materials at a steady pace with bio-based resources and principles (Dietz et al., 2018). This economy was believed to be more sustainable since the use of fossil-based materials will be replaced with biological resources (Mohan et al., 2019). The bioeconomy comes in many definitions. According to the German Bioeconomy Council (2020), bioeconomy is defined as "*the production and utilization of biological resources (including knowledge) to provide products, processes and services in all sectors of trade and industry within the framework of a sustainable economy"*. The European Union adopted the Europe's Bioeconomy Strategy in 2012 and defined bioeconomy as *"the production of renewable biological resources and the conversion of these resources and waste streams into value added products, such as food, feed, bio-based products as well as bio-energy"* (European Commission, 2017). The Global Bioeconomy Summit (2018) defined bioeconomy as *"the production, utilization and conservation of biological resources, including related knowledge, science, technology, and innovation, to provide information, products, processes and services in all economic sectors aiming toward a sustainable economy"*. European Commission (2018) stressed that a sustainable bioeconomy is the renewable segment of the circular economy.

5. Future directions and concluding remarks

We understand that it has always been a challenge to utilize biowastes for production of any types of value-added products. In commercial aspect or large scale production, the availability, purity as well as composition of wastes have always been a topic of debate. However, the many examples of successful cases described in this review is a testament of the worldwide research effort in materializing biowastes in order to create a viable circular economy model. The production of value-added materials using wastes needs to be addressed in both up- and downstream processes especially when is involves the use of microorganisms. By adopting next-generation biotechnology approaches in bioconversion of biowastes, it is possible to design optimal processes for maximal output. For example, using robust microbial strains which can be cultivated under non-sterile conditions or manipulation through genetic engineering. Engineered and versatile microbes can grow in stressed and impure conditions under cost effective methods. The valorization of biowastes and establishment of consolidated process of pre-treatment, microbial fermentation and extraction processes enables sustainable utilization of renewable resources.

This review has highlighted the opportunities and potential of biowaste used as feedstock for microbial fermentation, circular economy implementation by countries and the future directions of biotechnologically important products. Based on the studies on the literatures, biowaste was used as feedstock because it is renewable and cheap. It is evident that recycling of biowaste as feedstock embraces the circular economy and the SDG realizing the waste management via bio-based approach. The sustainability of microbial factories is unquestionable because of the vast amount of biowaste produced by the world. With this 'waste manager', biowaste can be more manageable leading to less capacity of landfill needed, less pollution and increased cost effectiveness. Not only that, the existence of microbial factories can redefine the term 'wastes' and the dependence on synthetic compounds can be reduced thus solving the rise in pollution and biowaste accumulation in landfills. In a nutshell, the interest towards bioeconomy or circular economy has spearheaded research towards developing bioprocesses based on renewable substrates and the efficient management of agro-industrial waste. A comprehensive regulatory in respect to environmental protection plays a key role in the development of a holistic and systematic evaluation of sustainability. It is also evident that government has coherently supported the development of circular economy based on agro-industry residue based products through the implementation of new legislation and policies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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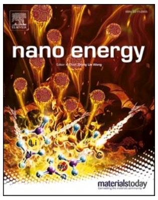

Biomemristors as the next generation bioelectronics

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ABSTRACT

Biomemristor has attracted a lot of attention due to its excellent scalability, high flexibility, easy processing and low fabrication cost. Natural biomaterial and polymer-based memristor has been demonstrated for promising applications because of their sustainable, non-toxic, environmental-friendly, degradable and biocompatible properties. Many biomaterials, which have abundant sources and simple extraction processes, have been widely explored as switching function layers for memristor applications. In addition, biomaterial-based memristors are expected to have fascinating applications in biomedicine because of their potential to combine with organisms and resorbable medical implants. This review will discuss the potential applications, physical mechanism and critical issues of the biomemristors as the next generation bioelectronics for information processing and human-machine interaction. In particular, we propose some cutting-edge potential applications of biomemristors, which may inspire future development for new types of bioelectronic devices.

1. Introduction

The utilization of organic materials has received extensive attention. Recently, they have been widely explored and applied in various types of electronic devices, such as organic biosensor, organic photoresponsive diode, organic field effect transistor, organic photosensor, organic solar cell, and so on [1–22]. Furthermore, the organic electronic devices are promising for commercial manufacturing because of their high scalability, easy processing, superior flexibility, wearability, and cheap production costs [23–32]. Due to the advantages of organic electronic devices, they are highly desirable to be employed as new memristors for the next generation information storage technology [33–40]. Therefore, enormous efforts have been devoted to the biomaterial-based memristors for developing memory based technology from laboratory to large-scale practical applications.

The existing memory devices, such as Si-based flash memory devices, ferroelectric random access memory (FeRAM) and magnetoresistive random access memory (MRAM), have shown some drawbacks for high performance requirements because they are closing to the storage limit. Among all the new concept memory devices currently proposed, resistive random access memory (ReRAM memresistor or resistive switching) is a promising candidate for the next generation of nonvolatile random access memory (NVRAM) because of the ultrafast reading-writing speed, high storage density, low power consumption, and nanoscale engineering capability [41–46]. The information memory in ReRAM is realized based on the memristive effect, by which the resistance of ReRAM cell can be reversibly switched between high resistance state (HRS) ("OFF" state) and low resistance state (LRS) ("ON" state) [47–49]. Before Chua proposed the concept of memristor in 1971 [50], the memristive phenomenon had been observed in some metal oxides [51], but it did not attract much attention. In 2008, Hewlett-Packard (HP) laboratory provided a substantial proof that the memristive effects were achieved in TiO_2-based device and can be further applied for information storage, which aroused widespread influence [52].

A typical memristive device is a sandwich architecture containing a function layer and two conductive electrodes [53–56]. Basically, the memory behavior is derived from the formation of conductive filaments, Schottky excitation, the tunnelling effect of charge, the traps and detraps of electrons, and the charge transfer memchanisms [57–60]. Therefore, it does not impose strict restrictions on the type of functional material.

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Fig. 1. A scene of the relationship between the natural world and the nanoscale electronic device systems.

This indicates the possibility to employ inorganic or organic materials as a function layer to prepare memristive devices.

Based on the above description, a fascinating nanoscale electronic device system involves the memory logic gates, logical circuit displays, data storages and neuromorphic computing. This can be constructed using the natural biomaterials in nanoscale electronic system, as shown in Fig. 1. This figure reflects the mutual conversion relationship between natural world (including various animals, organisms and microorganisms) and nanoscale electronic device systems (including various electronic components). The use of natural biomaterials and polymer in electronic devices can possibly realize the recycling of electronic devices for sustainable electronics industry due to its degradability. The sustainability between natural world and electronics industry can be achieved. Therefore, the development of natural biomaterial and polymer-based bioelectronics for information processing is of great potential for an integrated sustainable electronics with environmental-friendly economy. With a respect to the significance of the biomaterial-based memristors, this review will discuss the research motivation, potential applications, research progress, and related physical mechanism on biomaterial-based memristors. Besides, a crucial property of non-zero crossing I–V hysteresis curve in biomemristive devices will also be analyzed. To be noted, although the consistent pictures and results have been provided in this review, many detailed mechanisms are still unknown. Thus, it will need to establish physical models for the mechanisms in the future studies.

2. Advantages of natural biomaterials and polymer for biomemristors

Materials used as functional layers of memristive devices are mainly three categories, including inorganic materials (compounds and metal oxides), organic materials (natural biomaterials and polymers) and organic-inorganic hybrid materials. The research on organic materials based memory effect began in the 1970s when the switching phenomenon between different resistance states was observed in polystyrene and copper-tetracyanoquinodimethane (Cu-TNCQ) film [61,62]. Since then, significant progress has been made in organic memory devices. In particular, organic small molecular materials with excellent structure stability will benifit long-term cycle performance during memory operation. In addition, the structure of small organic molecules can be calculated through theoretical simulations for a comprehensive understanding of the physical mechanism [63]. Recently, polymers and natural biomaterials, including polymer mixtures and inorganic-organic composites, are expected to combine the advantages of each material component for high performance memory devices [64–66].

On the other hand, it is urgent to use environmental-friendly and sustainable organic materials to minmize the usage of metal oxides and compounds due to the excessive consumption of resources and the deterioration of environment. Moreover, natural biomaterials can be extracted directly from plants or animals. These biological ingredients are supposed to be inexhaustible and more environmental-friendly. Besides, biopolymers can be produced from living organisms, which does not require complex chemical synthesis and processing. This waste recycling can effectively mitigate the current environmental problems and the cycles of sustainable energy. Therefore, these biocompatible materials should be actively promoted in the advanced manufacturing of bioelectronic devices. Such bioelectronic devices can naturally degrade within a specified time without causing the environmental degradation. Once the biomaterials, including plant, animal and microbial materials, are used as functional layers to prepare biomemristive devices, it will

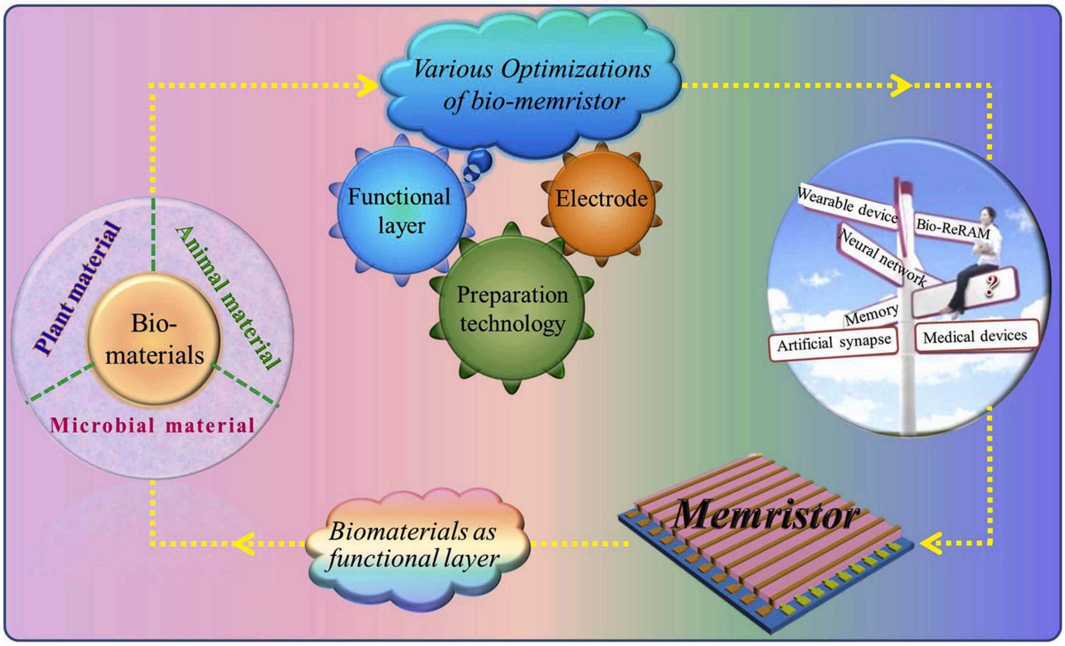

Fig. 2. Long term development goals of biomemristors as the next generation bioelectronics for information processing and human-machine interaction.

Fig. 3. A variety of proposed applications of the natural biomaterial and polymer-based biomemristor.

have an impact to meet long-term development goals, as proposed in Fig. 2. It not only expands the choice of materials for memristive device, but also increases the diversity of memristive applications. Furthermore, significant progress has been made in the biomaterials based memristive effect with sources coming from plants and animals [67–70].

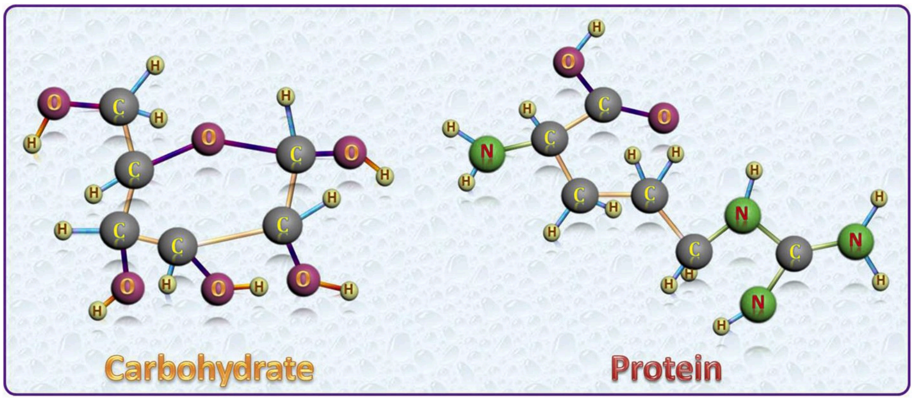

Fig. 4. Schematic diagram of the molecular structure of carbohydrate and protein.

Table 1
Experimental results of resistive switching effect in natural biomaterials.

Year	Functional layer	Top electrode	Bottom electrode	ON/OFF ratio	Mechanism	Ref.
2013	Sericin	Ag	Au	10^6	Trapping/detrapping of charge carriers	[89]
2014	Protein nanocage	Au	Au	4.75	Redox reactions of Fe	[90]
2015	Ag-doped chitosan	Mg	Mg	$>10^2$	Trap controlled SCLC and metallic filament formation	[82]
2015	Silk protein	Ag	Au	$>10^7$	Conductive channels	[91]
2016	Egg albumen	Mg	W	10^2–10^4	Metal filaments accompanied by hopping conduction	[92]
2016	Starch	Au	ITO	10^3	Carbon-rich filaments	[93]
2017	Pectin	Ag	FTO	450	Conductive filament	[94]
2017	Eggshells	Ag	FTO	10^3	Ag metallic conduction filaments	[95]
2018	Egg albumen	Ag	ITO	$>10^4$	Trap-based charge transfer	[96]
2018	DNA	Ag	ITO	10^2	Conductive filament	[97]
2018	Dead leaves	Ag	Ti	50	Conductive filament	[98]
2018	Glucose	Al	P^+ Si	10^3	Formation of local conducting filaments	[99]
2019	Cu^{2+}-doped salmon DNA	Pt	FTO	$>10^3$	Conductive filament	[100]
2019	Human hair keratin	Ag	FTO	10^3	Ag filament	[101]
2019	Natural pectin	Ag	ITO	10^2	Conductive filament	[102]

3. Potential application of biomemristor

Biomaterials based memristive devices have a wide range of potential applications, such as artificial synapses for neuromorphic computing, wearable electronics and implantable device for personalized health, ReRAM device for artificial intelligence, as proposed in Fig. 3. Although the reported applications are very limited so far, these proposed applications will be realized and play an essential role in information processing and human-machine interaction. Recently, lots of attention is attracted to the exploration of memristive effects based on biomaterials due to its great potentials. First, the memristive device made by biomaterials has an impact on sustainability and renewability [71–73]. Biomaterials are also inexhaustible and can be used for printable memristive device [74–77]. Moreover, biomaterial-prepared memristive devices have many other advantages, including implantability, wearability, renewability, degradability, and so on [78–82]. Biomemristor based synaptic and artificial intelligence, in particular, are very attractive. Recently, a significant progress and potential applications of biomaterial-based memristors has been developed with advanced versatility [83–88].

4. Natural biomaterials based biomemristors

4.1. Research progress

Natural biomaterials based memristive devices are made by biopolymers produced by organisms. These biopolymers can be divided into two categories: carbohydrate and protein. Their molecular structures are shown in Fig. 4. The molecular structure of carbohydrates contains only three elements: carbon (C), hydrogen (H), and oxygen (O). However, besides C, H and O, proteins usually contain nitrogen (N) from amino acid, and some trace element such as iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), and so on. Therefore, their memristive effect should be different because the addition of trace elements may help the formation of conductive filaments and redox reaction, which can effectively improve the performance of the memristive effect.

The reported characteristics of biomemristors have been listed in Table 1 for comparison. Firstly, Chen's group prepared a resistance switching device on flexible substrates using natural sericin in 2013 and achieved multilevel nonvolatile memory [89], as shown in Fig. 5. They found the resistance switching device using sericin as function layer displayed high resistance memory performance. This provides an example for the development of electronic device using waste as a raw material. Moreover, their work laid a foundation to utilize biomaterials as a functional layer for the preparation and application of multistate memristor. Subsequently, they developed a fabrication strategy for memristive nanodevices with stable and tunable performance based on protein nanocages [90]. This research work proves that higher Fe loadings contribute to better memristive performance. This work provides a reliable evidence for the use of hybrid biomolecular nanostructures to produce functional nanodevices, and shows that biomaterial-based electronic devices can achieve higher performance applications, paving the way for future development of bioelectronics can be used to make integrated electronic devices such as neuromorphic computers. Furthermore, Lee's group prepared a flexible and transparent resistive switching memory with a coplanar structure of Mg/Ag-doped chitosan/Mg on a natural organic polymer [82]. This provided an important step towards developing flexible and biodegradable resistive switching memory device. Besides, Wang et al. optimized the preparation process of resistive switching devices with

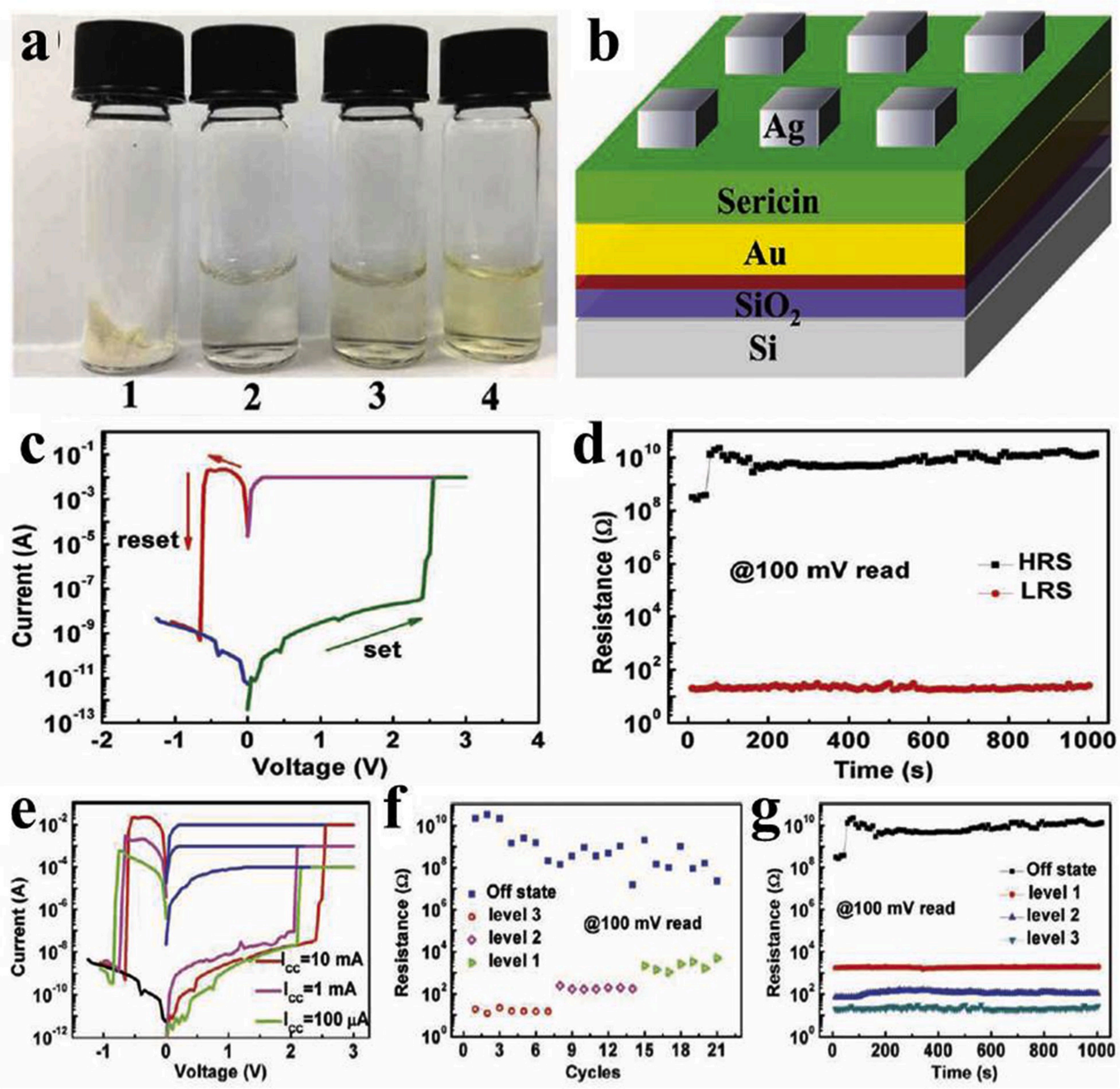

Fig. 5. (a) Optical images of sericin; 1: powder; 2–4; aqueous solution of sericin at concentrations of 16, 26, 35 mg/mL, respectively. (b) Schematic of the fabricated device with Ag/sericin/Au configuration. (c) Typical current versus voltage (I–V) curves of the Ag/sericin/Au device with an area of 120 × 120 μm^2 in voltage sweeping mode at ambient condition. A compliance current of 10 mA is used to prevent the breakdown of the device in set process. (d) Retention characteristics of both resistance states under a continuous 100 mV readout voltage at room temperature. (e) Typical I–V curves of the device under different compliance currents of 10 mA, 1 mA, and 100 μA. (f) The resistance of the device over 21 cycles with different compliance currents of 10 mA, 1 mA, and 100 μA. (g) The retention characteristics of different resistance states under a continuous 100 mV readout voltage at room temperature. All panels reproduced with permission [89]. Copyright 2013, Wiley-VCH.

configurable functionality based on naturally silk protein [91]. They showed the memory behaviors can be effectively and exactly controlled by adjusting the compliance current during the set process. This suggests the potential application of silk protein for sustainable electronics and effective data storage.

Due to the development of the preparation methods for bio-memristive devices, the selection of biomaterials becomes more diverse. Wang and Luo's groups made a transient resistive switching device by egg albumen dielectrics and dissolvable electrodes (Mg and W as the top and bottom electrodes) [92]. This provides high performance of resistance switching. Moreover, the Mg and W electrodes, and albumen film can be dissolved in water within 72 h, indicating the advantages of transient and self-degradation. Zhou et al. utilized hydrogen-peroxide-modified egg albumen to assemble transparent and flexible resistive switching memory device [96]. The results showed that the 10%-hydrogen-peroxide-modified egg albumen presents maximized electrical characteristics. They proposed a new mechanism, which is a trap-based charge transfer physical model to interpret the resistive switching memory behavior, as shown in Fig. 6. Based on this work, our group prepared ultra-flexible egg albumen paper with a dielectric constant of about 15–21, which is nearly 300% higher than that of natural egg albumen. The study demonstrated that the wearable memristor array made from the egg albumen paper showed high performance information storage and the logic gate function under dual photoelectric control (Fig. 7). This work laid the foundation for egg albumen-based memristors in logic circuits. Furthermore, it should be mentioned that Niloufar et al. demonstrated a robust, nonvolatile, flexible, and transparent memristive device based on potato starch [93]. In particular,

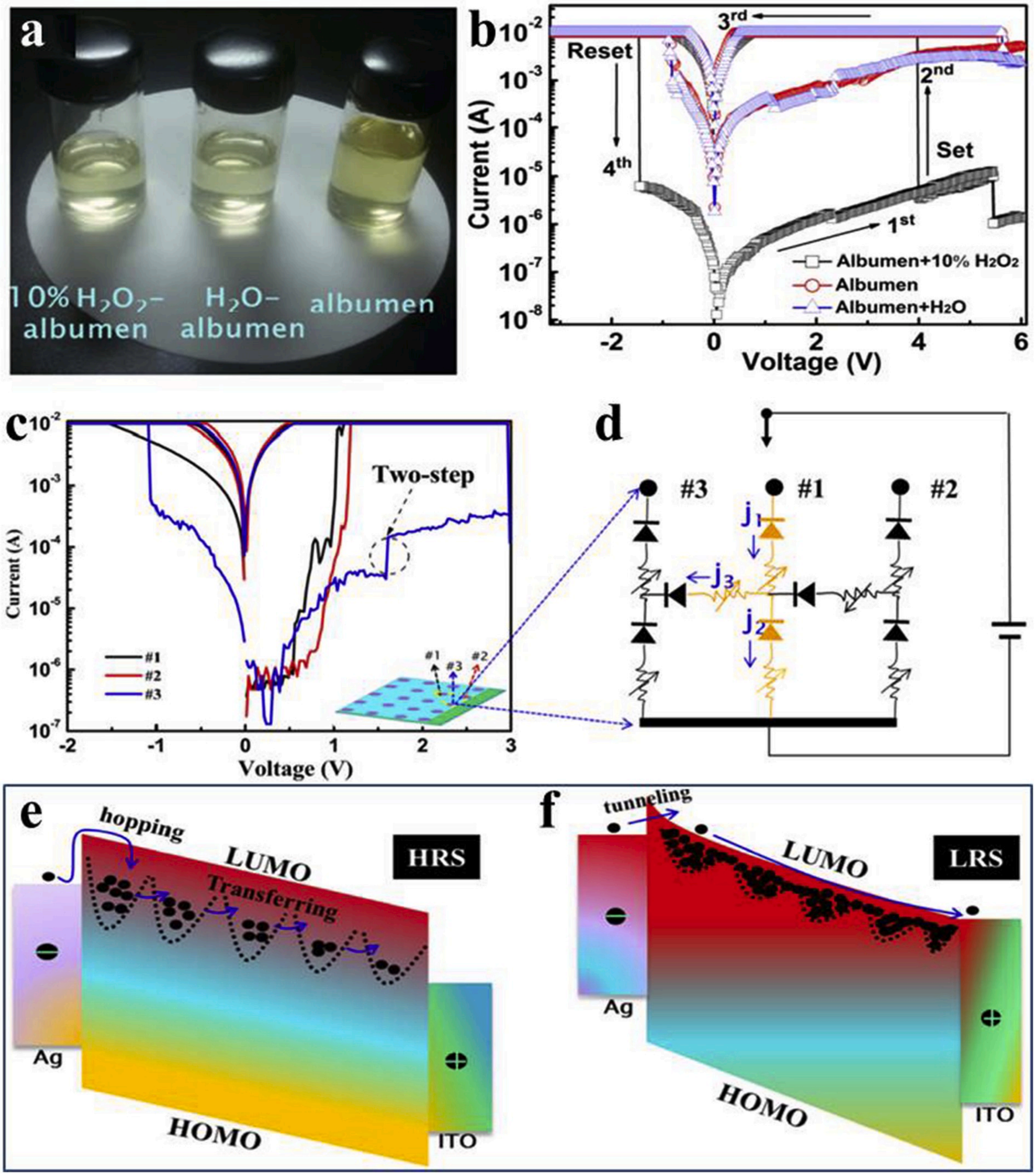

Fig. 6. (a) Solutions of pristine albumen, H_2O-albumen and 10% H_2O_2-albumen at a volume ratio of 1:10, respectively. (b) The current–voltage (I–V) characteristics of the memory cells with the active film of pristine egg albumen, H_2O-egg albumen and 10% H_2O_2-egg albumen, respectively. Resistive switching memory effects were observed in all the memory cells, but enhanced behavior was obtained in the 10% H_2O_2-egg albumen-based memory cell. (c) The typical I–V characteristics for neighboring cell numbers 1, 2 and 3, respectively. Before carrying out the I–V test using the optimized device, all of the memory cells except numbers 1, 2 and 3 are in low resistance states. (d) The logical equivalent circuit for the neighboring memory cells. (e, f) A schematic diagram of the charge transfer physical model. All panels reproduced with permission [96]. Copyright 2017, IOP Publishing.

memory devices using starch-chitosan mixtures exhibit gradual set/reset behavior, and such excellent performance devices can be used in neuromorphic devices.

Pectin, a biomaterial from plant that is thought to be not recyclable, was first introduced as a functional layer to create a new type of organic resistance switching memory device with Ag/Pectin/FTO structure [94]. The device exhibited long-lasting switching endurance accompanied by a large HRS/LRS resistance ratio (resistance memory window) of ~450 with promising application for nonvolatile memory applications. Besides, it was observed a large resistance ratio of ~10^3, wide memory voltage window of ~3.5 V, high endurance and retention performances in eggshells-based memristive device [95]. A recent report introduced DNA as a functional layer in the biomemristors. Specifically, Hung assembled successfully natural DNA into memristive devices by solution-processed method [97]. The device exhibited a reliable resistive switching behavior with retention time of 10^4 s and no sign of obvious deterioration after 200 operation cycles. Meanwhile, the device showed multilevel operation with low switching voltages [97].

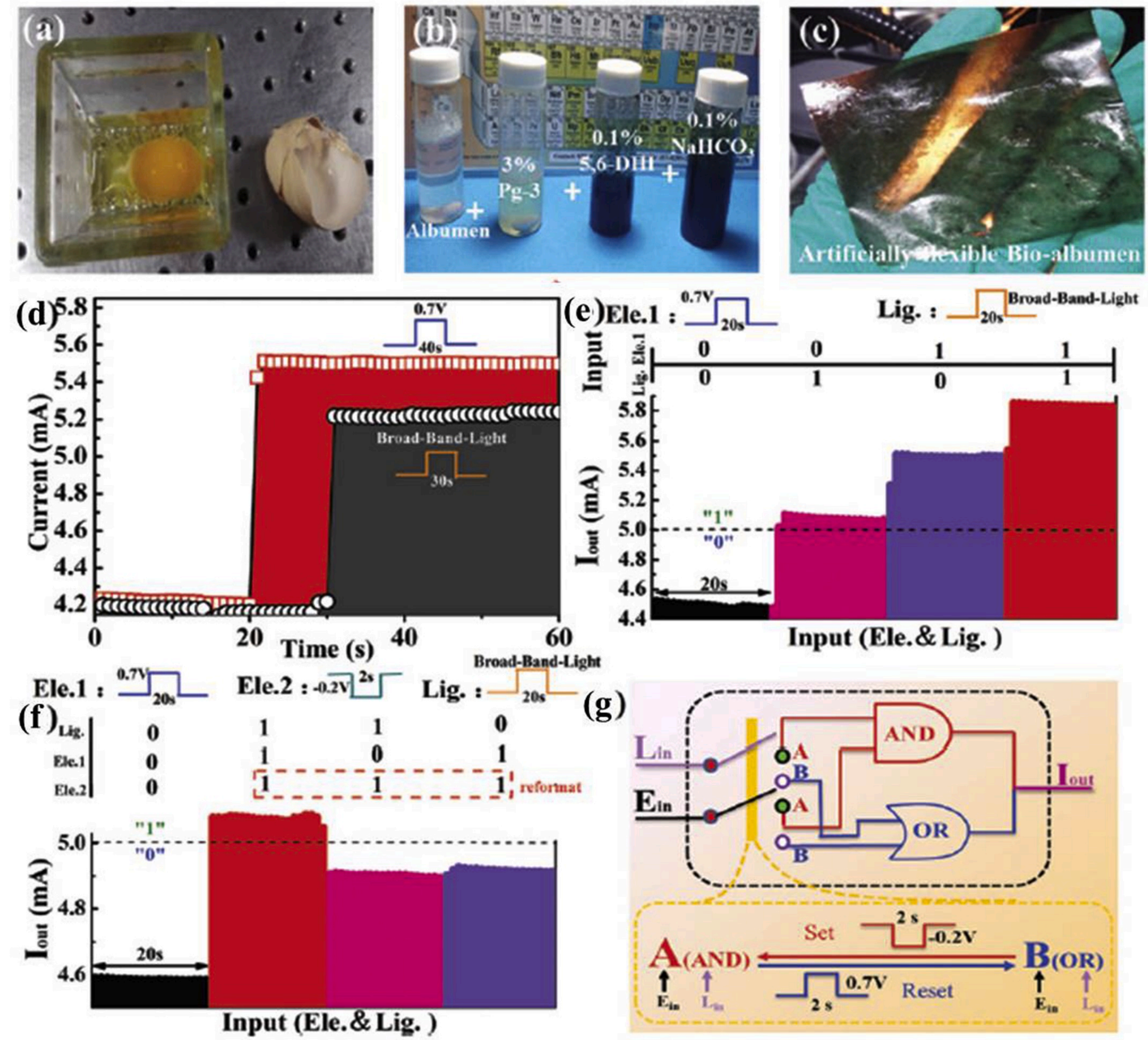

Fig. 7. (a) Optical images of native egg albumen solution. (b) Precursor solutions after native solution was sequentially reacted with polyglycerol-3(Pg-3), 5,6-dihydroxyindole (5,6-DHI) and $NaHCO_3$. (c) The artificial egg albumen substrate. (d) Two input signals: a broad-band light signal and an electric signal. (e) By applying the light or electric signals, an output current indicating "0″ or "1″ can be obtained under the defined current line of 5.0 mA. (f) A reformation electric signal of −0.2 V is added to the former input signals. (g) A schematic diagram of the memory logic gate switching between "OR'' and "AND'' states. All panels reproduced with permission [44]. Copyright 2019, Royal Society of Chemistry.

Reutilization and degradability are two crucial concepts for the development of biomemristor. Dead leaves, the most common type of waste material spreading across the earth, can be employed to fabricate organic resistive switching memory device with Ag/Leaves/Ti/PET structure on a flexible polyethylene terephthalate (PET) substrate [98]. The devices showed obvious resistive switching memory characteristics, large switching resistance ratio and stable cycling performance [98]. In addition, S. P. Park et al. reported a transparent memristive device with bipolar resistive switching behavior based on biocompatible glucose film, dissolvable Mg electrode, and edible substrate (rice paper) [99]. The biodegradability and switching characteristics of the memristive devices were analyzed illustrated in Fig. 8. It shows that the low-cost and biodegradable glucose-based memristor has attractive potential applications, such as biocompatible medical electronics and green electronics.

Recently, Y. Abbas et al. fabricated and characterized the transparent and biocompatible resistive switching random access memory (ReRAM) device with the structure of Pt/Cu^{2+} doped salmon DNA/FTO where Cu^{2+} was doped into salmon DNA by solution-processes [100]. This device showed excellent bipolar switching characteristics with set and reset processes during negative and positive sweeps, respectively [100]. Meanwhile, Tang's group reported that the thin films of biocompatible keratin from human hair can be used as solid electrolyte layer in resistive switching memory devices [101], as another environmental-friendly, sustainable and inexpensive candidate for memory applications. Furthermore, natural orange peel can be introduced to fabricate resistive switching memory devices and excellent resistive switching characteristics (Ag/pectin/ITO) [102]. Additionally,

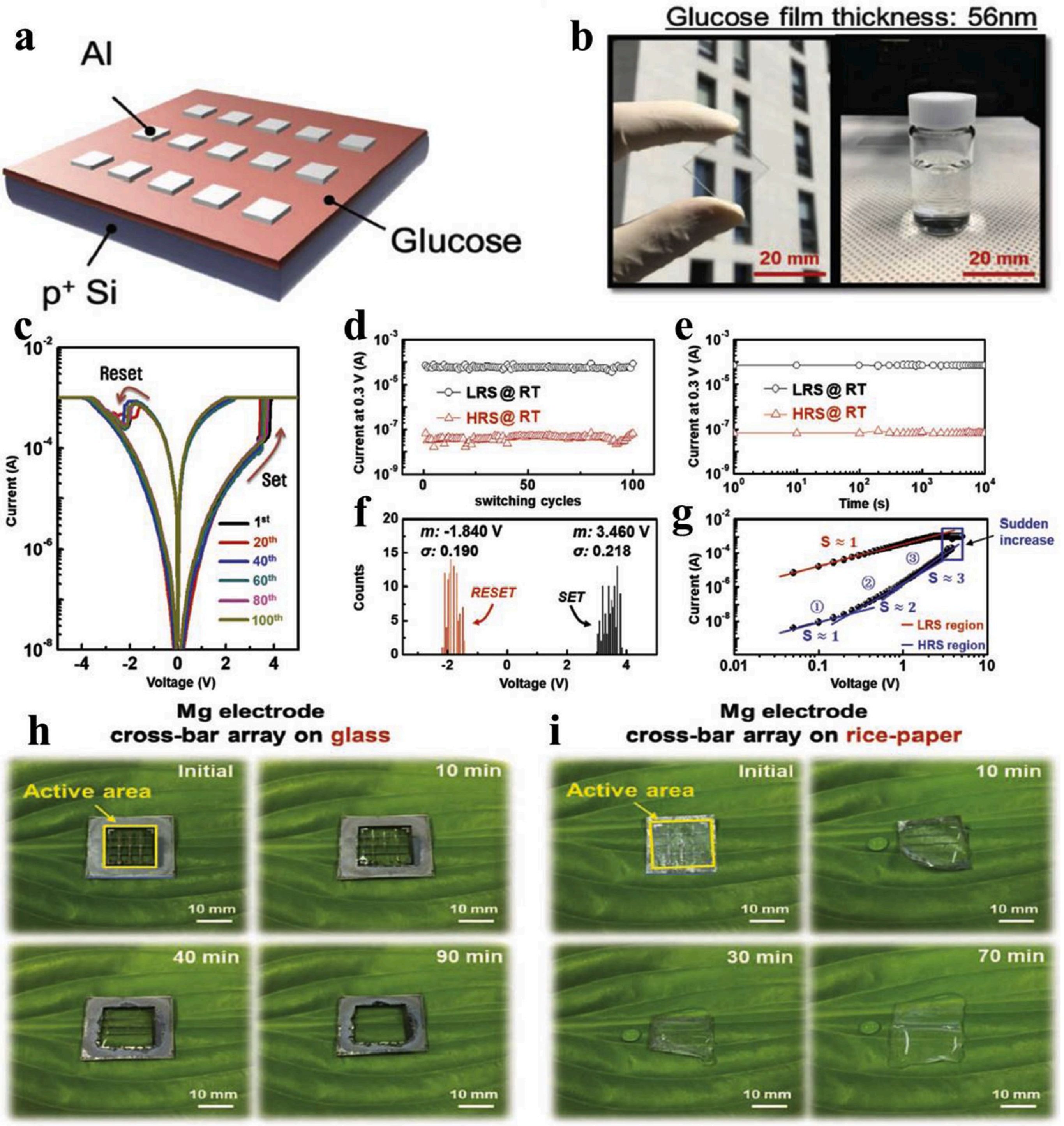

Fig. 8. (a) Device structure of glucose-based ReRAM. (b) Photograph of glucose film with thickness information on glass substrate and synthesized solution. (c) Extracted I–V switching characteristic of glucose-based ReRAM for 100 repetitive cycles. (d) Switching endurance results measured up to 100 cycles. (e) Data retention results for 10^4 s. (f) Histogram with average and standard deviation value of set/reset voltage distribution. (g) Double logarithmic fitting of I–V switching characteristics. (h, i) Procedure of degradability test and photograph of glucose-based ReRAM devices with Mg electrode fabricated on glass and rice paper with elapsed time. All panels reproduced with permission [99]. Copyright 2018, Wiley-VCH.

when acid solution was used, the Ag/pectin/ITO memory device can be dissolved rapidly in deionized water within 10 min. This is due to the good solubility arising from ionization of its carboxylic groups, which shows a promising application for green electronics.

It should be noticed that a chitosan-based resistive-switching memory device was demonstrated based on natural solid polymer electrolytes by Jang-Sik Lee et al. [103]. Fig. 9a shows the schematic illustration of device architectures, and the chemical structure of the bioactive layer and the thickness information of each layer of the device can be found in Fig. 9b. The optical photo of a single device unit is presented in Fig. 9c. The inset of Fig. 9d is a schematic diagram of a connection circuit for measuring the memristive performance of the device. The semi-logarithmic I–V characteristics of a chitosan-based resistance switch memory device with an $AgNO_3$ concentration of 5 wt% at room

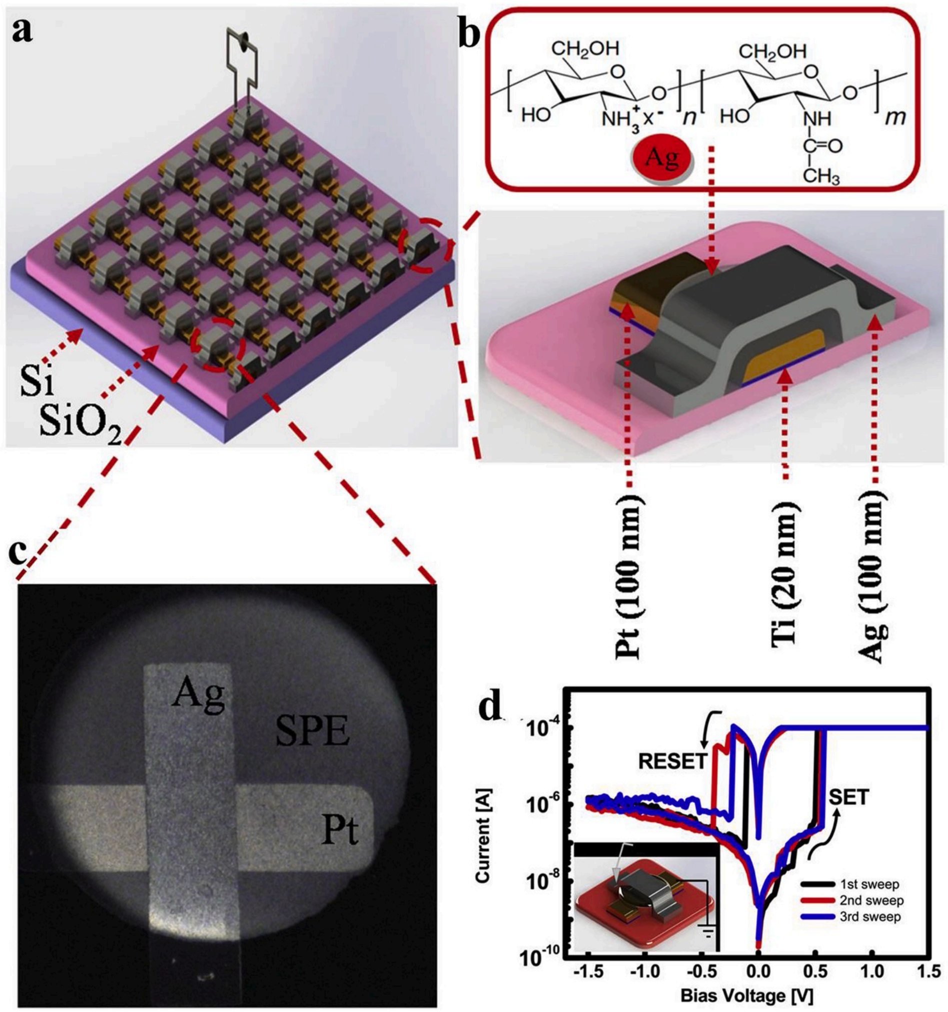

Fig. 9. (a) Schematic illustration of device architectures, (b) a unit device configuration with Ag-doped chitosan as resistive switching layer, (c) optical image of cross junction electrodes with drop-casted chitosan solid polymer eletrolyte, and (d) semilogarithmic I–V characteristics of the chitosan-based resistive switching memory device with an $AgNO_3$ concentration of 5 wt % at ambient temperature; inset: illustration of a unit device configuration to measure the electrical properties. All panels reproduced with permission [103]. Copyright 2015, American Chemical Society.

temperature are shown in Fig. 9d. This work shows that the use of biomaterials as functional layers can achieve biocompatible and flexible memristors. Chitosan usually comes from the shells of shrimp, a biological waste. Thus, by using chitosan to prepare electronic devices can achieve sustainable development goals.

The above research works show that natural biomaterials can be used as functional layers in the preparation of resistance switching devices. These natural biomaterials were extracted from plant or animal tissues through a simple chemical process. In future work, we propose the following strategies to improve the resistance switching performance of natural biomaterials. (1) One can improve the extraction process or extraction method of natural biomaterials to prepare high-quality functional layers in resistive switching devices; (2) One can doping conductive nanoparticles in the functional layer because conductive nanoparticles can effectively improve the carrier migration in the functional layer, thereby significantly improving the resistance switching characteristics of natural biomaterials; (3) Organic-inorganic heterojunctions can be prepared as the functional layer, thus forms a charge-limited interfacial layer, thereby improving resistance switching performance. New preparation and processing methods will enable the large scale preparation and application of natural biomaterials based memristive devices.

4.2. *Physical mechanisms of natural biomaterials based biomemeristors*

It is a consensus that the practical application of any new physical effects is based on a comprehensive understanding of the physical mechanisms. Several mechanisms are proposed to explain the resistance switching process in metal/insulator/metal (MIM) structure. These include conductive filaments, the Schottky barrier, tunnelling effect, the filling of electrons, thermochemistry, charge transfer, and interfacial effects [104–113]. The instinct nature of natural biomaterials determines that they contain rich chemical ions instead of strict physical band structure. Therefore, the mechanism of biomemristor is mostly related to the redox reaction of ions or the formation of conductive filaments [114–128]. Physical mechanism in biomemristors will be discussed in the following paragraphs.

Conductive filament has been widely used to explain resistance switching phenomenon. Jeng et al. proposed an formation and dissolution of Ag filaments based on natural DNA-derived biomaterials as functional layer in a biomemristive device, as shown in Fig. 10a [97]. Ag, a popular top electrode in memristors, is an active metal to accept and lose electron under the electric field [129–131]. The Ag^+ ($Ag \rightarrow Ag^+ + e^-$) can penetrate the active layer and migrate to the bottom electrode under the electric field. Simultaneously, a cathodic reaction occurs at the interface between inert electrode and the functional layer. Ag^+ will be reduced to Ag atoms ($Ag^+ + e^- \rightarrow Ag$) to build the Ag conductive bridge between top and bottom electrodes. Thus, the conductive bridge provides a transport pathway and leads to the dramatic decrease of resistance. Therefore, the device switches to LRS. When the polarity of the voltage reverses, the conductive filament consisting of Ag atom will be dissolved ($Ag \rightarrow Ag^+ + e^-$). Ag^+ ions will move to the active electrode. Thus, the device switches back to the HRS. Besides Ag filaments, other active materials can also undergo redox reactions to form

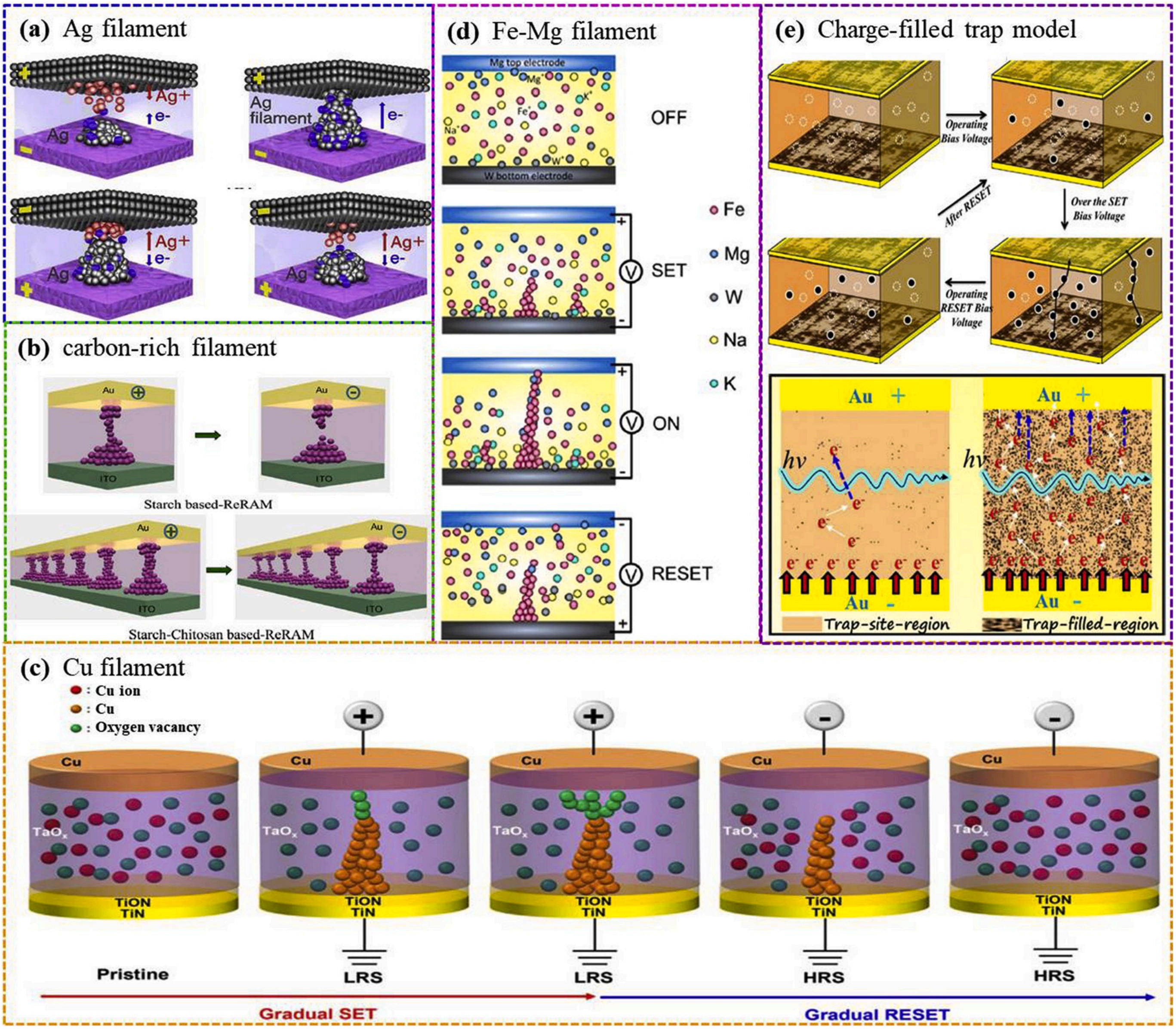

Fig. 10. Various physical mechanisms have been reported in biomemristive devices in the previous literatures. (a) Ag filament. Reproduced with permission [97]. Copyright 2018, Elsevier. (b) Carbon-rich filament. Reproduced with permission [93]. Copyright 2016, American Chemical Society. (c) Cu filament. Reproduced with permission [132]. Copyright 2015, Elsevier. (d) Fe–Mg filament. Reproduced with permission [92]. Copyright 2016, American Chemical Society. (e) The charge-filled trap model. Reproduced with permission [44]. Copyright 2019, Royal Society of Chemistry.

conductive filaments.

N. Raeis-Hosseini and J. S. Lee reported a starch-based flexible biomemristors, in which the resistive switching behavior is controlled by adding chitosan into the function layer [93]. The chitosan can influence the formation and rupture of carbon-rich filaments and further adjust the resistive switching behaviors (Fig. 10b). H. Y. Jeng et al. prepared a nonvolatile resistive memory devices based on solution-processed natural DNA biomaterial. The switching mechanisms can be explained by the formation and dissolution of Cu filaments [100]. At the same time, H. Jeon et al. combined oxygen vacancy/Cu conductive filaments to understanding the resistive switching behaviors of Cu/TaOx/TiN device, as shown in Fig. 10c [132]. Besides, the investigation of Mg/Egg albumen/W biomemristor proved that Fe^{3+} and Mg^{2+} can form conductive filament, as shown in Fig. 10d [92]. The device can realize the switching of resistance between LRS and HRS to complete the storage of information. The above work shows that the redox reaction of the active metal can help the formation of conductive filaments in the functional layer, which ensures that the effective switching characteristics of the resistive switching device driven by an external voltage. Therefore, the use of active metal electrodes or the doping of active metals into the biological functional layer may help improve the memristive effect and increase the durability of the memristive effect.

On the other hand, another physical model of trap-filled physical dynamic mechanism has been proposed shown in Fig. 10e [44]. In albumen protein based memristor devices, de-trapping and hopping processes of the photo-generated charges are happened under light illumination. This can directly contribute to the current increase. In the LRS, all trap locations are almost filled with charged carriers. The density of de-trapped charges in hopping processes will significantly increase under the light-illumination and cause a sharp increase of current value. By contrast, the detrapping and hopping processes are greatly weaker under the low density of charges in HRS without light. Thus, it can barely change the current value at HRS. Thus, the switching processes can be adjusted under light modulation. This provides a prototype

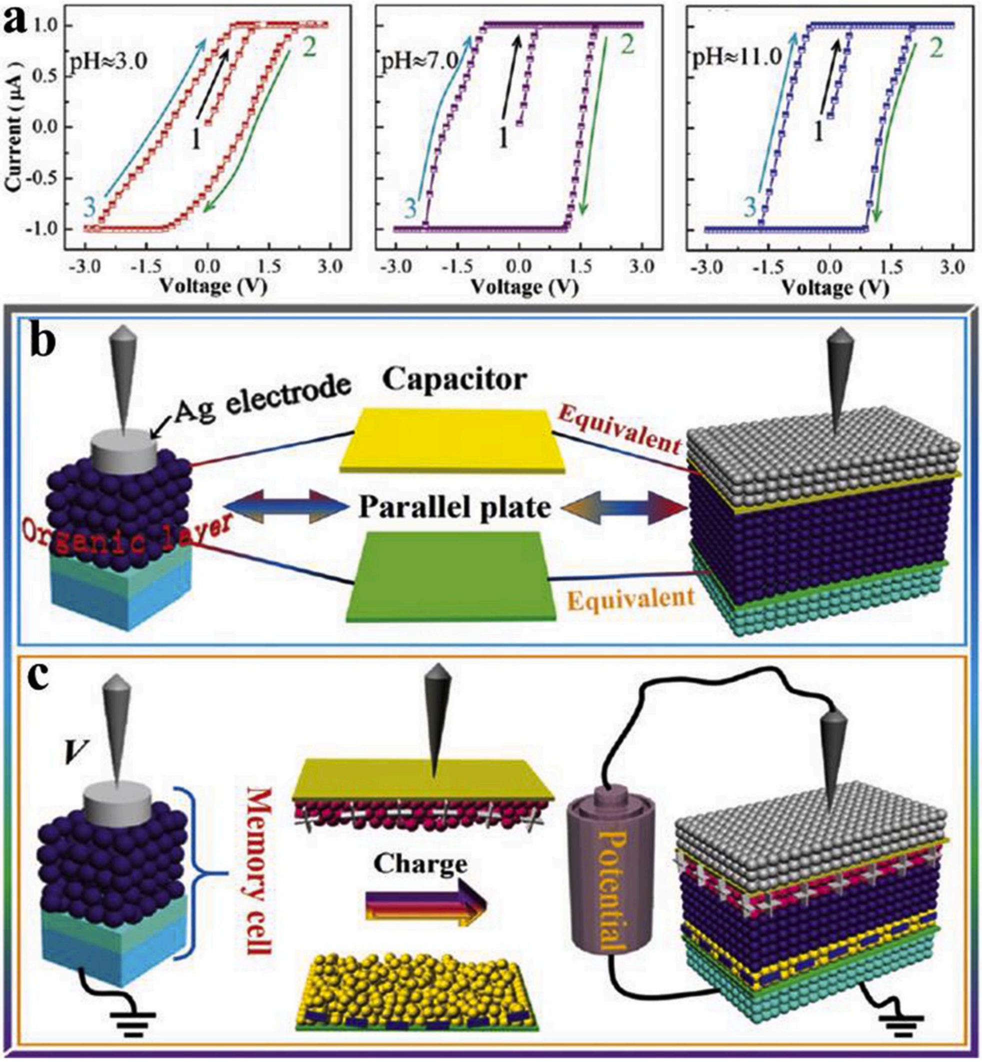

Fig. 11. Capacitive effect induced non-zero-crossing I–V hysteresis behavior in the natural biomaterial-based memristor. (a) Non-zero-crossing I–V hysteresis curves. (b) The equivalent circuit diagram of the memristor and capacitor. (c) The change of the memristor between the HRS and LRS is equivalent to the charging and discharging processes of the capacitor. All panels reproduced with permission [133]. Copyright 2019, Royal Society of Chemistry.

of light-controlled biomemristor.

The mechanisms reported in natural biomemristors are summarized as above. Although they can explain the corresponding physical phenomena relatively well, it is still under debate. Future research in the mechanism of natural biomemristors is still needed.

5. Non-zero crossing I–V hysteresis curve in natural biomaterials based biomemristor

5.1. Phenomenon of non-zero crossing I–V hysteresis curve

In many previous studies, the non-zero-crossing I–V hysteresis behavior in natural biomaterial-based memristors was observed [133–137]. It is believed that these non-zero-crossing phenomena are correlated with capacitive effects. For example, a pH-controlled resistive switching memory device was prepared using self-colored $(C_7H_7O_4N)_n$ extracted from a lichen plant [133]. We observed a capacitive effect induced non-zero-crossing I–V hysteresis behavior in this natural biomaterial-based memristor [133]. The non-zero-crossing I–V hysteresis curves are shown in Fig. 11a. The equivalent diagram of the memristor and capacitor is displayed in Fig. 11b. In this biomemristive device, the change of the memristor between the HRS and LRS is equivalent to the charging and discharging process of the capacitor (Fig. 11c). In previous reports, non-zero-crossing I–V curves in memristive effects have also been reported in some inorganic oxides and composites [138–144]. The related physical mechanisms are discussed later.

It is well known that capacitor is one of the basic components in the integrated circuits. It has a very broad and important application in the semiconductor industry and complementary metal oxide semiconductor (CMOS) circuits. This non-zero-crossing I–V behavior indicates that capacitive and memristive effects can occur in the same device [145, 146]. This multiple physical effects in the same device is the basis for a multifunctional device that can simultaneously achieve the functions of capacitive effect and memristive effect.

The property of natural biomaterials can be adjusted by changing the concentration of H^+ and OH^- (pH value) to control the performances of biomemristors. The pH-controlled memristive devices can perform a similar function as neurons. This can be used to simulate neurons in biological systems. The schematics illustrates the pH-controlled steps of signal processing [134], as a potential application using neuromorphic functionalities. For example, the pH-controlled memristor can be designed as a pH sensor to detect the pH level of organisms in real time, as shown Fig. 12. This work paves a new way for the development of medical devices. Therefore, biomemristive devices based on natural biomaterials have a wide range of potential applications in biomedicine,

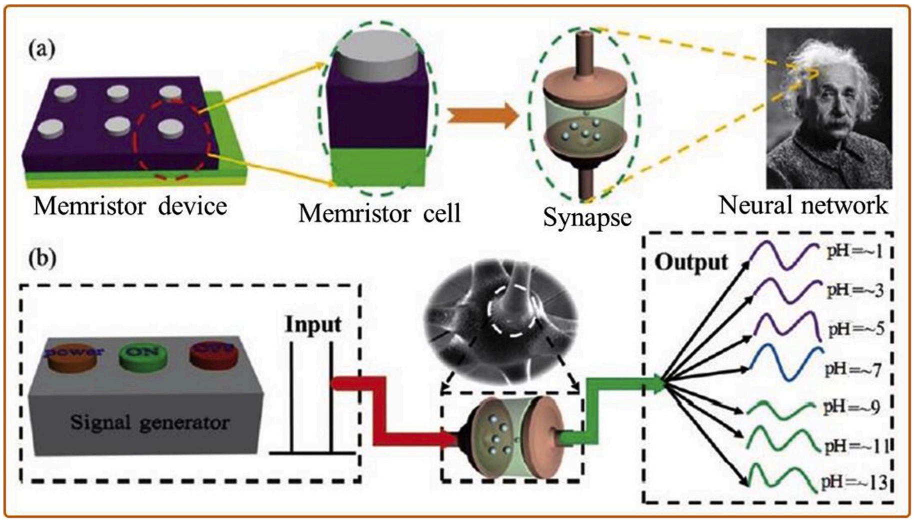

Fig. 12. (a) A schematic diagram of a memristor simulating the human brain in the future. (b) The regulation of pH on the neural network under ideal conditions. All panels reproduced with permission [134]. Copyright 2019, Royal Society of Chemistry.

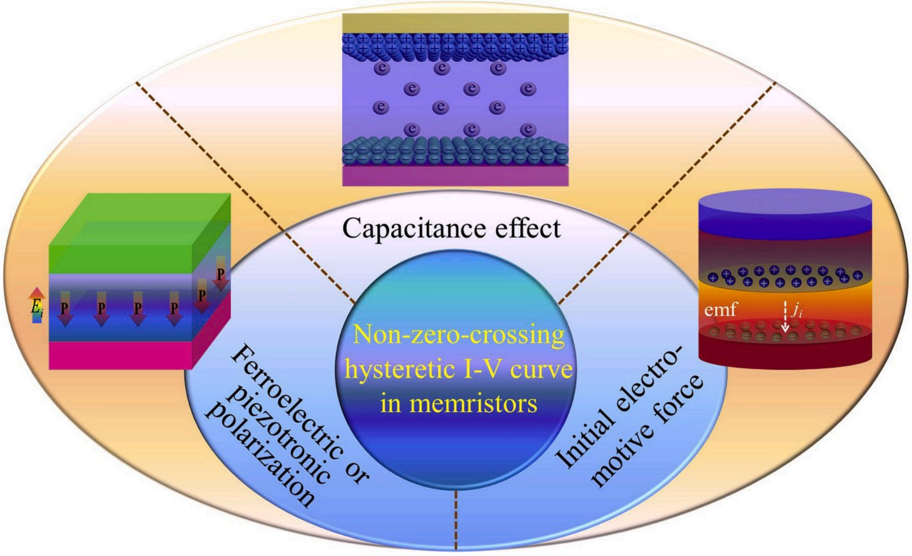

Fig. 13. The physical mechanisms of non-zero-crossing I–V hysteresis curves in memeristive systems. Reproduced with permission [149]. Copyright 2020, Elsevier.

biosensing, biodiagnosis and other fields.

5.2. *Physical mechanisms of non-zero crossing I–V hysteresis behavior*

Non-zero crossing hysteresis I–V curves have been reported [144–148]. In our previous research, we analyzed and summarized all the cases of non-zero crossing I–V curves in memristors [149]. The physical mechanism of generating non-zero crossing I–V curves can be summarized into three categories: the appearance of capacitive effects, the generation of ferroelectric or piezoelectric effect, and the generation of internal electromotive force, shown in Fig. 13. For natural biomaterials based memristors, the appearance of non-zero crossing I–V curves is mainly due to the capacitive effect. When an external voltage is applied to the device, the positive and negative ions in the functional layer are separated, and then distributed near the top and bottom electrodes of the device, which leads to the appearance of a significant capacitive effect. When the external voltage decreases to zero, there will be a non-zero internal current in the functional layer due to the capacitive effect [150,151]. Thus, we can observe a non-zero crossing I–V hysteresis curve. Therefore, the capacitive effect is an important physical mechanism that causes non-zero-crossing I–V curve in biomemristors. In addition, other physical mechanisms, including internal electromotive force, ferroelectric polarization and piezoelectric effect, can also cause the non-zero-crossing I–V curve in the memristor, which are discussed in detail in our previous work [149].

6. Biomemristor based on polymers

6.1. *Research progress of polymers based biomemristor*

Synthetic conductive polymers have been used as promising biomaterials in the preparation of electronic devices [152]. They have many potential applications in biomedicine, such as biosensors, drug delivery systems, and biomedical implants, and so on [153]. Because conductive polymers have many excellent physical properties, conductive polymers have also been used as functional layers in the preparation of biomemristors. This has opened up new research directions for the preparation of bioelectronic devices [154–156].

A. A. Talin and A. Salleo's group designed an electrochemical neuromorphic organic device using a poly(3,4-ethylenedioxythiophene):

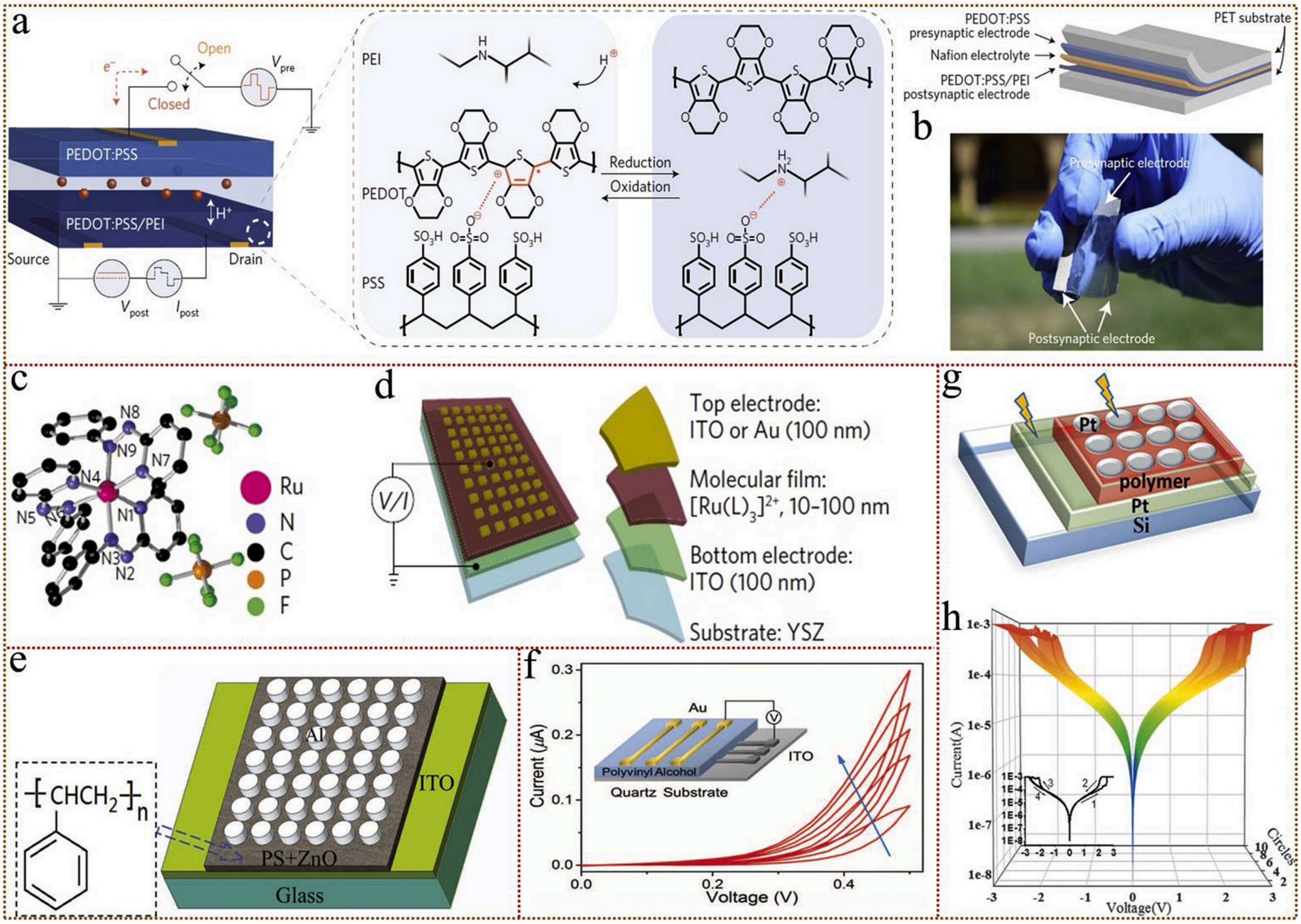

Fig. 14. (a) Sketch of the device structure, and a positive V_{pre} drives protons into the postsynaptic electrode, which results in the compensation of some PSS^- by the protonated PEI and (b) schematic of the device and photograph of the device while being flexed. Reproduced with permission [154]. Copyright 2017, Nature Publishing Group. (c) Molecular view of the compound mer-$[Ru(L)_3](PF_6)_2$ and (d) schematic of our device with the molecular film sandwiched between two electrodes. Reproduced with permission [155]. Copyright 2017, Nature Publishing Group. (e) Schematic diagram of the ITO/PS + ZnO/Al device architecture, and inset: Chemical structure of polystyrene (PS). Reproduced with permission [156]. Copyright 2018, Royal Society of Chemistry. (f) The I–V characteristics of the polymer memristor respond to positive scanning voltage sweeps, and the inset in (f) shows the schematic of the two-terminal cross-aligned structure of Au/PVA/ITO devices. Reproduced with permission [157]. Copyright 2014, AIP publishing. (g) Schematic illustration of the Pt/polymer/Pt structure and (h) consecutive I–V cycles of a Pt/P1/Pt device. Reproduced with permission [158]. Copyright 2014, Wiley-VCH.

polystyrene sulfonate (PEDOT:PSS) film partially reduced with poly (ethylenimine) (PEI) (PEDOT:PSS/PEI) [154], as shown in Fig. 14a. Its working principle is based on the protonation induced polaron change, which is completely different from the ion migration mechanism of other reported memristors. The structure of the functional layer PEDOT: PSS/PEI before and after the redox reaction under an external electric field is shown in Fig. 14a. Further, they fabricated an all solid-state plastic device with nafion as the electrolyte between two flexible PEDOT:PSS films coated on polyethylene terephthalate (PET) sheets and permeated with PEI [154]. The device structure and photography are shown in Fig. 14b. Their work shows an application of memristors using polymers as functional layers for neuromorphic computing [154]. The devices have good biological properties, flexibility and low cost fabrication. It is worth noting that Sreetosh Goswami et al. prepared a memristive device using ruthenium (Ru) and an azo-aromatic ligand as a functional layer with excellent memristive performance [155]. The chemical structure of $[Ru(L)_3](PF_6)_2$ and device structure are shown in Fig. 14c and d, respectively. The functional layer materials have three redox active centers probed by the in situ Raman spectroscopy [155]. They demonstrated two sets of redox reactions. These two reactions can lead to two different conductance states, thereby achieving binary resistive switching memory behavior. They claimed the hysteresis originates from the displacement of the counterions in the aromatic ligand [155].

In addition, Yanmei Sun et al. prepared a memristive device using a zinc oxide (ZnO) nanoparticle-doped polystyrene (PS) as a functional layer [156]. Fig. 14e shows the schematic diagram of the ITO/PS + ZnO/Al device architecture and chemical structure of PS. A changing transport behavior was observed due to the different charge transfer under different resistance states. It is because ZnO particles are electron acceptors in the functional layer, which can be used as charged trap sites when the device is applied with an external voltage [159]. Yan Lei et al. used a polymer of polyvinyl alcohol (PVA) as a functional layer to prepare a biomemristive device, and realized learning and memory functions that are similar to biological systems [157]. The schematic of the Au/PVA/ITO devices is shown in inset of Fig. 14f. It can be found that the device conduction continuously increases during five sequential positive sweeps from the I–V characteristics of the polymer memristor in Fig. 14f. This work demonstrates that PVA-based biomemristive devices can be printed on flexible substrates on a large scale, which can enable the use of low-cost and efficient artificial neural networks in future neuromorphological devices. Similarly, Cheng Wang et al. designed and

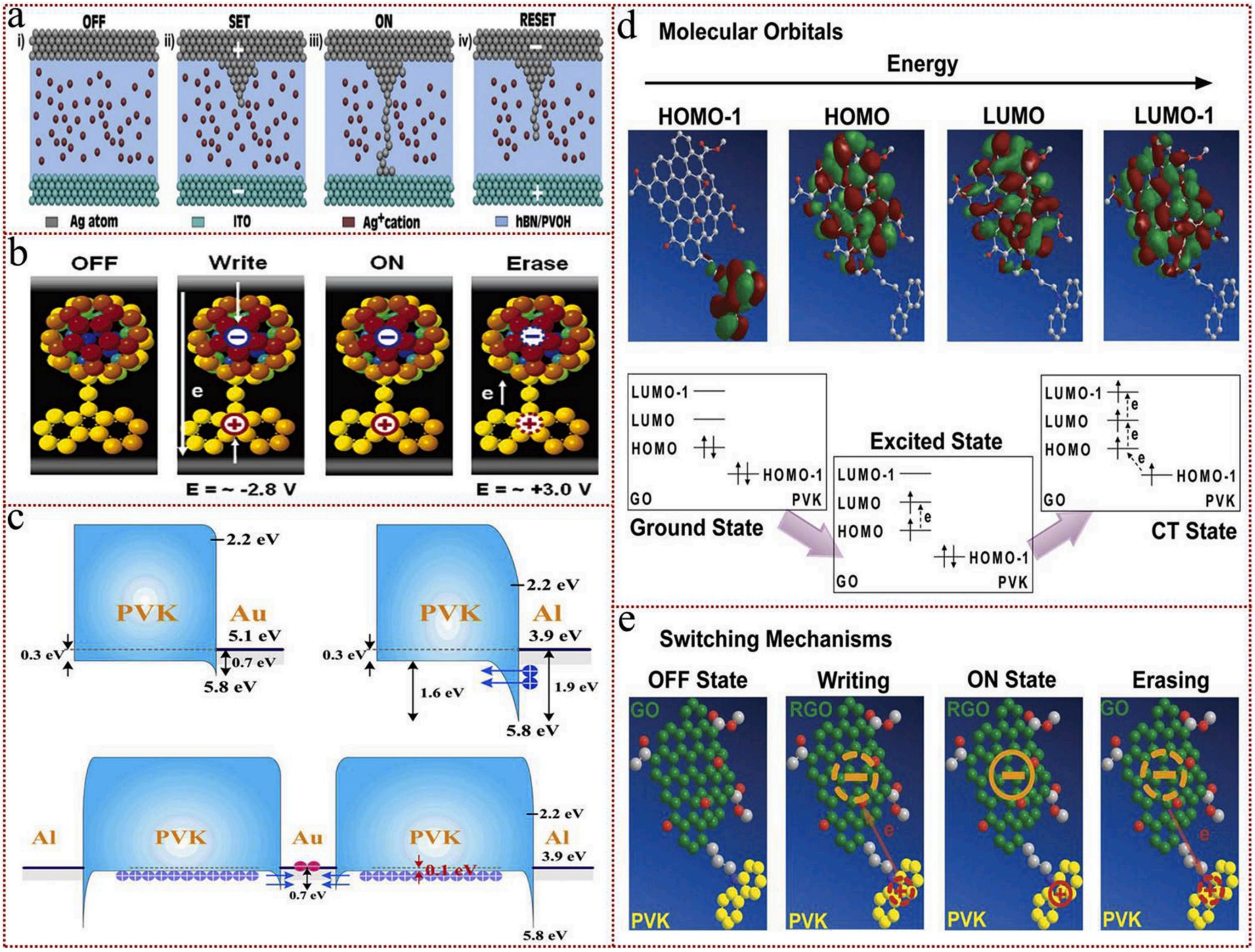

Fig. 15. (a) Illustration of the formation and rupture of a metallic filament from the top electrode to the bottom electrode under the influence of a strong electric field. Reproduced with permission [160]. Copyright 2017, Royal Society of Chemistry. (b) The electronic processes in a molecule of VK-C60 producing the memory effects. Reproduced with permission [161]. Copyright 2007, American Chemical Society. (c) The schematic energy-level diagrams for PVK–Au and PVK–Al junctions. Reproduced with permission [162]. Copyright 2009, Elsevier. (d) Molecular orbitals and electric field-induced electronic processes from the ground state to the charge transfer state and (e) plausible switching mechanism of GO-PVK. RGO stands for reduced graphene oxide. Reproduced with permission [163]. Copyright 2009, AIP Publishing.

synthesized two new donor (D)–acceptor (A) copolymers: poly({4,4'-[4,4-(9H-fluorene-9,9-diyl)bis(4,1-phenylene)]bis-(oxy)diphthalonitrile}-alt-DTP) (P1; DTP = dithieno[3,2-b:2′,3′-d]pyrrole) and poly({4,4'-[4,4'-(9H-fluorene-9,9-diyl)bis(4,1-phenylene)]bis(oxy)diphthalonitrile}-alt-BDT) (P2; BDT = [1,2-b:4,5-b]dithiophene) [158]. They fabricated a memristive device with Pt/Polymer/Pt/Si structure, as shown in Fig. 14g, and the consecutive I–V cycles of a Pt/P1/Pt device is shown in Fig. 14h.

From the above works, we can see that polymer is a very promising functional material in the preparation of biomemristive devices. We believe that polymer-based biomemristors will have more important applications. However, it needs to explore the design and synthesis of conductive polymers with good electrical properties, the electrode selection, the preparation process of devices, and the working mechanism. Next we will discuss the physical mechanism of polymer-based biomemristors.

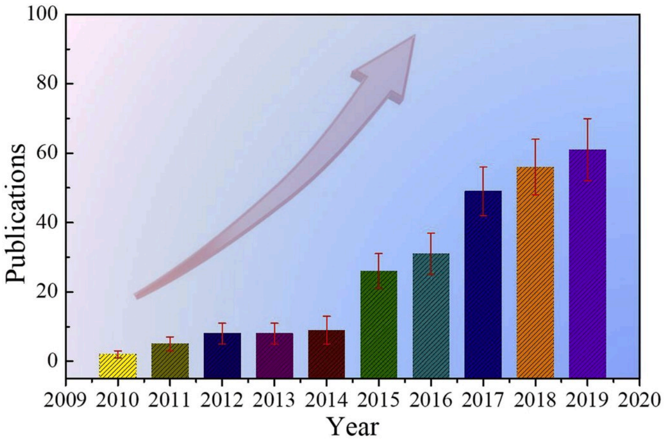

Fig. 16. The number of papers about biomemristors published from 2010 to 2019 by google and web of science.

6.2. *Physical mechanisms of polymers based biomemristor*

A switching mechanism of the formation and rupture of conducting filament based on a 2D material: boron nitride (BN) and a polymer,

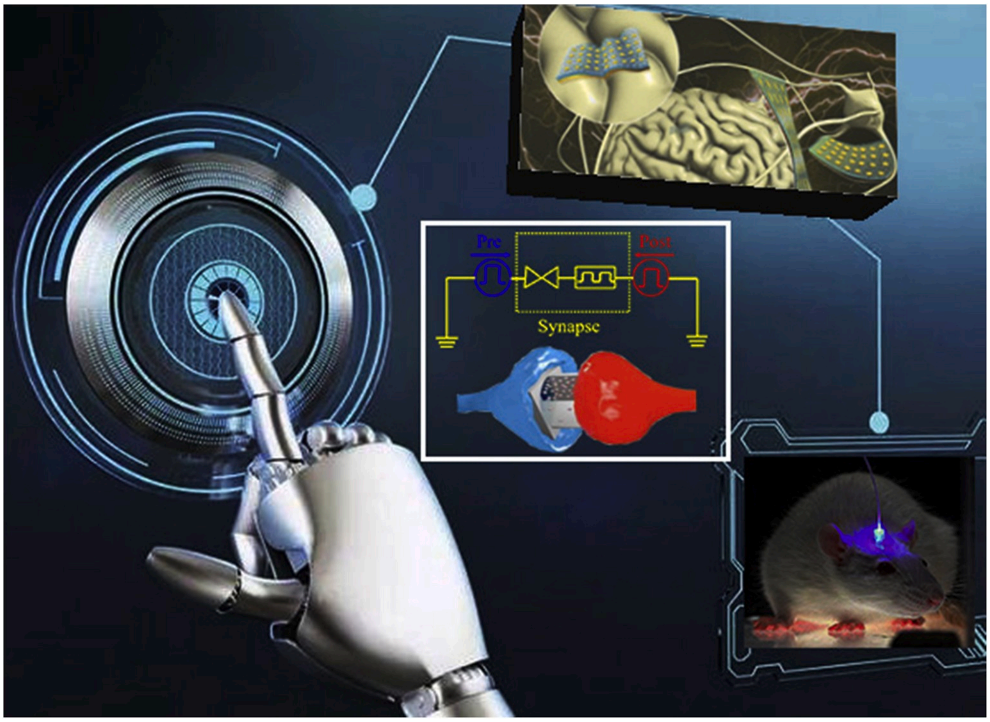

Fig. 17. The proposed conceptual diagram of control to animal brain using biomemristor as artificial synapse implanted into animal brain.

polyvinyl alcohol (PVOH) was suggested [160], as shown in Fig. 15a. In their work, the formation of conductive filaments was caused by the redox reaction of the Ag top electrode under the external electric field. The oxidation reaction results in the formation of Ag^+ ions and implantation into the functional layer. Because of Ag^+ ions cannot freely migrate in the hBN-PVOH functional layer, the Ag^+ ions were reduced to Ag atoms where the Ag^+ ions were captured, thereby forming a Ag conductive filament as an extension of the Ag top electrode. When the external electric field was turned off, the formed conductive filaments will not break, which reflects the non-volatile memory behavior of the device [160].

Qi-Dan Ling et al. synthesized a functional polymer (PVK–C60) via covalent tethering to prepare a resistive switching device with ITO/PVK-C60/Al sandwiched structure [161]. It is critical to the performance of the memristor that the valence band (highest occupied molecular orbital (HOMO)) and conduction band (lowest unoccupied molecular orbital (LUMO)) energy levels of the functional layer materials match the work functions of the top and bottom electrodes of the device. The high HOMO energy level of the carbazole moiety indicates that PVK-C_{60} is a p-type material with holes as the main charge carriers because carbazole is the main part in PVK-C_{60} [161]. Meanwhile, at a low bias voltage (0 to −2.8 V), C_{60} with a low HOMO level (−6.01 eV) partially prevents hole mobility in PVK-C_{60}. The device maintain at a HRS. The slight increase in current density may be due to inter-chain hopping of charge carriers. When the electric field exceeds the barrier (~0.7 eV), it injects holes into the HOMO of the carbazole group and electrons into the LUMO of C_{60}. The charged HOMO of the carbazole part and the charged LUMO of C_{60} form a carrier channel through a charge transfer interaction, as shown in Fig. 15b. The protonation induced polaron change in PEDOT:PSS can decrease the conductivity of the polymer. This can tune the resistivity from LRS to HRS [154]. The bias induced the multi redox states switching on azo aromatics gives a different scenario of tuning conductivity on polymers [155].

In addition, P. Y. Lai and J. S. Chen prepared a polymer memory device using Au nanoparticles (Au NPs) incorporated poly(N-vinylcarbazole) (PVK) as the active layer with Al films as the electrodes [162]. The switching mechanism of the device between HRS and LRS is explained in a band diagram in Fig. 15c. After applying an external voltage, the PVK carbazole group will continuously transfer electrons to Au nanoparticles. Thus, the number of hole carriers will be increased. The high carrier concentration will reduce the Fermi level E_F, so that the width of the depletion region at the Al–PVK Schottky barrier junction will be reduced [162]. This will eventually lead to the hole tunneling at the Al–PVK junction, shown in Fig. 15c. As a result, a sharp increase in current corresponds to the switching from HRS to LRS. According to the band diagram in Fig. 15c, when an electron is transmitted through the Au-PVK junction, it needs to overcome the Fermi level E_F and the potential barrier between Au and $LUMO_{PVK}$. Due to the large Fermi level E_F of $LUMO_{PVK}$, the captured electrons will be stably collected in Au nanoparticles. Therefore, the current immediately reached Ohmic conduction when a voltage scan was switched to LRS. After that process, holes accumulate in a thinner depletion region at the Au-PVK Schottky barrier junction. Therefore, it has a great possibility that holes tunnel through thin depletion regions and neutralize electrons in Au nanoparticles. As a result, the carrier concentration in PVK is significantly reduced, and the Fermi level E_F moves upward. Therefore, the device will be switched back to HRS. Similarly, Gang Liu et al. developed a Al/GO-PVK/ITO device with poly (N-vinylcarbazole)-derivatized graphene oxide (GO-PVK) as functional layer [163]. The electronic structure of GO-PVK is calculated in Fig. 15d. A simplified GO-PVK model with only 16 aromatic rings and 1 carbazole unit was used for the calculation. The conductivity of functionalized graphene oxide is several orders of magnitude lower than that of graphene due to the scattering on the surface or edge defects by epoxides and carbonyl groups. Therefore, the device is in HRS at the initial stage. Under the applied voltage, electrons are transferred from the HOMO of vinyl carbazole group to the LUMO of graphene oxide through an intramolecular charge transfer interaction, as shown in Fig. 15d. Electrons can propagate with less scattering in the graphene nanosheets. Thereby, to improve the electrical conductivity of the composite, graphene oxide was reduced. An effective charge transport path will be formed by the interplane-plane hopping between the thin films of the reduced GO nanosheets. Thus the device switched from HRS to LRS (Fig. 15e) [163]. At this time, the electrical conductivity of the

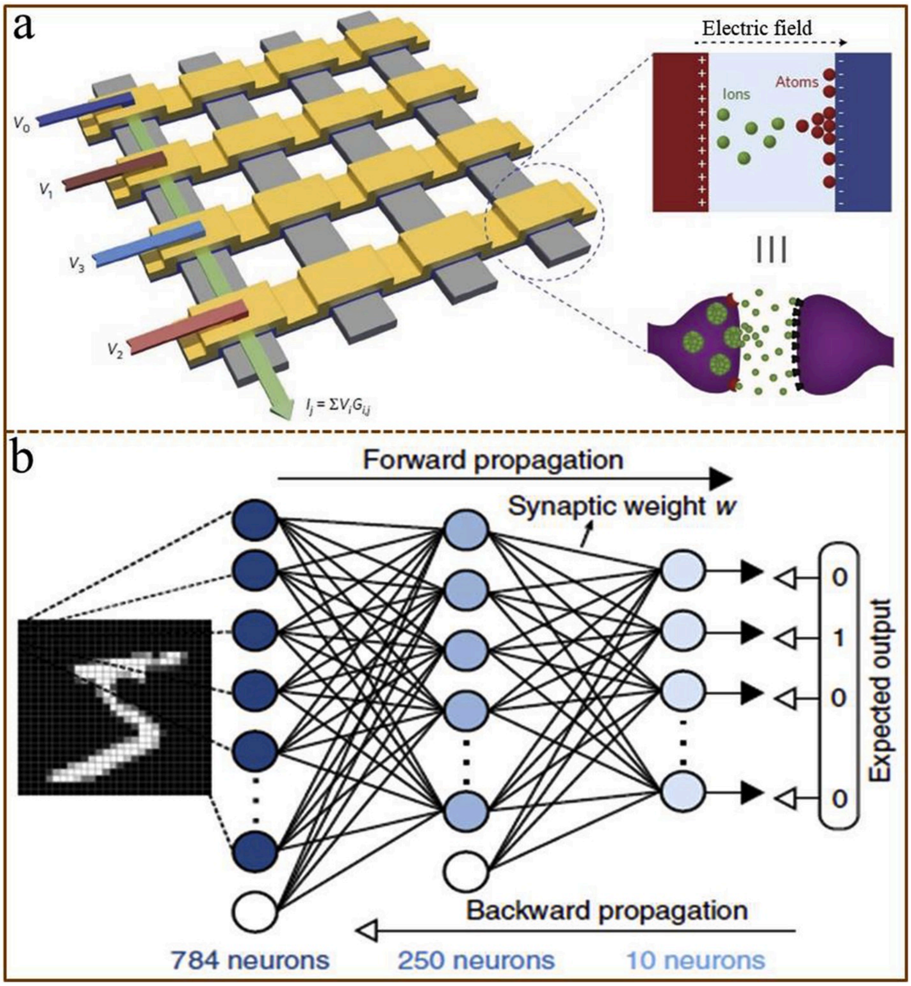

Fig. 18. (a) Hardware implementation of artificial neural network using memristor crossbar. Reproduced with permission [190]. Copyright 2018, Nature Publishing Group. (b) An artificial neural network is trained using backpropagation to perform handwritten digit classification. Reproduced with permission [199]. Copyright 2018, Nature Publishing Group.

functional layer is still lower than that of the intrinsic graphene nanosheets. Thus, the device is nonvolatile. However, when a reverse positive bias was applied to the device, it can extract electrons from the graphene nanosheets, returning the complex to its original form of the less conductive oxide, so that the device returns to HRS again.

The physical mechanism of polymer-based memristive devices is more complicated than that of natural biomaterials based memristors. It is mainly because polymers have a more defined molecular structure and energy level. The transport of carriers in conductive polymers obeys the characteristics of semiconductors. Therefore, the mechanism of polymer-based memristive devices includes the formation of conductive filaments, the formation of interfacial barriers, the trap and tunneling of electrons, and the filling of electrons and holes between different energy levels of HOMO and LUMO, the proton induced polaron modulation on conductivity, the multi redox states on configurations, and so on. This gives great opportunities for the design of polymer based biomemristors.

7. Trends and challenges of biomemristor

Nowadays, memristor shows a broad application prospect in ultra-high-density memory, artificial synapses, neural networks, artificial intelligence, and neuromorphic computing [164–174], Fig. 16 shows the number of papers published on biomemristors from 2010 to 2019. An obvious upward trend indicates that biomemristor has attracted great attention.

Biomemristor grows rapidly with benefits of reutilization, degradable and medical applications [175]. Biomemristors are regarded as a potential bioelectronics to compete with conventional complementary metal oxide semiconductor (CMOS)-based nonvolatile memristive devices. Biomemristive devices are promising due to the biodegradability, which enables the development of environmental-friendly sustainable electronic devices. Besides, the biocompatibility of biomemristors is indispensable for resorbable medical systems, such as biomedical monitoring, biotherapy, biosensing, memory devices, and neuromorphic systems [176–180]. In particular, flexible biomemristors have the function of simulating synapses which can potentially be implanted in the synapses in animal brains for real-time monitoring and controlling of the brain proposed in Fig. 17. Thus, the integration of flexible biomemristor into biological systems shows a great potential in human-machine interactions.

The memristor outputs a corresponding current under the applied voltage to complete the multiplication calculation function. The output currents from the plurality of memristors can also be used for addition calculation function [181–184]. Through the combination of multiplication and addition, the memristor can be used for neuromorphic computing. In particular, the resistance of memristor can be quickly and reversibly controlled under an applied voltage. This makes the neuromorphic computing chip, integrated by memristors, not only able to perform energy-efficient computing, but also repeatable programming [185,186]. These characteristics bring unparalleled advantages for neuromorphic computing [187–191]. Furthermore, it is considered that neuromorphic computing is one of the very important application branches of memristive devices in the future [192,193]. We can understand mathematically that neuromorphic computing can be understood as a series of multiplication operations of vector matrices, as shown in Fig. 18a [190]. These operations can be realized through the matrix structure of memristors array, so that this structure can perform various operations of input and output [191]. Therefore, it is foreseeable that the memristor-based neuromorphic computing chips have a great potential as an artificial brain that resembles or even surpasses human brain both in intelligence and energy efficiency. As mentioned above, memristors have very obvious advantages as neuromorphic computing. More importantly, the use of vector matrix operations can also solve some traditional mathematical problems [193]. Therefore, the memristor is a very promising way to implement memory computing, so that it can be prepared into a hardware system with low power consumption and high performance in future ultra-high density computing systems [194–198]. Furthermore, for neuromorphic computing applications of multi-memristive synapses, it should be noted that Irem Boybat et al. reported a method for representing synaptic weights using the conductance values of a multi-memory synaptic models, as shown in Fig. 18b [199], the classification accuracy increases as the number of devices per synapse increases. For a conventional differential architecture with two devices, its classification accuracy is less than 15%. With multi-memristive synapses in the differential architecture, it can achieve a test accuracy of more than 88.9%, and its performance is better than the latest field learning experiments on phase change memory (PCM). Therefore, this research work opens a new design method for realizing large-scale and energy-efficient neuromorphic computing application systems.

In addition, once this artificial intelligence chip using memristors is applied to the mobile phone, the power consumption of the phone will be greatly reduced [200]. Potentially, the mobile phone can be used for longer time without charging. The memristor and human brain have similar synaptic functions, which act as an “electronic synapse”. The built-in smart chip has the ability for machine learning and can potentially handle tasks that are previously incapable by the machine system.

Finally, for the development of biomemristors, some impediments of biomemristive devices should also be considered. For example, biomaterials may be damaged by joule heating of electronic current. Degradability of biomaterials may have an impact on the endurance of the devices. In addition, biomaterials such as proteins and polysaccharides can absorb moisture in the air, which may lead to degradation of device performance. Therefore, the packaging of the biomemristive device is necessary, which can effectively prevent the declining of device performance due to absorption of moisture during device operation.

8. Conclusions

Recent progress of the natural biomaterial and polymer-based biomemrsitors as the next generation bioelectronics has been reviewed, regarding the material designs, device fabrication, physical switching mechanisms and prospects. Great progress and breakthrough have been made for the biomemristors as the ultrahigh information storage devices, but the endurance needs to be considered for industry manufacturing. Therefore, it is necessary to develop new natural biomaterials or conductive polymers with excellent electrical conductivity, stability, and flexible device structures. Materials design strategies, including electrode selection, functional layer design, and interface reaction, are needed to design on novel device based on the fundamental understanding of the physical mechanism. With continuous efforts, the natural biomaterials and polymer-based biomemristors, are promising as next generation bioelectronics for ultrahigh information storage and processing, image recognition, medical diagnosis, artificial synapse, neuromorphic computing, and human machine interactions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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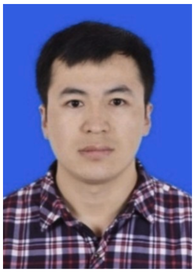

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Challenges With the Development of Biomaterials for Sustainable Tissue Engineering

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The field of tissue engineering has tantalizingly offered the possibility of regenerating new tissue in order to treat a multitude of diseases and conditions within the human body. Nevertheless, in spite of significant progress with *in vitro* and small animal studies, progress toward realizing the clinical and commercial endpoints has been slow and many would argue that ultimate goals, especially in treating those conditions which, as yet, do not have acceptable conventional therapies, may never be reached because of flawed scientific rationale. In other words, sustainable tissue engineering may not be achievable with current approaches. One of the major factors here is the choice of biomaterial that is intended, through its use as a "scaffold," to guide the regeneration process. For many years, effective specifications for these biomaterials have not been well-articulated, and the requirements for biodegradability and prior FDA approval for use in medical devices, have dominated material selection processes. This essay argues that these considerations are not only wrong in principle but counter-productive in practice. Materials, such as many synthetic bioabsorbable polymers, which are designed to have no biological activity that could stimulate target cells to express new and appropriate tissue, will not be effective. It is argued here that a traditional 'scaffold' represents the wrong approach, and that tissue-engineering templates that are designed to replicate the niche, or microenvironment, of these target cells are much more likely to succeed.

Keywords: template, biocompatibility, scaffold, biomaterial, biodegradation

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INTRODUCTION

This paper, and this journal issue in general, is concerned with sustainability in the field of tissue engineering. It is an opportune time to reflect on this topic; sustainability refers either to a position that is demonstrably correct and defendable or an activity that can be continued and developed within the foreseeable future. In reality these meanings are linked since it should not be possible to successfully continue an activity, especially a complex activity such as tissue engineering, without it being correct and defensible. We should, therefore, examine the sustainability of tissue engineering, and, in particular, the role that biomaterials play in this.

In order to make it absolutely clear what sustainable tissue engineering means here, a few definitions and concepts need to be addressed. Tissue engineering is the creation of new tissue for the therapeutic reconstruction of the human body, by the deliberate and controlled stimulation of selected target cells through a systematic combination of molecular and mechanical signals (Williams, 2006). While this does not directly imply that tissue engineering has to involve biomaterials, the delivery of those molecular and mechanical signals cannot take place in a vacuum, and there will usually have to be a vehicle that accurately controls the relevant processes. Such vehicles have usually been described as scaffolds. However, the term "template" is preferred as this involves a different concept and avoids the old-fashioned ideas of scaffold biomaterials. Tissue engineering may be considered as one of the scientific platforms of regenerative medicine, the others being cell therapies and gene therapies.

As discussed by Vacanti back in 2006 (Vacanti, 2006), tissue engineering has its origins in the late 1980s; in other words, we now have ∼30 years-worth of developments in this field. Many people, including myself, have written about the "promise" of tissue engineering, albeit with commentaries on the difficulties of achieving success. In 2004, I reviewed the benefits and risks of tissue engineering (Williams, 2004) referring to the uncertainty that exists with respect to its commercial and clinical exploitation. I noted that, during the previous decade, a number of companies had been formed with the objective of commercializing tissue engineering and that investment looked attractive; however, the tide had turned, with a number of high-profile bankruptcies and changes in company positions, with little hope of recovering initial investments. Two fundamental issues were at stake; on the one hand, the R & D costs were very high and on the other hand there was little prospect of these companies being able to sell their products for a reasonable sum, since the investigational nature of the work meant that treatment was not reimbursable under most insurance schemes.

I returned to this theme over 10 years later (Williams, 2017a) stating that the field had still not yet resulted in the widespread clinical and commercial successes that were initially predicted; there were also some problem areas with the conduct of clinical research, which had set the field back. There are many reasons why tissue engineering has not yet fulfilled the initial promises, and many of these, as alluded to above, are concerned with the infrastructure, including those related to health economics and reimbursement, regulation, ethics and bioprocessing. However, if the scientific principles upon which these promises rested had been fully developed, ways forward or around these logistical hurdles would almost certainly have been found. The scientific factors largely relate to the ability to deliver those molecular and mechanical signals mentioned earlier, such that new tissue, with appropriate morphological and functional characteristics, can be generated and maintained. Within this complex milieu, the roles of, and effects on, the target cells, on the whole array of biomolecules and on the biomaterial templates all have to be considered. In order to determine how these templates have performed, and have contributed, either positively or negatively, to tissue regeneration, it is necessary to consider the clinical outcomes that have emerged.

THE CLINICAL PERFORMANCE OF TISSUE ENGINEERING BIOMATERIALS AND TEMPLATES

Skin Tissue Engineering

With hindsight, the major problems with tissue engineering biomaterials were apparent from the early experiences with skin tissue engineering products and processes. The very public failure of Advanced Tissue Sciences Inc., and the difficulties with commercialization of its flagship product Dermagraft®, serves as a good example (Pangarkar et al., 2010). All of the infrastructure issues mentioned above were certainly involved, and the company was undoubtedly unlucky with respect to the reluctance of the FDA to approve new products following controversies such as the silicone breast implant scenario and the general economic situation, but it should not be overlooked that the product contained not only neonatal allogeneic fibroblasts but also a poly(lactic acid)-poly(glycolic acid) synthetic material.

From biomaterials and bioengineering perspectives, it was already becoming clear by the early 2000s that such synthetic polymers were unlikely to provide optimal substrates for tissue engineered skin. Metcalfe and Ferguson reviewed the relevant issues in 2007 (Metcalfe and Ferguson, 2007), indicating that no then-current bioengineered skin completely replicated the anatomy, physiology, biological stability or aesthetic nature of uninjured skin, with significant problems of under-vascularization, excessive scarring, a lack of complexity of differentiated structures and poor biocompatibility of the supporting membranes. These issues were stressed by van der Veen et al. (2010), who emphasized that fibroblasts need to be offered binding locations and chemotactic signals that can guide cell function and that the foreign body response to the degrading synthetic material will inhibit the wound healing process. Similar positions have been taken by Kamel et al. (2013) and Groeber et al. (2011), and in 2017, Vig et al. referred to continuing unavailability of an engineered skin substitute, with the properties of the biomaterial substrate being a major factor (Vig et al., 2017). Some indication of the better success that could be achieved with alternative substrates to the synthetic biodegradable polymers has been seen with products such as Apligraf (Stone et al., 2017); this is a skin substitute consisting of human foreskin-derived neonatal fibroblasts in a bovine Type I collagen matrix and a further layer of human foreskin-derived neonatal epidermal keratinocytes. This has been used in the treatment of venous leg ulcers, where it appears to induce a shift from a non-healing to a healing tissue response, with a modulation of inflammatory and growth factor signaling, keratinocyte activation and attenuation of Wnt/ß-catenin signaling. Clearly, the collagen matrix is far more capable of inducing such responses than synthetic polymers. This point was recently underlined by Ter Horst et al. (2018) when reviewing keratinocyte delivery in burn wound care, noting that natural biopolymer hydrogels, such as those of chitosan, alginate, fibrin, and collagen can act as supportive matrices in cell delivery, but not those of synthetic polymers.

Articular Cartilage Tissue Engineering

Articular cartilage received similar attention to skin in the early days of tissue engineering and the transition from R. & D. to clinical and commercial applications has followed a somewhat parallel trajectory. As recently reviewed by Huang et al. (2016), there are several clinical techniques available for the treatment of focal lesions in articular cartilage, including microfracture and autologous chondrocyte implantation, but in view of the limited capacity of the avascular, low cellular, cartilage to heal, these techniques do not consistently produce hyaline repair tissue. A number of cell-based tissue engineering products have been designed over the last two decades, some of which have been subject to clinical trials. The tissue engineered cartilage constructs involved here are generally formed by the integration of chondrocytes, signals, and scaffolds. These scaffolds are, strictly speaking, of exogenous origin, although, confusingly "scaffold-free" techniques have been introduced, in which an endogenously-generated "scaffold" that is generated by cells is involved. At the present time, very few of these constructs employ a synthetic polymer scaffold. Bioseed®-C and INSTRUCT® contain either polyglactin 910/polydioxanone or poly(ethylene oxide terephthalate)/poly(butylene terephthalate) biodegradable polymers. Development of these products has been slow, with mixed results.

More products have used natural biopolymers as scaffolds. Biocart ™ II uses autologous chondrocytes within freeze-dried fibrin and hyaluronan, Cartipatchç uses an agarose-alginate hydrogel, Hyalograft®-C a non-woven mesh of hyaluronic acid-based microfibres, NeoCart® a bovine type I collagen and so on. One good example here is the Novocart® product, a 3D autologous chondrocyte implant system composed of *ex vivo* expanded autologous chondrocytes seeded on a bioresorbable biphasic collagen scaffold, which is in Phase III trials. Overall, the pre-clinical results seem better with the natural biopolymer constructs or scaffold-free approaches than with the synthetic polymers, and more of these products have entered Phase II or III clinical trials, but the huge time delay from study inception to reimbursable clinical usage is still inconsistent with a concept of sustainable tissue engineering biomaterials. A very recently published systematic review of clinical evidence in the area of therapies for focal chondral defects (Gao et al., 2019) suggests that the general difficulty of this tissue repair has resulted in a significant lack of high-quality randomized controlled clinical studies on techniques such as microfracture and autologous matrix induced chondrogenesis; few recommendations on optimal methods can therefore be made.

With biodegradable polymers such as PLGA it is interesting to note their history of pre-clinical evaluation. Just as with polymer-based skin tissue engineering products, there was initial enthusiasm about the possibility of chondrogenesis and cartilage repair within porous scaffolds seeded with chondrocytes. However, two problems emerged with such systems, concerned first with the ability of either chondrocytes or stem cells, to attach to, and function on, these polymer surfaces and secondly with the effects of polymer degradation on tissue regeneration. For example, Zanatta et al. showed that adherence of mesenchymal stem cells to a PLGA copolymer scaffold is heavily dependent on the presence of integrin- ß1 receptors (Zanatta et al., 2012), while Asawa et al. showed that inflammatory cells associated with the response to degrading PLGA scaffolds significantly affected proteoglycan and type II collagen production during autologous transplantation of tissue engineered cartilage (Asawa et al., 2012).

During the last decade or so there have been many attempts to 'modify' these synthetic scaffolds and the literature is replete with *in vitro* and small-animal studies on cell responses to morphological and biochemical variants of degradable polymers, especially the aliphatic polyesters. It is certainly true that nanofibrous architectures can have some influence (Xin et al., 2007), as can pore size and orientation (Zhang et al., 2012), but these rarely provide improvements of clinical relevance since they do not substantially address the main underlying problems. This does not mean that degradable polyester systems do not have any role in cartilage tissue engineering, but it would appear that their role is most likely to be as carriers (or microcarriers) of biomolecules or genes rather than as structural scaffolds or templates. Tan et al. (2009) were among the first to use PLGA microspheres to modify the properties of natural biopolymer scaffolds (gelatin/chitosan/hyaluronan). This was taken to a new level by Morille et al. (2016) who incorporated TGF ß3 into PLGA microspheres that were suspended in mesenchymal stem cell preparations. In a murine arthritic knee joint model, these encouraged chondrogenesis and the formation of cartilage-like tissue. Im et al. used a similar approach by impregnating a PLGA scaffold with plasmid DNA containing a SOX-5, -6, and -9 genes, which induced chondrogenesis of adipose stem cells (Im et al., 2011).

Bearing in mind the far greater complexity of regulatory approval and reimbursement procedures for products that contain active biomolecules and/or genes, such developments are highly unlikely to enhance the sustainability of tissue engineering biomaterials.

Tracheal/Airway Tissue Engineering

A paper published in 2017 asked a question in its title "Tissue engineering of the trachea: what is the hold-up?" (Siddiqi, 2017). This was a sensible question, but with a complex answer. As an editorial in The Lancet in 2018 (Editorial, 2018) revealed, intensive investigations by The Karolinska Institute in Sweden and by University College, London had confirmed that experimental and clinical work by Macchiarini and colleagues on tracheal tissue engineering constituted scientific fraud and unethical behavior. This resulted in the death of several patients and the retraction of some, apparently pivotal, studies and reviews (Jungebluth et al., 2011; Badylak et al., 2012). This called into question the validity of tracheobronchial transplantation using tissue engineering techniques, and the translation of these concepts to the arena of engineered whole organs and complex tissues. There were many factors that lead to the deaths, but the scaffolds used in the procedures were clearly inadequate. Several constructs were employed, including cadaveric tracheas and a biodegradable synthetic composite material described as "POSS-PCU", polyhedral oligomeric silsesquioxanes and poly (carbonate-urea)-urethane. It is difficult to know why the latter material failed since there were both intrinsic problems with its biocompatibility and non-compliant manufacturing issues, but this disastrous approach did not help at all with the development of sustainable tracheal tissue engineering. In reviewing the possibility of clinical translation of tissue engineered tracheal grafts, Chiang et al. (2016) referred to the inappropriate nature of this material in terms of "*..the stiffness of the material led to compliance mismatch, granulation tissue formation, the development of fistula at distal anastomotic sites, poor vascularization and epithelialization and susceptibility to infection.*" In other words, pretty well everything went wrong from a biocompatibility perspective.

Concerning the alternative scaffolds, Chiang et al. (2016) discussed decellularized tracheas, which are intended to work through removal of cellular and immunogenic material from the ECM of donated tracheas, ostensibly to preserve the mechanical and bio-inductive properties of the tissue. While conceding that variations in decellularization protocols results in significant differences in outcomes, the overall impression was that the rate of chondrocyte repopulation does not usually match the rate of ECM degradation. This point was amplified by Maughan et al. in a 2017 review of autologous cell seeding in tracheal tissue engineering (Maughan et al., 2017), for although considerable remodeling of the ECM can occur, some critical ECM signaling molecules may be removed during decellularization, while the biomechanical properties may be unfavorably modified and the resulting material may still elicit adverse immunological responses. These latter complications are consistent with current theories of biocompatibility described in detail by the present author recently (Williams, 2017b).

The current situation with tracheal tissue engineering was critically discussed by Elliott et al. (2017) (the same team that produced the review cited as 28 above), who presented the results of a case where a stem-cell seeded decellularized tissue-engineered tracheal graft was used on a compassionate basis for a girl with critical tracheal stenosis. In spite of following full GMP procedures and appropriate clinical techniques, the patient died 3 weeks post-transplantation following an intrathoracic bleed and sudden airway obstruction (Elliott et al., 2017).

While making it clear here that, in the very difficult clinical area of tissue-engineered approaches to airway reconstruction, biological materials such as decellularized tissues are far from ideal and synthetic biodegradable polymers appear to have very little chance of success, there are other biomaterials-based options. Hollister and colleagues published an experimental model of treating tracheomalacia using 3D-printed bioresorbable airway splints in 2013 (Zopf et al., 2014); this approach was used clinically in compassionate cases of tracheobronchomalacia over the next few years (Zopf et al., 2013; Morrison et al., 2015). The splint, referred to as a personalized medical device rather than a scaffold is polycaprolactone homopolymer. This is biodegradable, its supportive presence allowing natural cartilage remodeling to take place over a matter of months. This technique is still with very limited clinical application, but may provide options for the very difficult management of tracheobronchomalacia (Svetanoff and Jennings, 2018).

One implication of the latter approach, which rarely if ever is described as "tissue engineering," is that ambitions for the biological role of biomaterials in what is essentially biomaterial-assisted remodeling, may have to be reconsidered.

Bladder Tissue Engineering

There are several serious conditions that affect the bladder, such as congenital or traumatic neurogenic bladder, bladder exstrophy, hemorrhagic cystitis and cancer, for which existing treatments are not always satisfactory and where regenerative medicine approaches appear attractive. Attempts to tissue-engineer bladder replacement or augmentation structures have been made for more than a decade. Atala et al. described the first successful procedures in 2006 (Atala et al., 2006). A Phase I study involved seven patients using autologous cells seeded into polyglycolic acid-collagen scaffolds that were wrapped in omentum to improve vascularization. As explained by Atala (2014), a Phase II study did not reproduce this success (Joseph et al., 2014). It was difficult to conclude what features of the process were significant causes of the disappointing outcome, but the editorial that accompanied this paper points to the unreasonable expectations from the scaffold materials: "*It is hard to believe that adding cells from a patient onto a scaffold will be enough to regenerate the organ without taking into account the normal physiological factors and necessary developmental cues. Although the bladder is a forgiving organ, it is complex, dynamic and normally expected to contract volitionally. These specific functional characteristics (contractile, impermeable, capacious, and compliant) should be considered when tissue engineering the bladder. Hence, the scaffolds used to tissue engineer bladders and the cells to be seeded on the scaffold need to be primed to work in harmony and with mutual reciprocity to allow the cell seeded scaffolds to maintain the resiliency and functionality of a normal bladder (contractile yet impermeable). The scaffold nature and its mechanical properties, the cells and their sources, and the in vitro factors before implantation may be critical but the in vivo post-implantation environment (prompt blood supply, altered scaffold mechanical properties, and seeded cell degradation and possible immune response) should not be underestimated.*"

Although some publications still suggest that there is good potential for tissue engineered bladders (Van Ba et al., 2015), the evidence for optimism is rather scant; some studies suggest a lack of understanding of bladder biomechanics may be a major factor (Ajalloueian et al., 2018). The poor prospects for synthetic biodegradable polymers has been emphasized (Pokrywczynska et al., 2014). Furthermore, the potential advantages for natural biopolymers (e.g., collagen-fibrin multi-layers, incorporating bioactive factors such as IGF-1), has been demonstrated (Vardar et al., 2016).

Cardiovascular Tissue Engineering

Outcomes of regenerative medicine approaches to the cardiovascular system in general, and biomaterials-based tissue engineering techniques in particular, are difficult to assess, but it is clear that success has been elusive. In relation to therapies for the failing heart, Vunjak-Novakovic has recently reflected on the fact that the main focus of cardiac tissue engineering, the development of a standard of care based on cell therapy, is still without clinical application after two decades of experimentation (Vunjak-Novakovic, 2017). She poses the question of whether cell engraftment is necessary for heart repair and suggest the possibility of cell-free heart repair using cocktails of cell-secreted factors, mass produced in culture, and delivered in biomaterial patches: "*One can envision a new cell-free approach to sustained delivery of regulatory factors, controlled over time by the degradation and release kinetics of a collagen patch.*"

With respect to the myocardium and the treatment of myocardial infarction, it is clear that the conventional view of tissue-engineering scaffolds will not apply; far more relevant is the concept of an injectable biomaterial that delivers signals, and possibly cells. As discussed by Camci-Unal et al. (2014), it is the environmental stress associated with the lack of a three-dimensional flexible biomimetic microenvironment and the direct exposure of any cells injected into the myocardium to oxygen tension, free radicals and inflammatory cytokines, that leads to the death of most injected cells. This gives rise to a need for engineered biomaterials to efficiently deliver cells to the myocardium, and hydrogels are the most likely candidates. Both natural and synthetic hydrogels have been considered. In the latter case, poly(ethylene glycol) (PEG), poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(N-isopropylacrylamide) (PNIPAAM) have some relevant properties, but without additional biological activity and functionalization are unlikely to satisfy all of the requirements. Since the cardiac environment is highly dynamic, tough elastomeric hydrogels should provide optimal compliance with the tissues and conductive materials may facilitate propagation of electrical signals during cardiac function (Camci-Unal et al., 2014).

Once again, native ECM molecules may form a better basis for the required hydrogels, with interest shown in collagen and fibrin. Since it is proving difficult to provide such hydrogels with appropriate stiffnesses, more subtle molecular engineering approaches may be necessary. Wu et al. (2017) have described the development of what they call "small molecular hydrogels" that are based on peptides such as ^{D}FEFK^{D}FEFKYRGD, which was shown to provide a scaffold for hepatocyte growth factor–modified mesenchymal stem cells that could preserve cardiac function after an infarction whilst alleviating ventricular remodeling in an animal model. These are, of course, very different to the historically-defined tissue engineering scaffolds, but it is in this direction we must look. There will be many other alternative, unconventional approaches, including cell sheet engineering, which has taken a long time to reach clinical trial stages after early enthusiasm (Miyagawa et al., 2017).

The area of heart valve replacement provides a different and interesting perspective on the role of tissue engineering. Generally this is not an area of un-met clinical need since there are perfectly adequate implantable devices, either surgically or catheter delivered for the vast majority of patients. The major potential for tissue-engineered valves lies in pediatric cases, where there is a need for devices that could adapt to growing children. This possibility received a significant setback nearly 20 years ago when cryopreserved decellularized porcine valves were implanted in 4 patients in a European clinical trial. Three of the patients died within a year (the valve in the fourth was explanted prophylactically just after implantation) because of severely inflamed and degenerated valve leaflets (Simon et al., 2003). Similar, although not so dramatic results were reported in 2012 when decellularized xenogeneic tissue-engineered pulmonary valve conduits were used for right ventricular outflow tract reconstruction in 93 patients (Perri et al., 2012). Histological analysis of explanted conduits showed inflammatory giant cells with poor autologous cell seeding, 35% of patients experiencing conduit failure and 29% conduit dysfunction. Whether better results will be obtained with synthetic polymer-based conduits remains to be seen; Benink et al. have reported "safety and functionality" in a sheep study of a synthetic polymer conduit made oif a hybrid structure of a polycaprolactone-based 2-ureido-4[IH] pyrimidinone and polycarbonate-based 2-ureido-4[IH] pyrimidinone (Bennink et al., 2018).

Vascular tissue engineering does represent a huge area of un-met clinical need. As discussed by Chang and Niklason (2017), the opportunities are considerable, but so are the challenges. Any tissue-engineered part of the vascular system has to withstand physiological pressures without leakage or aneurysm formation, which remains as a formidable barrier to reconstructing vessels in the major circulation. There have been a few successes but the vast majority of experience has been confined to animal studies. Most synthetic degradable polymers, including polycaprolactone and poly(lactic acid), tend to show limited cell infiltration with poor neotissue formation. Combining such polymers with natural biopolymers may give better performance, such as the PCL-chitosan combination used by Fukunishi et al. in a sheep model (Fukunishi et al., 2016) but it seems that we are a long way off providing a clinically-acceptable template material for arterial regeneration.

Spinal Cord Injury

A final potential clinical application to be discussed, briefly, is that of spinal cord regeneration after injury (SCI). To date, therapies for SCI have largely been ineffective, primarily because of the need for mechanical support around the lesion in order to guide and support axonal regeneration, the absence of sufficient neurotrophic stimulation and growth-factor mediated neuroprotection, and the presence of various myelin or reactive glia derived inhibitors of axonal growth. This would seem to be a strong candidate for tissue engineering solutions, involving some form of template that could guide regeneration together with the delivery of appropriate cells and bioactive molecules that could stimulate the desired regenerative activity whilst inhibiting the undesirable negative effects. There have been many attempts to use synthetic biodegradable tubular conduits, for example the recently published trimethylene carbonate—caprolactone copolymer conduit that contains oriented poly-p-dioxanone microfilaments (Novikova et al., 2018), but such work is still mostly confined to small animal studies, where results may show some attractive features but tend to be inconclusive.

Once again, results with natural polymers have generally proven to be better. Dai and colleagues have worked with bovine collagen scaffolds, showing good results in a chronic SCI canine model when seeded with umbilical cord mesenchymal stem cells (Li et al., 2017), and then in human clinical trials with both acute (Xiao et al., 2018) and chronic (Xiao et al., 2016) spinal cord injuries.

THE CRITIQUE OF SCAFFOLDS AND THE NEED FOR ACTIVE TEMPLATES

Conventional Scaffolds

A recent conference on definitions in biomaterials science (Zhang and Williams, 2018) determined that a scaffold is "A biomaterial structure that serves as a substrate and guide for tissue repair and regeneration." This represents the generally-perceived concept of tissue-engineering scaffolds that has persisted for the 30-year history of regenerative medicine. It is clear, however, that this conceptual definition does not even hint at what type of biomaterial can act in this way, let alone imply what are the broad specifications for scaffold materials, a point discussed by the present author a few years ago (Williams, 2014a). The reality is that there were two main specifications for tissue-engineering scaffolds at the beginning of this era; the first was that the material had to be degradable so that it could be replaced by the engineered issue that was forming, while the second was that this degradable material had to have had prior approval by the FDA for use in medical devices. This is why the first scaffold biomaterials were the bioabsorbable materials used in approved devices such as sutures, plates and drug delivery systems.

That tissue-engineering scaffolds could be (although not necessarily invariably) bioabsorbable is not contentious, but, by itself, is an insufficient criterion. This will be discussed a little later in this section. The requirement for prior FDA approval in medical devices is, however, not just irrelevant but dangerous. As the present author has discussed on several occasions (Williams, 2009, 2014b) regulatory approval for medical devices, which encompasses the biomaterials from which they are made, is predicated on the ability to show that the material does no harm; in regulatory and standards language, this determines that the materials are "biologically safe." Thus, depending on the precise application, the materials are subjected to the biological safety tests of ISO 10993 (International Standards Organization, 2018) to show that they pass the tests that demonstrate a lack of cytotoxicity, acute systemic toxicity, reproductive toxicity, thrombogenicity, complement activation and so on. Most of these tests require that the material or device is incubated in a specified solution (typically saline) for a short period of time, then the resulting extraction solution that contains any substance that is leached from the material is exposed to cells in culture, or to an appropriate *in vitro* or *in vivo* test system, and the results compared to actual or historic controls. Any hint that the extract produces a greater response compared to a control is interpreted as a failure, such that the material or device is considered biologically unsafe, and unsuitable for implantation in humans.

For biomaterials in medical devices, this requirement for minimal biological activity has resulted in the restriction of acceptable materials to those that have maximum chemical and biological inertness; that is the reality, inertness wins. Whenever the choice has deviated from inertness, problems have usually been encountered. There is some suggestion with implantable devices that inert materials themselves do not necessarily produce optimal results in all situations. For example, vascular grafts need help from endothelial cells to generate a superior neointima (Zilla et al., 2007) intravascular stents require help from anti-proliferative drugs to control in-stent re-stenosis (Otsuka et al., 2012), spinal fusion devices may give better outcomes when assisted by locally-released bone morphogenetic proteins (Axelrad and Einhorn, 2009) and thrombosis of heart valves is deterred by systemic anticoagulants (VanderLaan et al., 2012). A detailed analysis of the biocompatibility of these materials and applications (Williams, 2017b) show that, at maximal inertness, the host response is controlled by biomechanical factors, the release of particulate matter (e.g., wear particles in joint replacements) and applied pharmacological factors.

If biomaterials are used in applications other than implantable devices, where mechanical and physical functionality dominate the specifications, for example in drug and gene delivery processes, imaging and diagnostic systems and regenerative medicine applications, quite different requirements apply. This is why conventional tissue-engineering scaffolds, based upon FDA predicate considerations, are unlikely to result in new tissue generation; the materials used have to do more than guide tissue regeneration.

Tissue Engineering Templates

The above arguments make it clear that the originally conceived requirements for scaffold materials were, at best, too simple and, at worst, very misleading. Several of the early tissue-engineering biomaterials were modeled on those absorbable materials that had been used in FDA approved surgical sutures, e.g., synthetic polymers based on the aliphatic polyesters such as poly(glycolic acid). It is true that some of these polymers could degrade in the body without any clinically relevant adverse responses. However, a surgical suture was not designed to take part, biologically, in wound healing; it was required to hold tissues together while the repair process tool place according to natural healing mechanisms, and then degrade and resorb with minimal host response. Nothing could be further from the main requirement of a tissue-engineering biomaterial, which should be to actively take part in the process of tissue regeneration. No wonder that in those clinical applications described in section Introduction above, the simple concept of using an FDA approved synthetic degradable polyester rarely worked, and that the more the biomaterial choice moved toward natural or naturally-derived substances, the chances of regenerating tissues improved.

This, of course, is not the full story; a scaffold made from collagen, fibrin or silk may have a better chance, but far more attention has to be paid to the morphology and architecture of the construct, since the ability to signal to the target cells is not solely based on chemistry. The more conventional polymeric (or even resorbable ceramics such as some calcium phosphates) scaffolds were usually made by solid free form fabrication techniques or electrospinning. The microscale porous structures had various morphological characteristics, often with a degree of anisotropy, but their design rarely attempted to replicate a biological microenvironment. The question then arises as to whether these structures specifically replicate the niche of the target cells, i.e., those that are intended to be the focus of tissue regeneration. Moreover, the niche of these target cells, often but not necessarily stem cells, changes with time during the process of extracellular matrix expression; will electrospun collagen fibers change in the same way in order to accommodate this natural process? Even, therefore, with biomaterials that have some latent or intrinsic biological activity that could potentially be harnessed for stem cell signaling, it is unlikely that such activity can be sustained during the tissue regeneration process.

This is why the simple concept of a scaffold guiding a tissue regeneration process is insufficiently robust to result in effective, sustainable, tissue engineering. This is also the reason why the concept of a template is preferred to a scaffold. In general usage, a scaffold is a structure that mechanically facilitates the building of a construct, which is then disassembled and removed at the end of a process, without actually playing any part of that building process. In tissue engineering, the biomaterial has to do much more than that; for example a tissue-engineering template could be defined as "a biomaterials-based structure of defined size, chemistry and architecture that controls the delivery of molecular and mechanical signals to target cells in tissue engineering processes."

It is, perhaps, surprising that the tissue-engineering field as progressed up to this point without any authoritative presentation of specifications for the biomaterials. The present author provided a reasonably comprehensive list of such specifications, some mandatory and some optional depending on the application (Williams, 2014a). The more important of these template specifications may be summarized as follows:

- The template should recapitulate the architecture of the target cells,
- The template should be capable of adapting to the constantly changing microenvironment,
- The biomaterial should be degradable if that is desired, with appropriate degradation kinetics and appropriate morphological and chemical degradation profiles,
- The biomaterial should be capable of orchestrating molecular signaling to the target cells, either by directing endogenous molecules or delivering exogenous molecules,
- The biomaterial should have appropriate elastic/viscoelastic properties that favor mechanical signaling to the target cells,
- The biomaterial should be injectable if that is desired, with appropriate rheological characteristics, and transformation mechanisms and kinetics,
- The biomaterial should be capable of forming into an architecture that optimizes cell, nutrient, gas and biological molecule transport, either *ex vivo, in vi*vo or both, and which facilitates blood vessel and nerve development,
- Where necessary, the biomaterial should be compatible with the processing techniques that simultaneously pattern both the material and the cells; this has become an important issue in the context of 3D bioprinting, with features such as viscosity having a significant role,
- The material should be intrinsically non-cytotoxic, non-immunogenic and minimally pro-inflammatory.

On the basis of these quite specific requirements, a series of essential characteristics emerge (see **Table 1**). In order to recapitulate cell microenvironments, a substance that resembles the architecture and biochemical features of the desired, but acellular, new tissue seems an obvious choice The use of decellularized tissue, which represents the complex extracellular matrix (ECM) environment, has become a popular choice, both experimentally and clinically, for these templates (Urciuolo and De Coppi, 2018). A very significant point here is that the ECM is not simply a collection of proteins, or even a three-dimensionally arranged collection of proteins. The ECM components interact with each other in specific ways; these interactions between components, and between different isoforms of the same component, are not only tissue-specific but site-specific within each defined tissue. Such interactions are unlikely to be efficiently achieved by chemical or processing manipulations of collections of ECM components, even if some micro- and nano-architectural features can be replicated. On the contrary, this is most likely achievable when the complete structural features of the normal ECM can be prepared, which can occur if natural tissues, most likely of xenogeneic origin, can be decellularized.

As discussed recently by Hussey et al. (2018), ECM based materials can be prepared in several ways. Tissue decellularization may involve tissues such as the small intestine, the urinary bladder or the dermis, which can be subjected to mechanical delamination and immersion in decellularization agents, yielding a 2D sheet or a hydrogel. Several commercial products have been approved by the FDA for use in soft tissue repair, including ventral hernia repair and breast reconstruction. The clinical outcomes are controlled by the surgical technique, the matching of the sourced material with the specific clinical conditions, the age of the sourced material and patient comorbidities. Mechanistically these outcomes are determined by the host response to the ECM derived material, including angiogenesis, innervation, stem cell recruitment and modulation of the immune response. Although it is often claimed that this decellularized tissue does not elicit adverse innate or adaptive immune responses, this may not be the case. For example, although the ECM product CorMatrix® continues to receive regulatory approval in several jurisdictions, a systematic review of cardiovascular applications for this porcine SIS material suggests that the long-term histopathological data indicates the presence of significant chronic inflammation; a dense eosinophilic inflammation with granulation tissue and fibrosis and without tissue remodeling is not consistent with the required biocompatibility (Mosala Nezhad et al., 2016).

An alternative to tissue decellularization is whole organ decellularization. This usually involves perfusion of the organ, for example heart, liver, lung or kidney, through the native vasculature, followed by recellularizaton using patient-derived cells and subsequent transplantation into the recipient. This, of course, is not a trivial process and, after a decade or more, progress toward clinical transplantation has been slow. With respect to the kidney, for example, Petrosyan et al. have described the challenges with the repopulation of the renal matrix with functional renal cell types (Petrosyan et al., 2016). Zhou et al. have reported on progress with porcine decellularized lung scaffolds

TABLE 1 | Comparison of synthetic polymers, biopolymers and ecm-derived materials for tissue engineering templates.

Synthetic polymers	Biopolymers	ECM-derived materials
Good control of essential material chemical characteristics (mol.wt etc.), giving acceptable quality control and regulatory processes	Material characteristics depend on source and processing conditions	Considerable variability in essential material characteristics, making quality control difficult
Usually very cost effective	Can be very expensive, especially if recombinant techniques are required	Cost effectiveness will vary with source and processing conditions
Mechanical properties usually tunable and cover wide range	Mechanical properties vary, some can be quite good, others poor	Mechanical properties vary, some can be quite good, others poor
Degradation characteristics can be tunable and cover wide range	Degradation characteristics can be tuned, especially by control of blends	Degradation properties not easily tuned
Materials are inherently incompatible with support of key cell functions; may be capable of functionalization for some limited improvement	Careful choice of formulation can give good compatibility with cell function	Structure most closely replicates normal cell microenvironment, with support of cell function
Most materials should be free from toxicological and immunological risks	Most, although not all, materials should be free from toxicological and immunological risks	Possibility of immunological responses
Only a few are compatible with 3D bioprinting	Several materials with excellent characteristics for bioprinting	Not ideal for bioprinting

seeded with human airway epithelial progenitor cells derived from rejected donor lungs and banked human umbilical vein endothelial cells (Zhou et al., 2018). When transplanted into porcine recipients, the grafts were able to withstand the recipient's pulmonary circulation and exchange gases during ventilation over a short period of time. This demonstrates the feasibility of this approach to lung tissue-engineering templates, but there is still a long way to go before full graft maturation can be achieved.

It should be mentioned in passing that one theoretical alternative to the decellularization and recellularization of animal-derived organs is the use of direct xenotransplantation. It could be argued that this would not constitute a tissue engineering approach, or possibly even a regenerative medicine approach but it should be considered here. Although xenotransplantation has been suggested, and experimented, for many decades, going back to the attempts to transplant baboon hearts into pediatric human patients in the 1980s (Bailey et al., 1985), the pathobiologic barriers, especially those of immunological and infectivity character, not to mention the ethical implications, have appeared insurmountable. Recently, however, with the advances in genetically engineered pigs and better immunosuppressive agents, the reality of xenotransplantation as a solution to organ donor shortage is becoming closer (Cooper et al., 2018), possibly rendering whole organ decellularization less relevant.

As a final point with respect to templates, several of the examples of improved success discussed in section Introduction referred to biomaterials, either synthetic or natural, which did have greater biological activity and whose selection was not predicated on inertness. Usually these may be considered as hydrogels (Williams, 2018) or elastomers (Coenen et al., 2018). Virtually all reviews and analyses of these materials point to the limited biocompatibility (with respect to tissue engineering) of synthetic versions and the limited mechanical functionality and irreproducibility of many natural versions. With synthetic materials, progress is undoubtedly being made, as, for example, with click chemistry approaches to polymer synthesis that can eliminate all toxic by-products of polymerization (Xu and Bratlie, 2018) but it does seem inappropriate that so much work is being performed on variations of these synthetic polymers, and thousands of papers on them published each year, when they are based on the wrong principles of tissue-engineering templates. With natural materials, even with some continuing disadvantages, there is far more hope that the correct principles can guide their development. It does seem likely that some single-protein based materials (such as tropoelastin or collagen) or some protein-protein hybrids, especially if they can be appropriately functionalized and prepared with optimal architecture, provide a better pathway to those template specifications.

CONCLUSIONS

This essay has shown, through a series of examples of attempts to regenerate tissues through a conventional scaffold approach, that any process that relies on biomaterials that have been determined to be biologically inert and, therefore "biologically safe" is highly unlikely to succeed. It is possible that some new tissue will form within the porosity of these scaffolds, but that is usually in spite of rather than because of their properties. It is stated clearly and unequivocally here that the conventional scaffold paradigm, especially when based on synthetic biodegradable polymers, is mechanistically inappropriate and that a far better paradigm is one that is based on tissue engineering templates which, far from being inert, actively take part, both biologically and mechanically in the stimulation of those target cells intended to regenerate new tissue. It is further believed that although some natural biopolymers, as hydrogels or elastomers, and especially when used in conjunction with the right signaling molecules, can produce some good results experimentally, these, in their present form, are not the basis for sustainable tissue engineering. The most attractive biomaterials from the tissue engineering perspective are those derived from decellularized tissues, although even here biocompatibility characteristics are not fully understood and sustainability is still some way off.

DATA AVAILABILITY

All datasets analyzed for this study are included in the manuscript and the supplementary files.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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Review

Food waste biorefinery: Sustainable strategy for circular bioeconomy

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ABSTRACT

Enormous quantity of food waste (FW) is becoming a global concern. To address this persistent problem, sustainable interventions with green technologies are essential. FW can be used as potential feedstock in biological processes for the generation of various biobased products along with its remediation. Enabling bioprocesses like acidogenesis, fermentation, methanogenesis, solventogenesis, photosynthesis, oleaginous process, bio-electrogenesis, etc., that yields various products like biofuels, platform chemicals, bioelectricity, biomaterial, biofertilizers, animal feed, etc can be utilized for FW valorisation. Integrating these bioprocesses further enhances the process efficiency and resource recovery sustainably. Adapting biorefinery strategy with integrated approach can lead to the development of circular bioeconomy. The present review highlights the various enabling bioprocesses that can be employed for the generation of energy and various commodity chemicals in an integrated approach addressing sustainability. The waste biorefinery approach for FW needs optimization of the cascade of the individual bioprocesses for the transformation of linear economy to circular bioeconomy.

1. Introduction

Food waste (FW) is one among the most generated bio-wastes around the globe. According to the Food and Agriculture Organisation (FAO) food losses refers to “the decrease in edible food mass throughout the part of the supply chain that specifically leads to edible food for human consumption” (Gustavsson et al., 2011). About 1.3 billion tonnes of food (Paritosh et al., 2017) and one-third of the total global food production is wasted each year (Fig. 1a), costing the world economy about $750 billion or INR 47 trillion (Gustavsson et al., 2011). In Asian countries, the urban FW generation is expected to mount annually from 278 to 416 million tonnes from 2005 to 2025 (Paritosh et al., 2017). India ranks seventh in overall food wastage, while the Russian Federation tops the list. The huge generation of FW is severely impacting the environment majorly due to emission of green house gases (GHG) (Gustavsson et al., 2011; Venkata Mohan et al., 2017) (Fig. 1b). The amount of FW generated can originate either from its production, handling, storage, processing, distribution or consumption (Gustavsson et al., 2011). Further, the major fraction of FW can be categorized into avoidable FW (edible) and unavoidable FW (non-edible) prior to it’s discard. The avoidable FW generation can be decreased by taking precautionary measures at each level from its production to consumption. For unavoidable FW there is an extreme necessity to have proper waste management and reuse practices and policies (Fig. 1c).

FW mainly constitutes of organic fraction viz., carbohydrates, proteins, lipids and traces of inorganic components, which can be further digested into simpler organic compounds viz., glucose, amino acids, fatty acids (Lin et al., 2013; Dahiya et al., 2015), etc. although composition varies source to source. FW can be converted into a spectrum of bio-commodity chemicals and bio-energy by employing bioprocesses (Lin et al., 2013; Kiran et al., 2014; Dahiya et al., 2015). Bioconversion of FW into sustainable platform chemicals offers new resource recovery alternatives for fossil based chemicals to certain extend. FW as a substrate in anaerobic fermentation for biogas production is highly exploited by the research fraternity (Sen et al., 2016) and in recent years the research has been extended towards the production of liquid biofuels (Karmee, 2016), commodity chemicals (Lee et al., 2014), biohydrogen (Pasupuleti et al., 2014), biohythane (Sarkar and Venkata Mohan, 2017), bioelectricity, etc. FW can also act as an abundant source of electrons for electroactive bacteria (EAB) capable of producing bioelectricity with simultaneous waste remediation (Elmekawy et al., 2014). Various pretreatment methods viz. physical, chemical, physio-chemical, enzymatic (Kondusamy and Kalamdhad, 2014), etc. have been adopted for hydrolysis of FW to enhance the biogas and biochemical production. Recently, apart from acidogenesis other bioprocesses viz. bio-electrofermentation, bio-diesel production, solventogenesis, etc., are gaining rapid interest. Integrating these bio-

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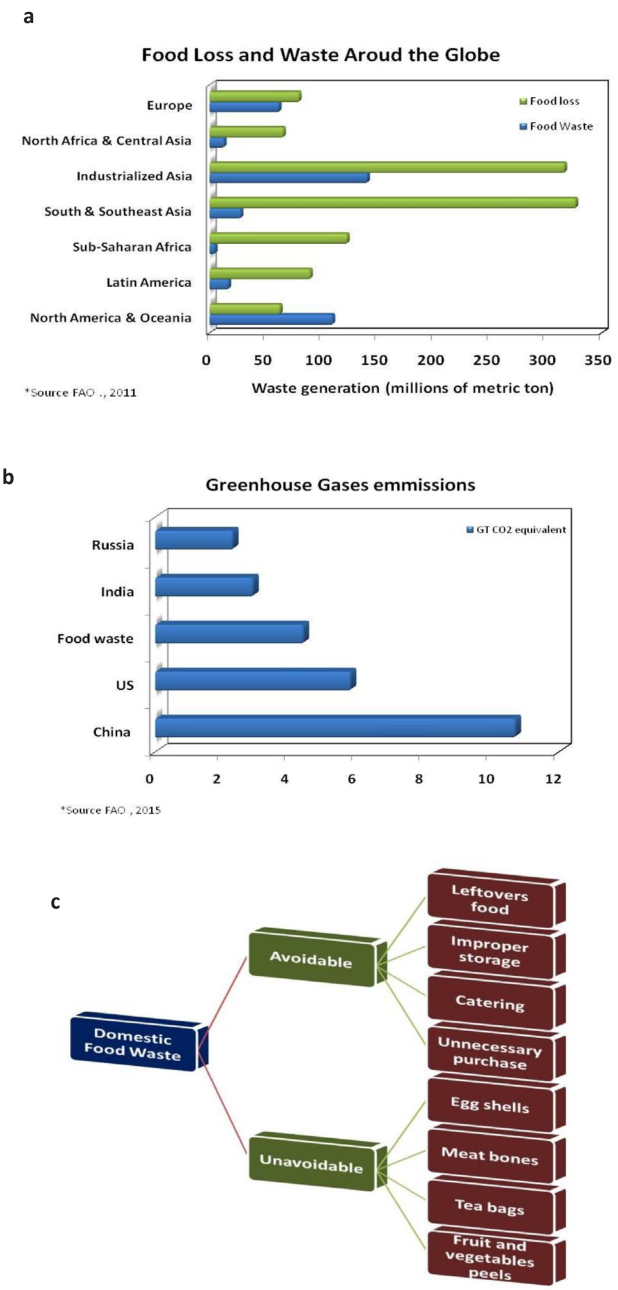

*Source FAO ., 2011

*Source FAO , 2015

Fig. 1. (a) Global food waste and food loss statistics (Source: FAO, 2011) (b) Global green house gases emissions in terms of GT CO_2 equivalents (Source: FAO, 2015) (c) Classification of domestic food waste. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

processes can further provide a new dimension in the frame-work of FW biorefinery. Thus, this review comprehensively discusses the key bioprocesses that are employed for FW valorisation. It also makes an attempt to depict various futuristic technologies and their integration in a biorefinery approach for developing a circular bio-economy.

2. Bioconversion processes and bioproducts

2.1. Anaerobic fermentation/Acidogenesis

Anaerobic fermentation (AF) is probably the most demanding process for the valorisation of FW towards methane (CH_4), hydrogen (H_2) and volatile fatty acids (VFA) viz., acetic acid (H_{Ac}), propionic acid (H_{Pr}), butyric acid (H_{Bu}), iso-butyric acid (H_{IBu}), valeric acid (H_{Va}) and iso-valeric acid (H_{IVa}) production (Fig. 2). AF is gaining immense interest when compared to other bio-platforms for biofuels and bio-commodity chemical production using biogenic waste including FW (Dahiya et al., 2015; Sarkar et al., 2016). AF is a sequential process wherein hydrolysis is the first step followed by acidogenesis, acetogenesis, dehydrogenation and methanogenesis. These steps are achieved by the action and syntrophic association of various bacteria viz. hydrolytic, acetogenic, hydrogen-producing, acetate-forming microbes, homoacetogens, acetoclastic methanogens and hydrogenoclastic methanogens (Venkata Mohan, 2009). Each stage of AF yields important bio-products, hydrolysis yields fermented sugars, etc., acidogenesis yields VFA's and H_2, acetogenesis yields H_{Ac} and H_2 while as the terminating process methanogenesis yields CH_4. For the enhanced production of VFA and $H_{2,}$ methanogenesis can be suppressed by implementing various inoculum pre-treatment strategies (Venkata Mohan et al., 2008a; Sarkar et al., 2016). Subsequently, the produced VFA can be biologically and/or chemically converted to bio-based products viz. alcohols, polymers, pharmaceuticals, etc. AF platform using mixed microbiome makes it particularly suitable for utilizing FW as feedstock and makes process relatively inexpensive. Integrating conventional AF with electrodes in bioelectrochemical systems (BES) can also generate bioelectricity. In comparison to the sugar platform, AF platform utilises organic fraction of biogenic wastes viz. carbohydrate, lipids, and proteins towards biofuels and commodity chemicals production, thus decreases the carbon load from the environment.

2.1.1. Sugars

Considering the various possibilities of resource recovery, production of sugars or sugar rich effluents from the FW is one of the key areas to be considered (Li et al., 2012). Sugars like glucose, fructose, galactose and ribose are mostly mined during the hydrolytic pre-treatment of the FW (Hafid et al., 2015). The composition of sugars may vary with respect to FW composition and origin. The sugars have industrial importance and the concentration of produced sugars in the hydrolysate is dependent on the adopted pre-treatment strategy. Thus, the method of pre-treatment is selected to achieve the following viz., acceleration of sugar yields, minimization of the sugar degraded compounds formation or losses, elimination of inhibitory by-products formation and finally to increase the economic viability of the process. There is a need to establish a comprehensive pre-treatment method to extract the maximum reducing sugars from FW. Pre-treatment can be either done individually with physical, chemical, physico-chemical, biological and enzymatic methods or in combination of the strategies (Hafid et al., 2015). Among the various pre-treatments, dilute acid pre-treatment is considered to be a promising methods for carbohydrate rich FW. Pre-treatment using hydrochloric acid and sulphuric acid at low concentrations are commonly applied directly or in combination with enzymatic method to avoid the formation of sugar degraded compounds (furfurals/hydroxyl methyl furfurals). Additionally, mixture of α-amylase, β-amylase and glucoamylase enzymes is also used for the transformation of starch into small monomeric sugars (Jianguo et al., 2014).

2.1.2. Biohydrogen

Biohydrogen (H_2) is considered as a sustainable green fuel and its production from waste has attracted attention of the research fraternity around the globe. Biologically, H_2 can be produced using photo-fermentation, bio-photolysis, and AF or integrating these processes (Venkata Mohan, 2009). H_2 is produced by the action of obligatory H_2 producing acetogenic bacteria (AB). Biological H_2 production was majorly studied using a variety of wastes viz. composite vegetable based market waste (Venkata Mohan et al., 2009), FW (Sarkar et al., 2016), wastewater, vegetable waste, co-supplemented domestic sewage supplementation, etc. The potential of FW for H_2 production is well established (Sarkar et al., 2016) with semi-pilot and pilot scale studies (Pasupuleti et al., 2014; Venkata Mohan and Sarkar, 2017). FW can be

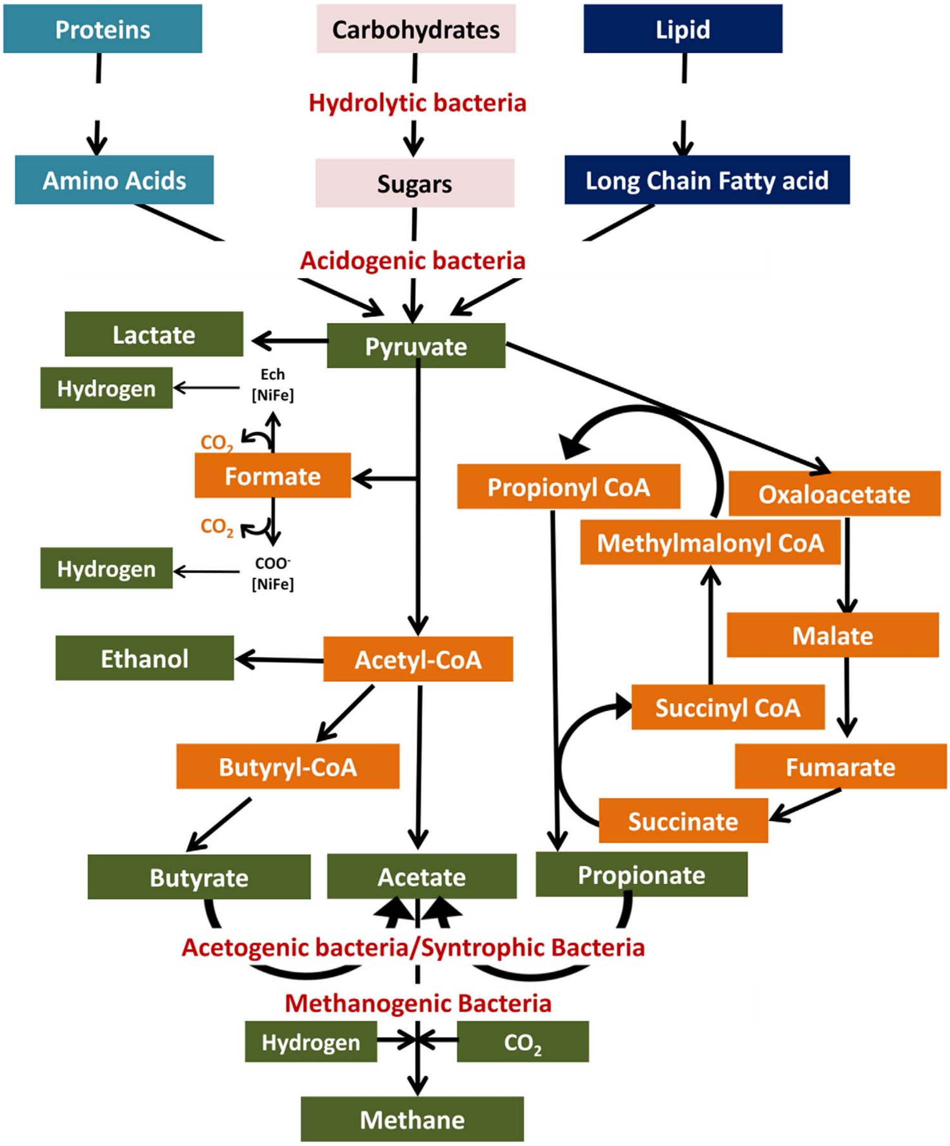

Fig. 2. Schematic pathway of anaerobic fermentation for biobased products generation.

considered as one of the ideal substrate as it contains high levels of easily degradable organic material, which can result in a net positive energy and economic balance. The H_2 production in AF is directly dependent on various process parameters viz., type/origin of inoculum, pretreatment procedure, inlet pH, co-substrate addition, reactor configuration, temperature and feed composition on the combined process efficiency (Venkata Mohan, 2009). Employing mixed consortia as biocatalyst and FW as feedstock for H_2 production has multiple advantages as it has economic viability, non-sterile operating conditions, operational flexibility, utilization of carbon rich substrates, multiple product synthesis with diverse biochemical functions, ease of process control and up-scaling feasibilty (Pasupuleti et al., 2014; Venkata Mohan, 2009; Goud et al., 2017). Combining AF with photo-fermentation is a strategy to enhance the biological production where the metabolites produced during AF can also be further utilized. The photo-fermentation and AF can be either performed in two-phase operation or single stage operation (Chandra et al., 2015a). Combining dark and photo-fermentation was found to be the ideal route for the highest possible theoretical H_2 yield. The advancements in the biological H_2 production from a variety of biogenic wastes specifically with FW may lead to worldwide setting up of pilot plants and usage of H_2 as major transportation fuel.

2.1.3. *Biomethane*

Biogas is mainly composed of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), moisture and traces of hydrogen sulphide (H_2S). CH_4 production is perhaps the most explored technology for the generation of bio-energy utilizing FW as substrate with AF. CH_4 production from FW is dependent on the various process parameters viz. reactor design (Kondusamy and Kalamdhad, 2014), inoculum type (Deepanraj et al., 2017), temperature, pH, carbon/nitrogen ratio (Zeshan et al., 2012), volatile fatty acid (Xu et al., 2014), organic loading rate (OLR), co-digestion (Agyeman and Tao, 2014) etc. Advancements in research for biogas production have lead to the development of high-rate bio-methanation technology with improved process efficiency (Dahiya and Joseph, 2015). Methane production in the form of biogas from FW have reached commercial level in India and abroad as several industries have developed and established full scale technologies.

2.1.4. *Biohythane*

Individually CH_4 and H_2 have their limitations, like H_2 is reactive and flammable causing storage issues whereas CH_4 faces a problem of low flammability. Blending CH_4 and H_2 in the ratio of 1:4 forms biohythane, which is emerging as an appropriate fuel that is clean and has good calorific efficiency (Pasupuleti and Venkata Mohan, 2015; Sarkar and Venkata Mohan, 2017; Sen et al., 2016). Blending a small

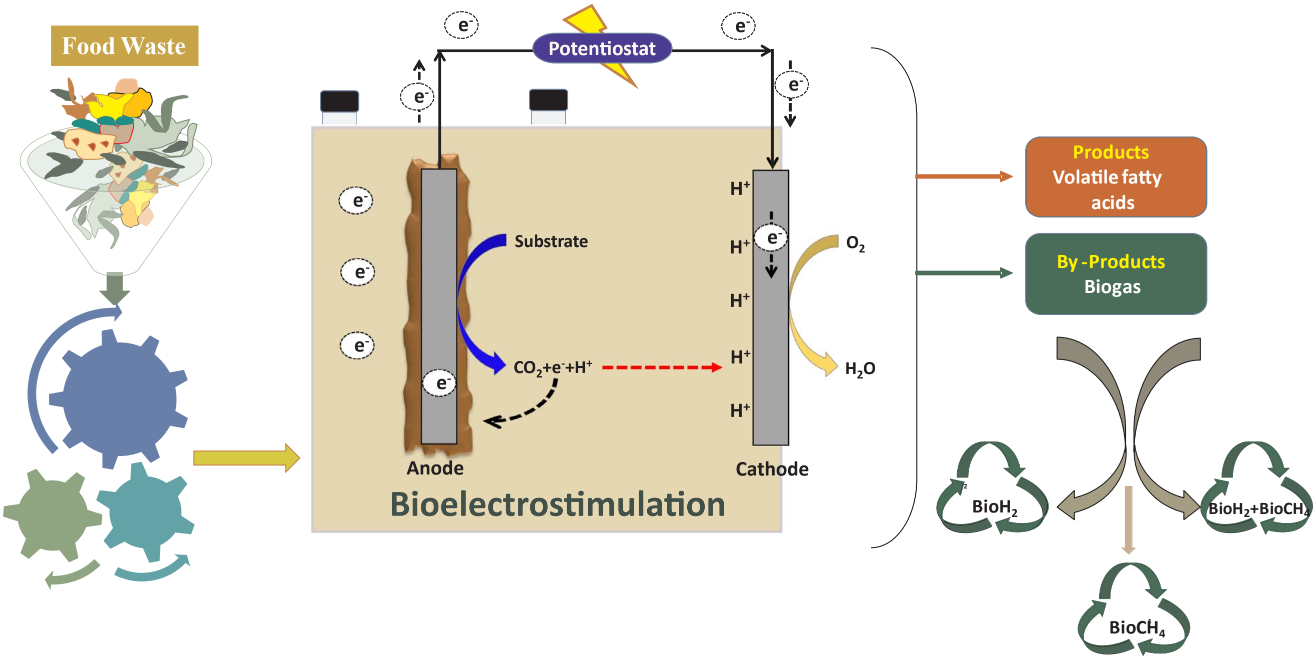

Fig. 3. Schematic of electro-fermentation.

percentage of H_2 with CH_4 enhances the combustion rate, which greatly increases the efficiency of CH_4 fueled vehicles. Various studies have been performed using FW (Cavinato et al., 2012; Yeshanew et al., 2016; Sarkar and Venkata Mohan, 2017) and distillery spent wash (Pasupuleti and Venkata Mohan, 2015) as feedstock for the production of biohythane. Biohythane production has been studied from lab scale to semi-pilot scale. Specific H_2 production of 66.7 L/kg of total volatile solid (TVS) feed and a specific biogas production in the second phase of 0.72 m^3/kgTVS fed, was claimed to be typical composition for biohythane (Cavinato et al., 2012). A semi-pilot scale study using distillery spent wash observed maximum biohythane production of 147.5 ± 2.4 L (Pasupuleti and Venkata Mohan, 2015). Highest H_2 yield in continuously stirred tank reactors (CSTR) and CH_4 yield in anaerobic fixed bed reactors (AFBR) were reported (Yeshanew et al., 2016). Cumulative biohythane production was observed to be varied from 128.7 L (control; 60 g COD/l), 144 L (60 g COD/l), 156 L (70 g COD/l), 156 L (80 g COD/l), 159 L (90 g COD/l), and 163 L (100 g COD/l) based on organic load of FW (Sarkar and Venkata Mohan, 2017). The research reveals the potential of FW as the future feedstock for biohythane production which can be easily commercialized.

2.1.5. *Volatile fatty acids (VFA; C_2-C_5)*

VFAs or short chain carboxylic acids viz. H_{Ac}, H_{Pr}, H_{Bu}, H_{IBu}, H_{Va} and H_{IVa} are the major co-products along with H_2 in AF. VFA production in anaerobic systems started when biomethanation came into limelight in the 18th century. Conventionally, these VFAs are produced chemically from petroleum derived compounds. These chemical processes are energy intensive and have negative impact on the environment, thus its biological production is gaining immense interest. For VFA production, sterile fermentation conditions are not required, hence AF it particularly suitable for utilizing waste biomass streams and is relatively inexpensive. FW as a substrate in AF for CH_4 production is highly exploited by the research fraternity where generation of VFA is considered as an important process parameter (Kiran et al., 2014; Sarkar et al., 2016; Sen et al., 2016). However, from the last two decades focus is shifted towards VFA production in AF, as these acids have importance in pharmaceuticals, textiles, food and beverages, plastics, polymers and many more industries. The amount of these acids production from FW depends on the composition, inoculum, reactor condition, temperature, organic loading rate and redox conditions (Lee et al., 2014; Dahiya et al., 2015). The type of VFA produced majorly depends on the composition and degradation of FW. The degradation of particular amino acid or the acidification of long chain fatty acids (LCFA) produces VFA in the form of H_{Ac} only. On the other hand, the acidification of monosaccharides by anaerobic bacteria produces H_{Ac}, H_{Pr}, and H_{Bu}. Thermodynamically, the production of H_{Ac} by anaerobic acidifying bacteria is more favourable than H_{Bu}, and H_{Va}. Thus, for FW that mainly contain carbohydrates, it is expected that acetate will be the highest proportion of VFA. Under stress conditions, H_{Pr} and H_{Bu} concentrations are expected to increase. For example, at high hydrogen concentration more H_{Pr} is produced. Biologically, these VFAs can be used for the production of bioplastics (anoxygenesis), biodiesel (oleaginous metabolism), bioelectricity generation (bioelectrogenesis), biofertilizers (Venkata Mohan et al., 2016a), etc.

2.1.6. *Medium chain fatty acids (C_6-C_{10})*

Biological production of medium chain fatty acids (MCFA) proceeds via reverse β-oxidation pathway and this pathway was described after studying metabolic pathway of *Clostridium kluyveri* (Steinbusch et al., 2011). In this MCFA synthesis pathway, instead of consuming VFAs into methane (CH_4), they can be elongated by two carbons per cycle to MCFAs (C_6-C_{10}). The process of reverse β-oxidation requires carbon source, reducing equivalent and energy from specific electron donors. Apart from the simple carbon source, electron donors such as ethanol, H_2, and lactate could also be used. Several experiments were reported for n-caprylate production using ethanol as electron donor (Steinbusch et al., 2011). MCFAs are superior to VFAs, due to more number of carbon atoms (C_6 to C_{10}) that provide longer hydrophobic nature and lower oxygen/carbon ratio compared to VFAs. Hydrophobic nature of MCFA also facilitates the ease of separation from the fermentation broth (Gildemyn et al., 2017). Moreover, longer hydrocarbon tail of MCFAs will also provide higher energy density and lower solubility compared to ethanol. Heating value of 1 mol of caproic acid (3452 kJ) is higher than the 2 mol of ethanol (2638 kJ) required for producing caproic acid (Grootscholten et al., 2013). MCFAs have wide range of applications in aviation fuels, renewable precursors for diesel, antimicrobial, fragrance and flavouring intermediates, etc. Synthesis of MCFAs using FW as feedstock address the waste management constrains with simultaneous high value products synthesis (Lee et al., 2014; Gildemyn et al., 2017).

2.1.7. Electro-fermentation

The regulation of the rate kinetics by the interference of electrodes in the microbial environment (electrofermentation (EF)) is an electrocatalysis mechanism (Fig. 3) towards regulated product formation (Venkata Mohan et al., 2016a; Schievano et al., 2016). The use of these electrode-based electron acceptors can enhance the electrode-linked rates by eliminating the redox constraints, benefits in enhancing the biobased targeted products and driving other unbalanced reactions to yield pure products (Chandrasekhar et al., 2015). The technique is still in its infancy and is hyped as a promising method to convert organic sources into valuable platform chemicals and biofuels. External stimulation on these electrodes with applied potential (positive or negative) creates a synergy of interactions on solid-liquid interfaces between electrode and microbes influencing their electrometabolic rates (Nikhil et al., 2015). Studies on decreasing electrochemical losses caused by the common disruptors involved in oxygen-reduction reaction (ORR) and hydrogen evolution reaction (HER) with relation to electrochemistry of substrate-hydroxide-oxide binding need to be given importance in effective FW utilization. The modifications specific to the carbon surface that lead to selective, sensitive and economic viability when compared to native electrodes need to be analyzed (Rahimnejad et al., 2015; Venkata Mohan et al., 2014a). Electrode potential is essential to determine the performance of a BES in EF so as to decrease the electrochemical losses towards maximum energy harvesting. Mostly bacteria are negatively charged and hence imposing a positive potential to the anode can accelerate the biofilm formation due to the electrostatic interaction (Arunasri et al., 2016; Srikanth and Venkata Mohan, 2012). To facilitate the reductive reaction in the cathode, the negative potential should be imposed. The syntrophic interactions and the optimized conditions that are at play in the bioelectrochemical systems (BES) effect the rapid and enhanced conversion of FW into value added biobased products (Venkata Mohan et al., 2014b). Production of electro-fuels viz., bioelectricity, H_2 and bioethanol and additional metabolites from FW in solid state bio-electrofermentation system (SBES), including formate, lactate, propionate observed in depicts the potential of electrofermentation towards FW valorization. The synergistic approach of integrating microbial environment with electrochemistry is an encouraging technology that establishes it as a futuristic, green and sustainable route in its approach.

2.2. Solventogenesis

Production of biosolvents from FW is gaining interest due to limited supplies, high economics and environmental impacts of exploiting fossil fuels. Biosolvents such as bioethanol and biobutanol production has the ability to replace the dependency on non-renewable conventional sources (Huang et al., 2015). These biosolvents can be produced as byproducts in the process of fermentation from FW by utilizing anaerobic microbiomes. Apart from the product benefits, the high economics is considered a major bottleneck in these biotechnology processes (Wang et al., 2016). Biological conversion of FW to biosolvents can also decrease the organic pollution load by 75–80% while deriving energy and making the process self-sustainable.

2.2.1. Bio-ethanol

Worldwide ethanol production demand worldwide has reached 100 billion litres in 2015 and is increasing significantly. Therefore, there is a need to shift from fossil based ethanol synthesis to renewable resources based production. Currently, pilot scale production of bioethanol is being practised using sugarcane and corn which are also consumed as food and animal feed, thus raising the food versus fuel competition. Additionally, studies were also performed using low-cost agricultural residues viz., wheat straw, rice straw, sugar cane bagasse and other cellulosic biomass (Humbird et al., 2011). Lignin interferences in the conversion of cellulose and hemicelluloses into monosaccharides is a major limit to the production of ethanol. Thus substrate like FW is a better option which can sustainably address the food vs. fuel condition. The potential of bioethanol from FW has been explored with vacuum recovery technology to avoid the high solid contents of FW. Maximum ethanol production with vacuum fermentation (357.5 ± 5.4 g/kg FW) was reported than the conventional fermentation (326.5 ± 5.4 g/kg FW). FW saccharification followed by fermentation was also evaluated using *S. cerevisiae,* in two stages resulted in 0.43 g ethanol/g TS. Simultaneous saccharification and fermentation in a single stage resulted lower ethanol yields 0.31 g ethanol/g TS (Walker et al., 2013). High organic content of FW acts as a potential substrate for the production of bioethanol and simultaneously addressing the food vs. fuel problems.

2.2.2. Bio-butanol

Bio-butanol also known as butyl alcohol is commonly used as solvent, extractant, supplements, elutent, precursor for other compounds etc. Conversely, it can also be used as transportation fuel by blending with gasoline. The properties of biobutanol are low vapour pressure, non-sensitivity to water, reduced volatility, lower toxicity, and flammability. Biobutanol is of particular interest due to its ability to directly replace gasoline, thus considered a drop-in-fuel. Starch-rich crops such as maize, wheat, rice, cassava, grasses, trees and energy crops and algae are widely used substrates for bio-butanol production and based on the substrate used it is designated as first, second and third generation bio-butanol (Stoeber et al., 2011). The main process for bio-butanol production is extraction of sugars from the substrate using various pre-treatment strategies later utilizing the extract using strains belonging to *Clostridiaceae* family. Thus, domestic FW being rich carbon source is utilized for bio-butanol production (Huang et al., 2015) but still there is a need to explore the potential of FW for biobutanol production.

2.3. Oleaginous metabolism

Oleaginous microorganisms belonging to the genera of microalgae, yeast, fungi and bacteria have been explored for lipid production. Lipid synthesis from oleaginous microorganisms offers several advantages over the conventional sources like short life cycle, less labour intensive, lower cultivation area, etc. Oleaginous microorganisms can accumulate lipids from 20% to 70% of dry biomass under specific cultivation conditions (Ratledge, 2002). The lipid biosynthesis in the form of triacylglycerol (TAG) starts when acetyl-CoA is transported from the mitochondria to the cytosol executed by the ATP citrate lyase (ACL) (Fig. 4). Acetyl-CoA carboxylase (ACC) then catalyzes the first step towards lipid biosynthesis, converting cytosolic acetyl-CoA into malonyl-CoA, which is the primary precursor for fatty acid elongation. The lipid biosynthesis is most commonly triggered by the limitation of nitrogen and excess of carbon. Malonyl-CoA is then converted to acyl-CoA chains that are transported to the endoplasmic reticulum (ER) or lipid body membranes for the final assembly of triacylglycerol (TAG).

2.3.1. Biodiesel- Yeast/Fungi

Biodiesel is a sustainable energy form produced from renewable resources. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids. Conventionally, biodiesel is produced from a variety of feedstocks including vegetable oils, waste cooking oils and animal fat. The limited supply of these feedstocks restrains the further expansion of biodiesel industry. Oleaginous yeasts and fungi (especially molds) can potentially use organic waste as feedstock for the synthesis of lipids. A variety of inexpensive carbon sources viz. molasses (Alvarez et al., 1992), grape must (Buzzini and Martini, 2000), radish brine (Malisorn and Suntornsuk, 2008), hydrolyzates of agricultural residue (Yu et al., 2011), distillery wastewater, municipal wastewater (Chi et al., 2011), food and feed waste (Schneider et al., 2012), cheese whey

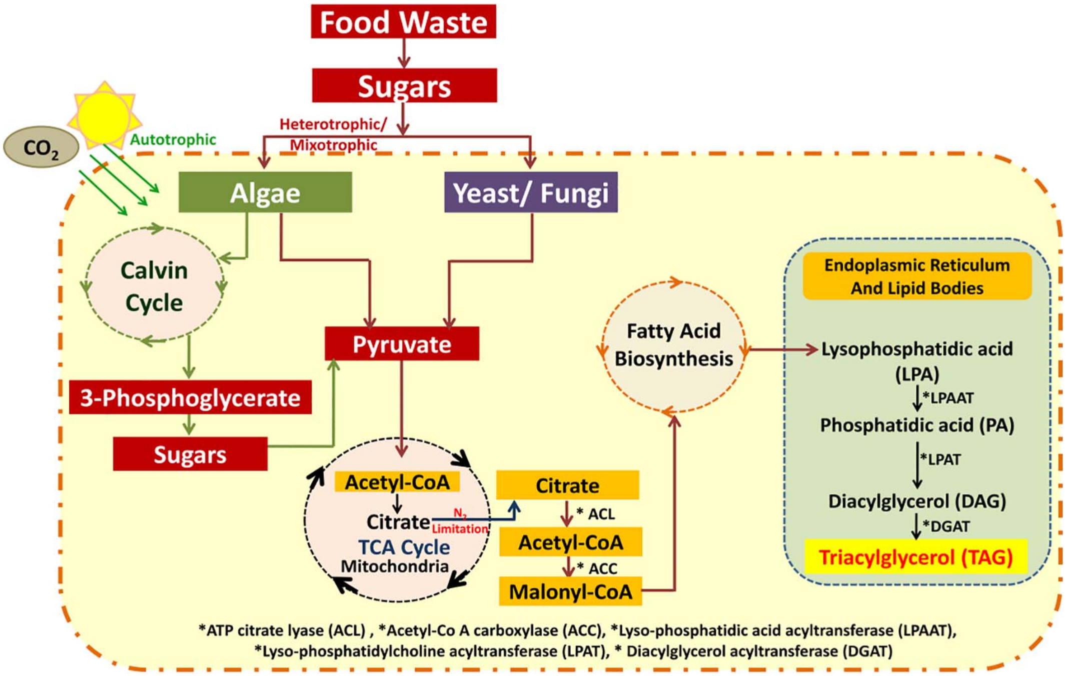

Fig. 4. Schematic pathway for bio-diesel production from oligenous micro-organisms.

(Castanha et al., 2014), food/municipal wastewater (Chi et al., 2011), flour extracts, etc., have been used as primary feedstock for cultivation of oleaginous yeast. Some yeast strains, such as *Rhodosporidium* sp., *Rhodotorula* sp. and *Lipomyces* sp. are reported to accumulate intracellular lipids as high as 70% of their biomass dry weight (Ratledge, 2002). *Crptococcus curvatus* when grown in sweet sorghum bagasse under N-limiting conditions showed to accumulate storage lipid up to 60% on a dry weight basis with 44% of saturated fatty acids (SFA) (Liang et al., 2012). Lipid accumulation by oleaginous fungi using different renewable substrates such as glycerol, rice hulls, wheat straw, waste cooking oil and corncob waste liquor were reported (Economou et al., 2011; Subhash and Venkata Mohan, 2011). Oleaginous fungi *Aspergillus sp*. showed 22.1% lipid productivity when grown on corncob liquor (Subhash and Venkata Mohan, 2011). *Mortierella isabellina* showed highest lipid content of 39.4% on liquid hydrolyzates of wheat. Therefore, FW can function as a promising feedstock for biodiesel production using microbial cell factories in the framework of biorefinery.

3. Integrated bioprocesses

Various bioprocesses used for FW valorisation has specific process efficiency and generates metabolites rich effluents. These effluents can serve as primary substrates for the generation of various products viz., algal biodiesel, bio-electricity, bio-fertilizers, bio-plastics, etc. The necessity of integrating various bio-processes to improve the process efficiency and generating gamut of bioproducts is essential for improving the economic viability of the process. In this context, various biorefinery models were discussed elsewhere (Venkata Mohan et al., 2016a) than can be implemented for the FW valorisation.

3.1. Biodiesel-algae

Microalgae can utilize both inorganic (carbon dioxide; autotrophic mode) and organic (heterotrophic mode) carbon along with micronutrients. The average lipid content of algae cells varies between 1% and 70%, and can reach up to 90% of dry weight under specific conditions (Li et al., 2008). Compared to phototrophic process, heterotrophic process has benefits of high cell density without light limitation, but one of its drawbacks is the high cost of feedstock. Therefore, acidogenic effluent as well as FW can be explored as a feedstock for cultivation of microalgae in mixotrophic and heterotrophic modes. Microalgae yielded higher biomass as well as lipids when grown in the heterotrophic and mixotrophic mode of operations using wastewater as feedstock (Devi and Venkata Mohan, 2012; Devi et al., 2012). *Chlorella sorokiniana* is reported to accumulate up to 22.9% of intracellular lipids when grown heterotrophically in food and municipal wastewater (Chi et al., 2011). *Schizochytrium mangrovei* and *Chlorella pyrenoidosa* when grown in canteen waste (rice, noodles, meat, and vegetables) produced 300 mg/g of lipid intracellularly (Pleissner et al., 2013). Acidogenic effluent from biohydrogen production process when used to cultivate microalgae under heterotrophic conditions showed a lipid productivity of 26% (Venkata Mohan and Devi, 2012). *Chlamydomonas reinhardtii* was reported to grow well with acetate under mixotrophic conditions (Moon et al., 2013). The highest FAME yield (19.02% of biomass) and biomass production (2.05 g/L in 5 days) were obtained with 5 g/l of VFA. High lipid content of 34% with acetate followed by 18% with butyrate and 3.5% with propionate was reported under mixotrophic conditions (Chandra et al., 2015b). *Chlorella ellipsoidea* and *Scenedesmus quadricauda* were tested to grow on effluent from anaerobic digestion of kitchen waste and reported good lipid productivity (Pei et al., 2017). Acidogenic effluent from biohydrogen production process can serve as a potential carbon source for lipid biosynthesis by integrating with heterotrophic cultivation of microalgae.

3.2. Biopolymers

Polyhydroxyalkanoates (PHAs) are group of biopolymers synthesized by various prokaryotic microorganisms as energy and carbon reserve materials in response to nutrient limiting or stressful conditions (Reddy and Venkata Mohan, 2012). The economic and environmental needs insists the development of sustainable and renewable biobased polymers (Amulya et al., 2015a). These biobased polymers have gained momentum not only due to their biodegradability but also due to their thermoplastic properties that are similar to the petroleum derived plastics. These have a range of different applications such as packaging, paints, adhesives and medical applications such as tissue engineering, implants, chiral substrates for drug synthesis and drug delivery.

Biogenic wastes like FW (Reddy and Venkata Mohan, 2012), spent wash effluents (Amulya et al., 2014), sugar cane molasses (Albuquerque et al., 2007) and bakery waste hydrolysate using *Halomonas boliviensis* (Pleissner et al., 2014) were used for PHA production. Integration of acidogenic fermentation with PHA production has also been reported (Reddy and Venkata Mohan, 2012; Amulya et al., 2015b). By integrating FW based acidogenic effluent to PHA production and implementing them in a multi-stage strategy, a PHA production of 23.7% was observed (Amulya et al., 2015b). PHA production of 39.6% from fermented FW was observed in comparison to unfermented FW (35.6%) due to ready availability of VFA in the acidogenic effluents. Integrating acidogenesis with bio-plastics production resulted in higher process efficiency than using the sole FW as substrate (Reddy and Venkata Mohan, 2012). Considering the abundance, use of FW or acidogenic FW as substrate is a propitious approach for PHA production that can have economic viability.

3.3. *Bioelectricity*

Microbial fuel cell (MFC) is a sustainable and futuristic technology that is capable of converting the chemical energy of waste directly to bio-electrical energy (Goud and Venkata Mohan, 2011; Ishii et al., 2013). The microorganisms in the anode function as biocatalyst, producing reducing equivalents (electrons and protons) that help in electrochemical oxidation of organic substrate. The presence of a terminal electron acceptor (TEA) in the cathode acts as an electron driving force, helping in transfer of electrons (e^-) through the external circuit, where they can be harnessed for bioelectricity production, whereas the protons (H^+) are delivered to the cathode via a membrane separating the anode and cathode (Butti et al., 2016). The transferred e^- and H^+undergo reduction in the cathode chamber to form valuable products along with FW treatment (Srikanth and Venkata Mohan, 2012; Xia et al., 2013). MFC when integrated with similar principle based technologies can become a hybrid technology for bioelectricity production along with waste treatment and value addition (Venkata Mohan et al., 2008b & 2014a).

3.4. *Bio-fertilizer*

Bio-fertilizers from FW can be produced by composting technology or by using effluent of AF. FW can be composted aerobically or anaerobically and are categorised into aerobic and anaerobic compost. The production and quality of the compost depends on the conditions viz., moisture content, composition, pH, temperature, aeration and carbon to nitrogen ratio. The use of effluents as biofertilizer is a sustainable approach in integrated waste management and utilization, as they are inexpensive and renewable sources of plant nutrients for sustainable agriculture. Acidogenic effluents usually contains many microorganisms like *Pseudomonas, Klebsiella, Salmonella, Penicillium, Shigella, Bacteriodes, Aspergillus* and *Bacillus* which can be exploited in the production of biofertilizers (Tamil Nadu Agricultural University, 2008). *Klebsiella* and *Clostridium* are free living nitrogen fixing biofertilizers while *Bacillus and Pseudomonas* are phosphate solubilizing biofertilizers (Alfa et al., 2014). These micro-organisms can fasten the microbial processes in the soil and increase the availability of nutrients to the plants. Liquid effluents comprises of significant amount of degraded organic matter and microbial biomass, which can be used to improve soil fertility (Alburquerque et al., 2012). It contains high amount of available nutrients which makes it better for crop fertilization in comparison to chemical fertilizers. Bio-fertilizers production from FW helps in diverting the negative carbon footprint from landfills and GHG towards nutrient rich organic fertilizer. Establishing local composters in households for FW turns into nutrient-rich biofertilizer, can also be seen as an efficient process for decreasing its environmental impact and transportation.

3.5. *Animal feed*

Animal feed from FW is kept in the third tier of Food Recovery Hierarchy of United States Environmental Protection Agency (EPA) (https://www.epa.gov/sustainable-management-food/reduce-wasted-food-feeding-animals). Utilizing FW as animal feed can reduce the pollution caused by FW, providing nutrition to the animals and thus giving economic benefit to the farmers. FW can be donated to people concerned with the animal care and husbandry. The FW can be processed majorly by dehydration, silage, and liquid feeding. FW like fish waste, meat waste, peels, old sweets and bakery products, extra cooked food, milk, dairy waste, poultry derived waste, fruits and vegetable waste, etc. can be used for animal feeding (Ghosh et al., 2016). Although, these wastes are of high nutrition value but inapt use can create major health problems to the animals and thus, major countries have regulations for the use of these waste as animal feeds.

4. Food waste and its energy analysis

Unavoidable FW if quantified and valorised rightly eventually leads to the economic and environmental benefit to the society. The calorific values of FW under STP conditions is 5.35 MJ/kg, signifies its potentiality as feedstock to harvest bio-energy (Li and Khanal, 2016). Theoretically, the complete oxidation of 1 g glucose gives 16 kJ of energy. One kg (kilogram) of COD from FW gives 15.62 mol of CH_4 (350 L CH_4) with a conversion efficiency of 50%, accounting for an energy output of 13,882 kJ and it contributes 3.85 kWh of electricity generation (Li and Khanal, 2016). Similarly, one kg of COD of FW can produce 20.83 mol H_2 (466 L H_2) through dark fermentation pathway with an energy output of 5906.97 kJ and that equals to 1.6 kWh. But H_2 produced through butyric acid pathway is 10.417 mol H_2 (233.33 L H_2; 2953.49 kJ). Though, photo-fermentation produces 62.5 mol H_2 (1400 L H_2; 17720 kJ), the major problems is the inhibition caused by high concentrations of VFAs and NH-N production and also requires severe control of physico-chemical conditions (Akroum-Amrouche et al., 2013). One kg of FW (5.208 mol of glucose) under STP conditions can produce 624.96 g of acetic acid (0.875 MJ/mole), 916 g of butyric acid (2.192 MJ/mole) and 385 g of propionic acid (1.534 MJ/mole) (Mohanakrishna and Venkata Mohan, 2013). The individual calorific values of the harnessed bio-based products from FW directly contributes to the commercial value at the industrial scale. The specific yields of biogas (H_2, CH_4) depends on the actual conversion efficiencies that can be calculated to evaluate the bioprocess performance. The utilization of energy intensive and commercially viable bio-based products from FW through integration of bioprocesses can lead towards environmental sustainability and significantly contribute in the development of bioeconomy. Further, this also reduces the negative impact of FW on environment to a certain extent by integrating various bioprocesses towards maximum resource recovery with simultaneous revenue generation.

5. Biorefinery and bioeconomy

The mounting need for energy and materials is forcing humankind to shift from fossil-based linear economy to sustainable circular bioeconomy. Bioeconomy demands renewable feedstocks which have potential to generate a spectrum of biobased products, involving multidisciplinary areas of science, management, and engineering (Amulya et al., 2015b). In this context, biogenic waste is considered as a potential feedstock for developing a bioeconomy (Venkata Mohan et al., 2017). Thus, the huge amount of generated FW can also be considered as a potential feedstock. The amount of avoidable FW can be controlled to a certian extent by implementing three strategies viz. eliminate, reduce and reuse. The generation of unavoidable FW cannot be controlled thus there is a need for proper disposal and reuse strategies. The amount of avoidable and unavoidable biogenic FW can be efficiently

Table 1
Bioproducts through fermentation of food waste.

Product	Inoculum	Yield	Substrate	Reference
Biohydrogen	Anaerobic activated sludge	23.96 mmol/day	Vegetable based market waste	Venkata Mohan et al. (2009)
Biohydrogen	Sludge	1.2770.51 mmol g-COD^{-1}	Kitchen waste and white rice	Wang et al. (2009)
Biohydrogen	Anaerobic activated sludge	370 mL-H_2 g^{-1} VS	Municipal food waste	Tawfik et al. (2011)
Biohydrogen	Anaerobic activated sludge	245 mL g-COD^{-1}	Municipal food waste, kitchen wastewater	Tawfik and El-Qelish (2012)
Biohydrogen	Anaerobic activated sludge	85.65 mL-H_2 g^{-1} VS	Vegetable waste	Marone et al. (2012)
Biohydrogen	Anaerobic activated sludge	9.67 l/h	Food waste	Pasupuleti et al. (2014)
Biohydrogen	Pre-treated anaerobic activated sludge	8.65 mol/kg COD_R	Glucose	Goud et al. (2017)
Biohythane	–	H_2: 66.7 l per kg of total volatile solid (TVS) CH_4: 0.72 m^3 per kg TVS fed	Food waste	Cavinato et al. (2012)
Biohythane	Anaerobic consortium	147.5 ± 2.4 L	Distillery Spent wash	Pasupuleti and Venkata Mohan (2015)
Biohythane	Digested Sludge	115.2 (± 5.3) L H_2/$kg_{VSadded}$ and 334.7 (± 18.6) L CH_4/$kg_{CODadded}$,	Food Waste	Yeshanew et al. (2016)
Biohythane	Anaerobic Sludge	163 L	Food waste	Sarkar and Venkata Mohan (2017)
Volatile fatty acids	Anaerobic activated sludge	29.1 g-COD/L	Food waste + sludge	Chen and Wu (2010)
Volatile fatty acids	Anaerobic digested sludge	0.690 g/g	Food waste	Jiang et al. (2013)
Volatile fatty acids	Anaerobic activated sludge	0.918 g/g	Food waste	Wang et al. (2014)
Volatile fatty acids	Anaerobic activated sludge	6.3 g/L	Food waste	Dahiya et al. (2015)
Volatile fatty acids	Anaerobic pre-treated sludge	11.1 g/L	Food waste	Sarkar et al. (2016)
Volatile fatty acids	Anaerobic activated sludge	18.4 g/L (as acetic acid)	Food waste	Li et al. (2017)
Bioethanol	*S. cerevisiae*	0.31 g ethanol/g TS	Food Waste	Walker et al. (2013)
Biobutanol	*C. beijerinckii P260*	12.3 g/L	Food Waste	Huang et al. (2015)
Biodiesel	*Cryptococcus curvatus*	30–35%	Cheese whey	Takakuwa and Saito (2010)
Biodiesel	*Cryptococcus curvatus*	28.6 ± 2.2%	Food Waste and Municipal Wastewater	Chi et al. (2011)
	Rhodotorula glutinis	19.6 ± 0.2%		
Biodiesel	*Rhodotorula glutinis*	19.6 ± 0.2%	Food Waste and Municipal Wastewater	Chi et al. (2011)
Biodiesel	*Aspergillus niger*	0.49 g/g	Waste cooking olive oil	Papanikolaou et al. (2011)
Biodiesel	*Yarrowia lipolytica*	34.02–57.89%	Waste oil from chicken products, frying fish, frying vegetables	El Bialy et al. (2011)
Biodiesel	*Chlorella sorokiniana*	20–22.9%	Food Waste and Municipal Wastewater	Chi et al. (2011)
Biodiesel	*Cryptococcus curvatus*	63.98–73.26%	Sweet sorghum bagasse	Liang et al. (2012)
Biodiesel	*Chlorella vulgaris*	43%	Agro-industrial co-products, ethanol thin stillage and soy whey	Mitra et al. (2012)
Biodiesel	*Schizochytrium mangrovei and Chlorella pyrenoidosa*	300 mg/g	Rice, Noodles, Meat, and Vegetables	Pleissner et al. (2013)
Biodiesel	*Cryptococcus laurentii*	2.96 g/l	Cheese whey supplemented with Molasses	Castanha et al. (2014)
Biodiesel	*Candida lipolytica*	19.4 g/L	Corn cobs hydrolysate	Kahr et al. (2015)
	Yarrowia lipolytica	11.3 g/L		
Biodiesel	*Torulaspora maleeae*	0.31 g/L	Sugarcane molasses	Papone et al. (2016)
	Torulaspora globosa	0.2 g/L		
Polyhydroxyalkanoates	*Aerobic mixed inoculum*	39.6%	Food waste based acidogenic effluent	Reddy and Venkata Mohan (2012)
Polyhydroxyalkanoates	*Aerobic mixed inoculum*	23.7%	Food waste based acidogenic effluent	Amulya et al. (2015b)

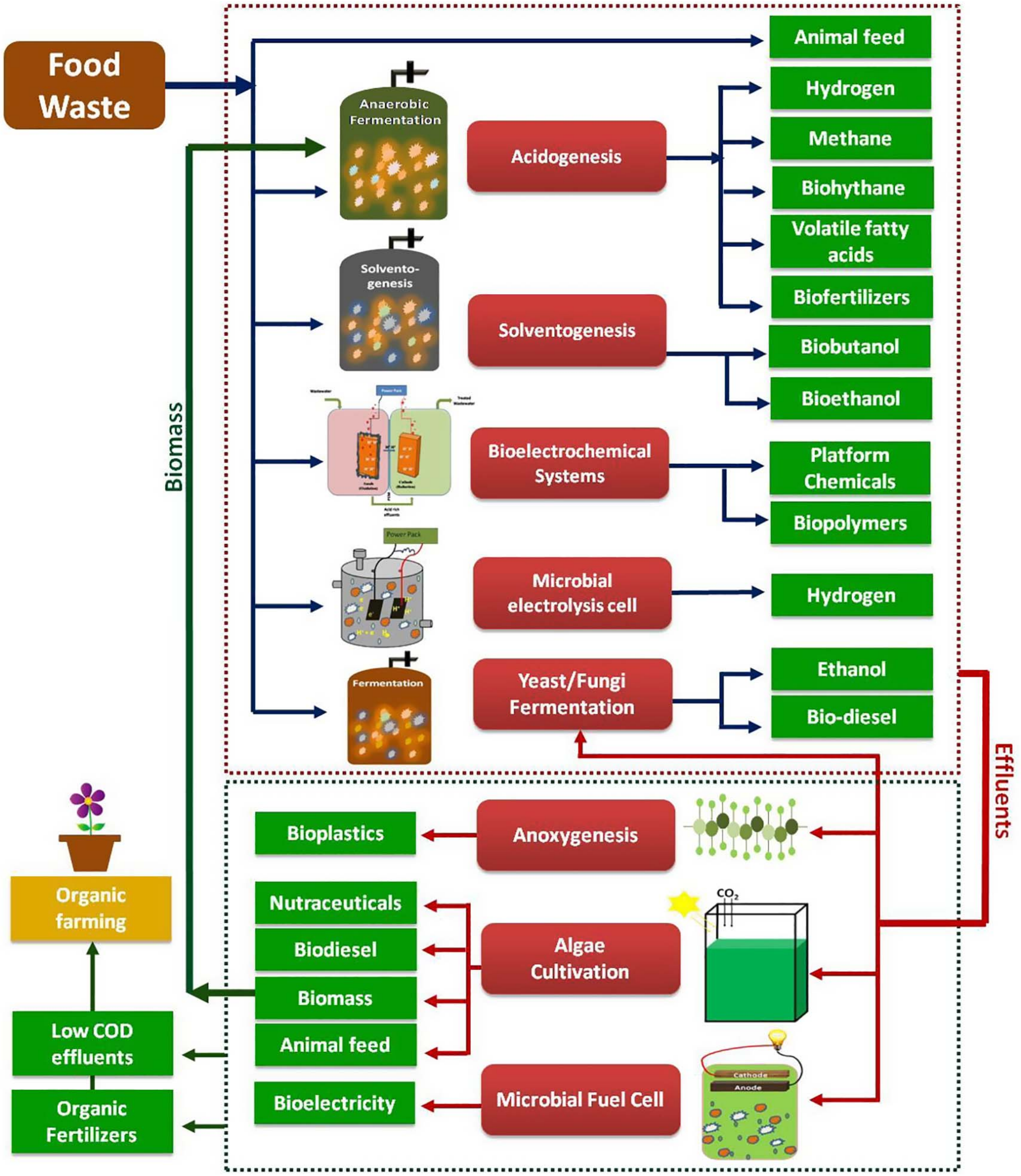

Fig. 5. Overview of multi-dimensional approaches for valorization of food waste to value added bio-based products in circular bioeconomy.

utilized in waste biorefinery. Implementing various bioprocesses viz., acidogenesis, fermentation, methanogenesis, solventogenesis, photosynthesis, oleaginous process, bio-electrogenesis, etc. can deploy strategic waste conversion to economically beneficial product recovery. The biorefinery approach can result in various products like biofuels (H_2, CH_4, biohythane, biodiesel), platform chemicals (sugars, carboxylic acids, bioethanol, biobutanol), bioelectricity, biomass, biomaterials (biopolymers), biofertilizers, animal feed, etc., with enhanced waste treatment efficiency (Table 1; Fig. 5). Integrating these bioprocesses have advantage of utilizing the organic rich effluents provides an additional product recovery benefit by surpassing the limitations of the individual processes. Integrated biorefinery for the production of bio-based products can lead to the development of a sustainable waste-based bioeconomy (Venkata Mohan et al., 2016a,b; O'Callaghan, 2016) and FW can play an important part in developing waste based circular bioeconomy. By producing a spectrum of biobased products ranging from biofuels to commodity chemicals and biofertilizers, FW biorefinery can compliment fossil based refinery to a certain extent and can address the major drivers for bioeconomy viz. climate, resource security and ecosystem services (Amulya et al., 2015b). FW biorefinery approach in near future can be able to achieve sustainable green route with least environmental impact.

6. Conclusions

This communication tries to delineate the in-built potential of FW in terms of resource recovery with a sustainable perspective. FW as a feedstock has a potential to produce a gamuts of biobased products and simultaneously reducing the carbon foot prints. The integrated biorefinery platform can address the futuristic bioeconomy which still needs process optimization, efficient integration, recovery/separation of the products, scaling up and simultaneously scrutinizing the ideal approach. Appropriate technical, economic and scientific strategies in multi-disciplinary approach can help to develop a sustainable FW biorefinery by addressing the circular bioeconomy goals and bridging the gap between waste remediation and product recovery.

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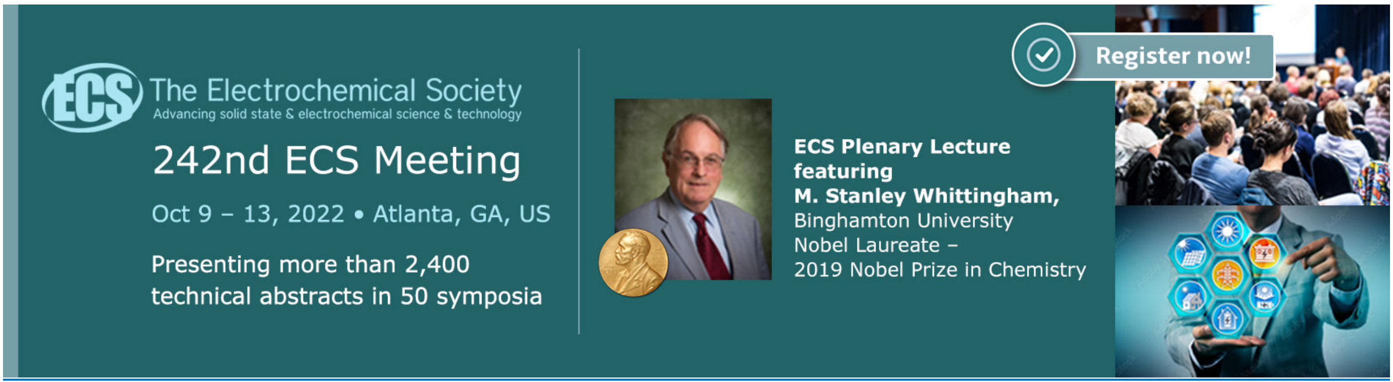

Integrated algal biorefinery and palm oil milling for bioenergy, biomaterials and biopharmaceuticals

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Abstract. The call for greener processes and eco-friendly products has been the essence of the 2030's core agenda on 17 Sustainable Development Goals. The major challenge is in bringing systems thinking and holistic worldview to the planning and strategies to develop the Economics whilst incorporating the Environment, and Socio-cultural diversity dimension as equal components. This means a total revamp of human activities such that the discussion on climate change, famine and poverty, destruction of eco-systems and habitat for wildlife, and the emerging infectious diseases, is as relevant as, if not more important than, discussing about artificial intelligence, robotics, flying and driver-less vehicles, and exploration to Mars. There is an urgent need for resource optimization, better biodiversity management and improved agro-practices for food production and distribution, affordable health care, and cleaner energy, air and water, with strict monitoring, regulation and enforcement to minimize emission, pollution and wastage. The focus of this presentation is to highlight research and development efforts towards the realization of sustainable bioenergy production, environmental remediation and conversion into biomaterials *via* integrated algal biorefinery and palm oil milling processes. Recent development in microalgal research with nanotechnology for biopharmaceuticals and anti-cancer products will be discussed. The image problem and the negative perception surrounding oil palm industries especially with regards to the impact on the environment, and the efforts towards a more sustainable production route will be highlighted. This hopefully could bring forth insights towards partnerships and collaboration among the industrialists, investors, economists, scientists, engineers, and social scientists to tackle the immediate and pressing problems facing the Planet and the People, whilst reaping the Profit, yesterday, today and tomorrow.

1. Introduction

Integrated algal biorefinery and palm oil milling has great potential to achieve the Global Sustainable Development Goals (SDGs) agenda especially with regards to addressing the issues of clean and affordable and energy, the development of sustainable cities and the communities within, with responsible consumption and production, and lesser or zero wastage. As the global CO_2 emissions from fossil fuels have also increased 15-fold [1], more effort should be made into the development of green technology and environmentally-friendly materials for cleaner production based on algal cultivation and palm oil milling [2]-[7]. Of great importance is to strive for optimal use of locally available resources, whilst reducing the costs and the environmental impact [8]. With the combined production of 64.2 million metric tonnes of crude palm oil, Indonesia (56.5%) and Malaysia (27.9%) are globally the two biggest palm oil producers [9]. The residues such as the oil palm empty fruit bunches (EFB), mesocarp fibres (MF), palm kernel shells (PKS), palm kernel cake (PKC), and palm oil mill effluent (POME) have great potentials to be turned into value-added products through technologies for composting, pelletizing, briquetting, pressing, pre-treatments, co-generation and pyrolysis [4]-[5], [10]-[14]. The microalgal biomass co-cultivation within the palm oil mill setting is attractive for renewable generation of biofuels [15]-[17], waste remediation [3], [15] and conversion into value-added biomaterials [4]-[5], and high-value biocompounds [2]-[3]. The objectives of this review article was to explore the implementation of the biorefinery concept for bioenergy production and value-added products based on palm oil milling and microalgal co-cultivation, making use of the bio/nanotechnology platform.

2. Integrated Biorefinery

2.1 Bioenergy Production and POME remediation

The palm oil methyl ester posses low engine emissions with high oxidation stability and nitrogen oxide emission [18]. EFB can be changed into bioethanol by hydrolysis, distillation and fermentation or into bio-oil by fast pyrolysis and gasification [19]-[20]. The EFB and palm kernel addition can be utilized in the anaerobic digestion process with POME and sludge inoculum [21]. Algal co-cultivation can be implemented in the palm oil mill for sustainable energy management, environmental remediation and high value biochemical and biomaterials [17], [22] (Figure 1). Co-digestion of *Chlorella* sp. (2 mL/mL POME) with the EFB (0.12 g/mL POME) has produced 5295.8 mL CH_4/L POME/day with equally high removal efficiency of BOD (95%), COD (98%), TOC (78%) and TN (78%) after 7 days [23]. The co-cultivation of *Nannochloropsis oculata* (2 mL/mL POME) and EFB (0.12 g/mL POME) also attains high biomethane (4606-5018 mL CH_4/L POME/day) and removal efficiency of BOD (84-98%), COD (90-97%) and TOC (65-80%) [24]. For co-cultivation of *N. oculata* and *Chlorella* sp. (1 mL/mL POME) with EFB (0.12 g/mL POME), the biomethane production (4651.9 mL CH_4/L POME/day) remains high [25]. The filtered POME at 10% composition in sea water used as an alternative medium for algal cultivation could enhance cell performance [26]-[27]. The cultivation of *Pavlova lutheri* at 5-300 L is successfully achieved, but the cell growth (0.35 g/L) in 300 L open-tank is far lower than that achieved in 250 mL reaction vessel (0.43-0.45 g/L) [28]. The 5 L photobioreactor (PBR) cultivation of *N. oculata*, *Tetraselmis suecica*, *Isochrysis galbana* and *P. lutheri* has attained considerably high biomass (0.62-0.96 g/L) and lipid content (31.6-42.2%) [29]. The fatty acids such as pentadecanoic, C15:0 (8.16%), palmitic, C16:0 (18.4%) and oleic, C18:1 (11.3%) in *N. oculata*; and palmitic, C16:0 (35.2%), palmitoleic, C16:1 (23.3%) and oleic, C18:1 (13.8%) in *P.lutheri*, are all highest in 5 L PBR [29].

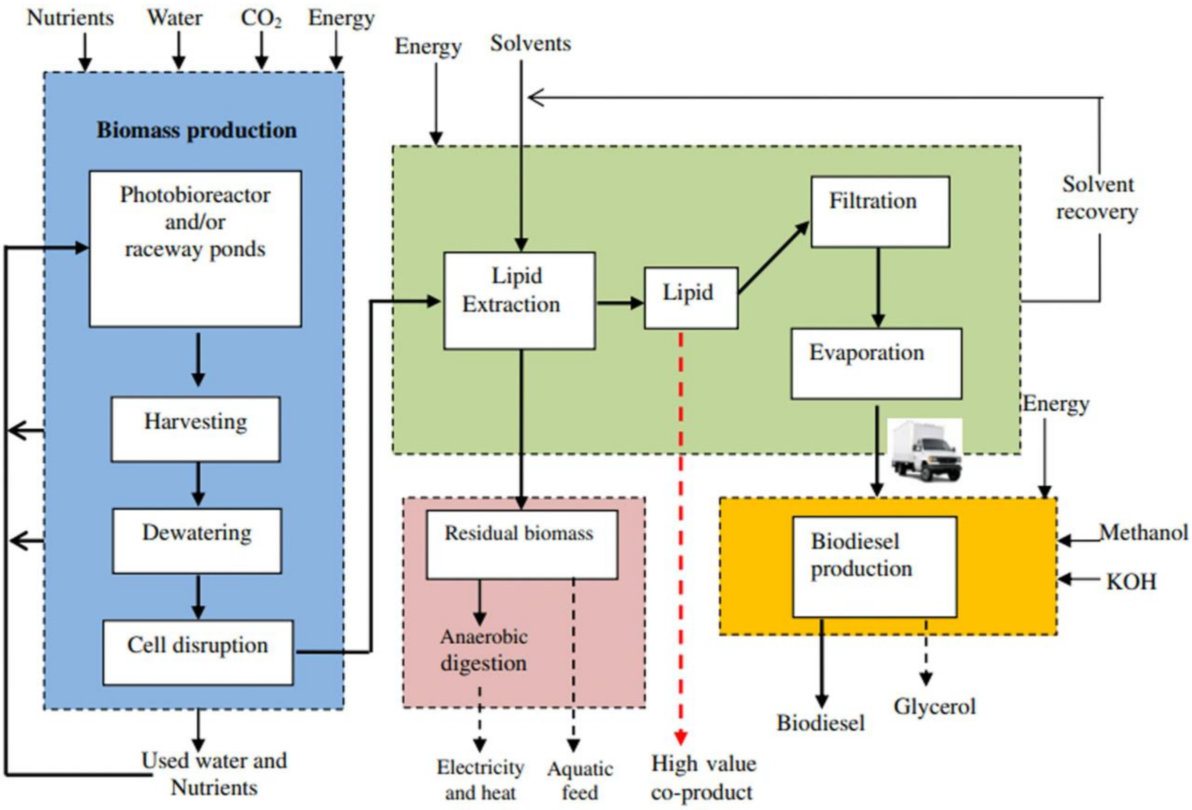

Figure 1. Schematic of microalgal biofuel production and the recovery of high-value compounds (Reprinted from [17], with permission from Elsevier).

2.2 *Biomaterials*

Eco-friendly technique based on autoclave has been developed with formic acid and hydrogen peroxide to yield 64% purely-extracted cellulose (PEC) of 93.7% α-cellulose content and 70% crystallinity [4], [30]. The polypropylene with 25% PEC composites attain 26.7-27.3 MPa tensile strength, without any addition of coupling agents [4]. The surface engineering of PECs with EDTA treatment and loaded with Pb achieves high desulphurization of diesel with 300-350 ppm sulphur removal as compared to 80-110 ppm without Pb-loaded modified sorbents [31]. EFB and the fibers can be manufactured into furnitures, electronics, packaging or building and automobile materials [32]-[33]. An agro-based magnetic biosorbents based on EFB, celluloses from EFB and *Ceiba pentandra* have been developed to achieve 97.7-99.4% Pb(II) removal efficiency from aqueous system which can be reused for 5 adsorption/desorption cycles [34]. Fabrication of a novel Cellulose-Hydroxyapatite (HAp)-Carbon Electrode has achieved successful detection of Pb(II) ions at trace level with the Limit of Detection (LOD) at 0.11 µg/L, and the Limit of Quantification (LOQ) at 0.36-0.37 µg/L, in blood serum and POME [35]-[36].

3. Biopharmaceuticals

Marine algal bioactive compounds can be developed as anti-cancer or other therapeutic drugs [22], [37]-[38]. The microalgal extracts and compounds such as silver nanoparticles (AgNPs) have great potentials in cancer therapy and for theranostics application. High cytotoxicity at the IC_{50} of 6.60 and 53.7 on MCF-7 and 4T1 breast cancer cells, respectively, has been achieved with the AgNPs-*T. suecica* chloroform extract at the 2:1 ratio co-application, but with no cytotoxicity exhibited on the normal Vero cells [39]. The phospholipids (PL) from microalgae, are suitable for the production of liposomes, providing the combination of the hydrophobic compounds of interest and omega-3 (ω-3) fatty acids and could enhance the adsorption of docosahexaenoic acid (DHA), and decrease the cholesterol and the hepatic fibrosis [40]. This could open up new avenue on the use of microalgal natural products with nanoparticles [39] and for liposomes as drug delivery systems [41], for high-value pharmaceutical applications.

4. Global Sustainable Development Goals and Life-cycle Analysis (LCA)

The integrated biorefinery concept based on palm oil mill [16] and microalgae co-cultivation (Figure 2) should meet the sustainable development goals on low cost and clean energy (goal 7), economic development and decent work (goal 8), and innovation, industry and infrastructure (goal 9). The spill-over impacts include in reducing inequalities (goal 10), creating sustainable cities and communities (goal 11), and responsible consumption and manufacture (goal 12) [42]. The optimal options should not only be based on economic performance indicators, but also on environmental and social indicators. Based on Life-cycle analysis (LCA), palm biodiesel can reduce greenhouse gases (GHG) by 46-73%, as compared to diesel, but the production of nitrogen-fertilizer and its application in the plantation, and the emissions from the ponds treating the POME could lead to major environmental impacts [43]. The palm oil mill-microalgae biorefinery should include options such as the oil recovery, biogas, sugar feedstock, thermo-chemical processes [44], with considerations for commodity chemicals, the aquaculture and animal feeds production, biofertilizers and biocomposites [45], and the high-value biopharmaceuticals, EPA-rich oil and protein extracts [44], [46] to make it a more socially-environmentally-economically viable venture.

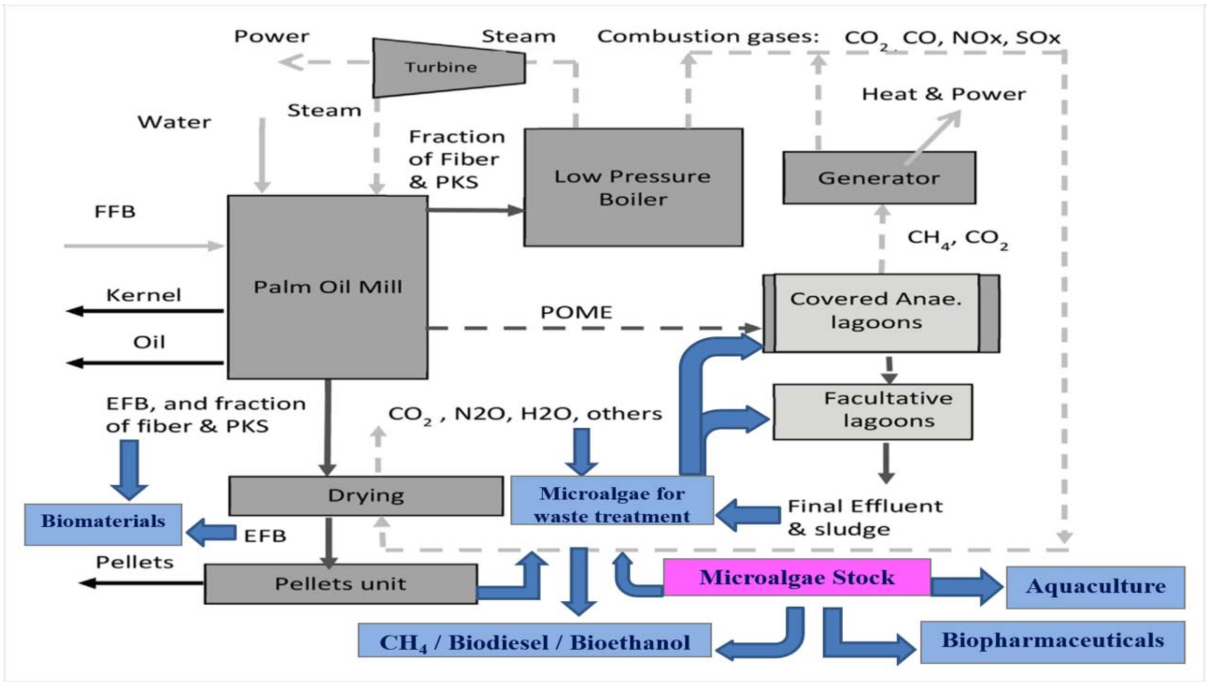

Figure 2. Integrated biorefinery based on Palm Oil Mill and Microalgae co-cultivation (Modified from [16]).

5. Conclusion

Integrated Microalgal Biorefinery and Palm Oil Milling could meet the global sustainable development goals in combating climate change and green house gas emission by achieving clean and more affordable energy, promoting decent work and economic growth through the promotion of green industry, innovation and infrastructure. At the same time, reduction of inequalities, creation of sustainable cities with civic conscious communities, practising responsible consumption and production, thus generating reduced, recycled or zero wastes, could be attained. These are achieved by the re-utilization of oil palm residues, bioenergy production, waste remediation and micro-algal co-cultivation with conversion into value-added products. Co-digestion of microalgae with POME and EFB could attain higher biomethane rate with high removal efficiencies of COD and BOD. The POME can also be utilized as an alternative medium for algal cultivation and at the correct cultivation conditions and reactor configuration, specific metabolites or fatty acids composition can be engineered for its final intended applications. Eco-friendly techniques can be adopted for cellulose extraction from oil palm fibres for use in the polymer composites development or surface engineered for environmental remediation application. Microalgal cultivation in a biorefinery concept can be further developed for biopharmaceuticals production or as feed for aquaculture.

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Review

Marine Collagen from Alternative and Sustainable Sources: Extraction, Processing and Applications

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Abstract: Due to its unique properties, collagen is used in the growing fields of pharmaceutical and biomedical devices, as well as in the fields of nutraceuticals, cosmeceuticals, food and beverages. Collagen also represents a valid resource for bioplastics and biomaterials, to be used in the emerging health sectors. Recently, marine organisms have been considered as promising sources of collagen, because they do not harbor transmissible disease. In particular, fish biomass as well as by-catch organisms, such as undersized fish, jellyfish, sharks, starfish, and sponges, possess a very high collagen content. The use of discarded and underused biomass could contribute to the development of a sustainable process for collagen extraction, with a significantly reduced environmental impact. This addresses the European zero-waste strategy, which supports all three generally accepted goals of sustainability: sustainable economic well-being, environmental protection, and social well-being. A zero-waste strategy would use far fewer new raw materials and send no waste materials to landfills. In this review, we present an overview of the studies carried out on collagen obtained from by-catch organisms and fish wastes. Additionally, we discuss novel technologies based on thermoplastic processes that could be applied, likewise, as marine collagen treatment.

Keywords: marine collagen; marine gelatin; sustainable sources; by-catch; discards; protocols

1. Introduction

Collagen is a complex macroprotein which groups 20%–30% of all proteins found in living organisms [1], and represents the main structural component of the extracellular matrix in all connective tissues (i.e., skin, bones, ligaments, tendons and cartilage) and interstitial tissues of the parenchymal organs.

Thanks to its unique properties, collagen is well-known as a structural support for biomedical devices, dermal implants and emerging health applications, as well as being largely used in nutricosmetic, food and beverages. Due to its high-water absorption capacity, collagen is a good candidate for texturizing, thickening and gel formation. Moreover, it has interesting properties related to surface behavior, which involves emulsion, foam formation, stabilization, adhesion and cohesion, protective colloid functions and film-forming capacity. Also, collagen is a good surface-active agent, with its ability to penetrate lipid-free interfaces [2].

Collagen can be utilized in a variety of applications because of its biocompatibility and excellent degradability [3,4]. Furthermore, it is known that collagen is a molecule with weak immunogenicity, which decreases the possibilities of rejection when it is ingested or injected into a different body. Although this molecule has already low antigenicity, this property can be enhanced by modifying it to suppress any immune response [5,6]. Additionally, collagen peptides and gelatin (denatured collagen) have been widely utilized in different fields such as food, medicine, cosmetics, leather and film industries, diagnostic imaging, and therapeutic delivery [7].

For many years, most available collagen was extracted from discards from the bovine and porcine processing industries, but during the last few decades the use of collagen from these sources has been limited. The use of porcine and bovine-derived products is occasionally prevented by dietary regimes, due to specific needs or personal choices. It is forbidden by religious constraints, to Muslims, Hindus and Jews who make up 38.4% of the global population [8]. Moreover, the use of bovine-derived products became a concern for a wider section of the population during the bovine spongiform encephalopathy (BSE), transmissible spongiform encephalopathy (TSE) and foot-and-mouth disease (FMD) crises that occurred over the last few decades in all areas of the world, mostly in the United Kingdom and Asia. Bovine-derived products might be a vehicle of transmission of these diseases and therefore their use has been severely limited (regulations CE n. 999/2001 and UE n. 142/2011). Hence, there is an urgent need to find novel alternative sources of collagen.

Recently, marine organisms have received consideration as promising sources of collagen, because they have no limitations in use for any religions and there are no reports of possible transmissible diseases. In particular, biomass derived from the activities of fish-processing industries and fisheries (fish and sea urchin wastes, undersized fish and by-catch organisms such as jellyfish, sharks, starfish, sponges) might become an important, yet underexploited, source of collagen [9–14]. The use of discarded and underused biomass will contribute to the development of a sustainable pipeline to obtain collagen with a significantly reduced environmental impact.

In this review, we present a general overview of the studies carried out on by-catch organisms and wastes from fish and sea urchin processing industries in order to isolate collagen. We discuss the structure of collagen, the established methodologies for collagen extraction from these marine sources, and its applications. We also discuss novel technologies based on thermoplastic processes that have been investigated for other types of proteins, and that might be applied to marine collagen.

2. Sustainable Marine Sources of Collagen

Collagen is found not only in terrestrial organisms, but also in a variety of marine species. In particular, the skin and bones of fish and sharks, sea urchin waste and by-catch organisms such as jellyfish and starfish, have high collagen content, as shown in Table 1.

Table 1. Collagen content in fish, sharks and scyphomedusae. The collagen content is expressed as percentage of wet or dry (*) mass.

Species	Tissue	Collagen Content	Reference
Pisces			
Priacanthus tayenus (Richardson, 1846)	bone	1.6	[15]
	skin	10.9*	[15]
Hemibragus macropterus (Bleeker, 1870)	skin	28.0*	[16]
Syngnathus schlegeli (Kaup, 1856)	skin	33.2*	[17]
Lagocephalus gloveri (Abe and Tabeta, 1983)	skin	54.3*	[18]
Takifugu rubripes (Temminck and Schlegel, 1850)	skin	44.7*	[19]
Saurida spp.	scales	0.79	[20]
Trachurus japonicas (Temminck and Schlegel, 1844)	scales	1.5	[20]

Table 1. *Cont.*

Species	Tissue	Collagen Content	Reference
Mugil cephalis (Linnaeus, 1758)	scales	0.4	[20]
Cheilopogon melanurus (Valenciennes, 1847)	scales	0.7	[20]
Dentex tumifrons (Temminck and Schlegel, 1843)	scales	0.9	[20]
Mollusca			
Illex argentinus (Castellanos, 1960)	skin	53	[21]
Sepiella inermis (Van Hasselt, 1835)	skin	16.2*	[22]
Elasmobranchii			
Chiloscyllium punctatum (Müller and Henle, 1838)	cartilage	9.59*	[23]
Carcharhinus limbatus (Müller and Henle, 1839)	cartilage	10.3*	[23]
Echinoidea			
Paracentrotus lividus (Lamarck, 1816)	whole	7*	[24]
Anthocidaris crassispina (Agassiz, 1864)	whole	35*	[25]
Asteroidea			
Patiria pectinifera (Muller and Troschel, 1842)	body wall	6.1	[26]
Scyphomedusae			
Aurelia aurita (Linnaeus, 1758)	whole	0.01	[27]
Chrysaora sp.	bell	9–19	[28]
Pelagia noctiluca (Forsskål, 1775)	whole	0.07	[27]
Catostylus tagi (Haeckel, 1869)	bell	2.7*	[29]
	bell	4.5	[27]
Cotylorhiza tuberculate (Macri, 1778)	oral arms	19.4	[27]
	bell	< 10*	[27]
	bell	8.3–31.5	[27]
Rhizostoma pulmo (Macri, 1778)	oral arms	26–90	[27]
	bell	< 10*	[27]
Rhopilema asamushi (Uchida, 1927)	-	35.2*	[30]
Rhopilema esculentum (Kishinouye, 1891)	mesoglea	0.28*	[31]
Stomolophus meleagris (Agassiz, 1860)	mesoglea	46.4*	[32]
Nemopilema nomurai (Kishinouye, 1922)	mesoglea	2.2*	[33]

Fish waste is very abundant worldwide and several studies, projects, and local and international authorities have focused on how to use this valuable waste [10,12,34–40]. Its utilization has recently increased in order to enhance the economic value of by-catch and fish by-products for biotechnological applications, and also because of the urgent need to reduce the amount of waste for contemporary societies.

Fish processing industries produce large amounts of fish waste every year that represent approximately 25% of the total production. The waste mainly consists of bones, skin, scales, and fins, which constitute over 70% of fish. Currently, part of these wastes are utilized as feedstuff because they contain almost the same amount of proteins as fish flesh [41]. Nevertheless, the majority of this waste is not fully used and most of it is discarded [42], creating a fundamental problem for the environment.

Determinations of the protein composition in fish discards have highlighted that skin, bones and scales of fish are rich in collagen, as displayed in Table 1. The yield of collagen extracted from these discards can reach up to higher than 50% in dry mass, even though the number of fish examined is relatively limited compared to the number of fish species used in food industries. Therefore, this waste material has the potential to be exploited as an eco-friendly and low-cost collagen source.

Waste is generated routinely by seafood and sea urchin processing and by fishing activities. The implementation of the landing obligation, as part of the recent reform of the EU Common Fisheries Policy (CFP), requires that catches of regulated commercial species, including undersized animals which cannot be used for direct human consumption, and endangered species (such as several shark species) to be landed and accounted for quota. An estimate of discards throughout the Mediterranean suggests that they constitute around 18.6% of the catches [43], which makes them a compelling ecological and economic problem.

The sea urchin peristomial membrane, a food industry waste, has been suggested as sustainable and eco-friendly source of fibrillar collagen to produce membranes for regenerative medicine applications [24].

In addition to fish waste and sea urchins, jellyfish (pelagic Cnidaria, in particular scyphomedusae) appear to be increasing worldwide [44–46] and are often abundantly caught in fish nets. Although jellyfish have been a primary ingredient in traditional Chinese food for many centuries [47], they are considered a nuisance because of their negative interactions with human activities, such as tourism, aquaculture, and fishery [48].

In light of the apparent increase of jellyfish abundance and their occurrence as by-catch in fishing nets, some studies focused on determining their protein content. Analyses indicated that their organic matter is made up mainly by collagen [49], thus they may be considered as a promising source of this fibrous protein.

Scaffolds for tissue engineering made of collagen extracted from the scytphomedusa *Rhizostoma pulmo* were successfully implanted into a mouse model and showed optimal adsorption and biocompatibility properties [50]. These findings suggest that collagen derived from scyphomedusae may become a suitable replacement for bovine-derived collagen.

A recent review has shown that rhizostome scyphomedusae contain more collagen than semaeostomeae scyphomedusae [51], as shown in Table 1. The collagen content in *Rhopilema esculentum* is significantly high, considering that the value in Table 1 is based on dry mass. The other two scyphomedusae, *Stomolophus meleagris* and *Rhopilema asamushi*, are commonly consumed by Eastern populations, and contain the highest percentage of collagen on a wet mass basis of all the scyphomedusae where determination of collagen was made, as shown in Table 1.

Table 1 displays that native rhizostome scyphomedusae, such as *R. pulmo* and *Cotylorhiza tuberculata* in the Mediterranean Sea also present high collagen content. The collagen extracted from the invasive rhizostome *Catostylus tagi* has already been considered for exploitation [29], suggesting this species as a suitable source of collagen.

3. Collagen Structure

There are 28 distinct types of collagen named with Roman numeral designations (I–XXVIII) in chronological order of discovery [3,52]. Collagens are generally made up of three long helicoidally-shaped chains of amino acids (about 1050 in each helix). The basic structure of the chains is the triplet, where glycine bonds with two other amino acids, and with the repeating sequence $(\text{Gly-X-Y})_n$; typically, proline or hydroxyproline are often located at position Y. The chains are organized in primary, secondary and tertiary structures, with a final shape of fibrils [53], as shown in Figure 1.

The different types of collagen are classified depending on domain structure and their suprastructural organization. Each collagen type has a specific alpha chain with its own domain structure which contributes to the classification by collagen type.

Collagens can be fibril-forming (i.e., collagen types I, II, III, V, XI, XXIV, XXVII), fibril-associated with interrupted triplex helix (i.e., collagen types IX, XII, XIV, XX), fibril-associated with interrupted triplex helix-like (i.e., XVI, XIX, XXI, XXII), and network-forming (i.e., the basement membrane collagen IV, beaded filament-forming collagen VI, anchoring fibril-collagen VII, hexagonal network-collagens VIII and X, transmembrane collagens XIII, XVII, XXIII and XXV, multiplexin collagens XV and XVIII, and other molecules with collagenous domains named collagens XXVI, XXVIII). Collagens in each class have their own specialized function and contribute to higher order tissue structures.

Collagen is the main component of membranes in most living organisms and has a structural function, as in bones and cartilages [54]. Slight differences in the composition of the triplet units determine differences in collagen types. According to the structure and supramolecular organization of the 28 known collagen types to date [53], they also have different allocation in mammalian tissues shown in Table 2; type I collagen accounts for 80%–85% of the collagen in the body.

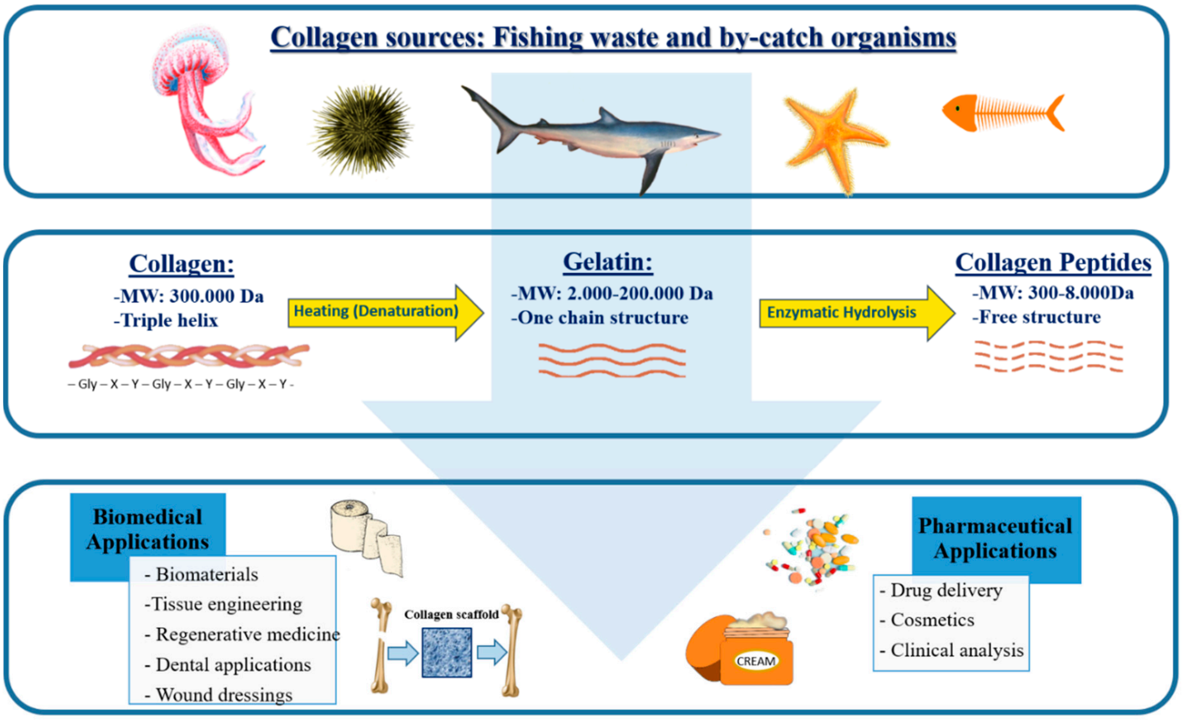

Figure 1. The classical structure and applications of marine collagen, gelatin, and collagen peptides extracts from sustainable marine sources.

Table 2. Distribution of the most common collagen types within mammalian tissues.

Collagen Type	Tissue
I	Bone, skin, tendon, ligaments, cornea
II	Cartilage, vitreous body, nucleus pulposus
III	Skin, vessel walls, reticular fibers of lungs, liver, spleen
IV	Basement membranes
VI	Cornea (often associated with type I collagen)

Partial hydrolysis of collagen followed by thermal treatment, produces gelatin with molecular weights from 3 to 200 kDa as shown in Figure 1, depending on the raw material used and handling conditions [55]. In particular, depending on the process used, two types of gelatin, namely type A (acid hydrolysis) and type B (alkaline hydrolysis) are generally obtained [56]. During hydrolysis, the natural molecular bonds between individual collagen strands are broken down into a form that rearranges more easily. Therefore, gelatin is a mixture of single or multistranded polypeptides, each with extended left-handed helix conformations and containing 50–1000 amino acids; its chemical composition is closely related to that of collagen. Gelatin contains many glycine residues (almost one in three residues, arranged every third residue), proline and 4-hydroxyproline residues. A typical structure is -Ala-Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro-. The approximate amino acid composition of gelatin is: glycine 21%, proline 12%, hydroxyproline 12%, glutamic acid 10%, alanine 9%, arginine 8%, aspartic acid 6%, lysine 4%, serine 4%, leucine 3%, valine 2%, phenylalanine 2%, threonine 2%, isoleucine 1%, hydroxylysine 1%, methionine and histidine $< 1\%$ and tyrosine $< 0.5\%$. These values vary, especially the minor constituents, depending on the source of the raw material and processing technique [57].

Collagen represents an excellent source of peptides with biological activities [58], obtained by several processes including chemical hydrolysis, enzymatic treatment, and fermentation with proteolytic bacteria. Enzymatic hydrolysis with appropriate proteolytic enzymes seems to be the most effective approach for the bioactive peptides generation [59]. It can be achieved under controlled conditions by specific proteases to obtain reproducible collagen hydrolysates. Moreover, the use of the mixture of several proteases and sequential enzymatic hydrolysis by enzymes with different specificities is also recommended to enhance collagen hydrolysis. Peptides in collagen hydrolysates (300–8000 Da) are subsequently fractionated by ultrafiltration and several chromatographic techniques [59]. Incubation time and the concentration of enzymes greatly influence the average molecular weight of obtained peptides which subsequently impacts their activities; a high degree of enzymatic hydrolysis with the release of small peptides produces collagen hydrolysate with interesting bioactivities [58].

4. Extraction of Marine Collagen

Depending on the marine sources, different techniques have been proposed to obtain collagen. Nevertheless, it is possible to establish a general methodology to isolate collagen from fish by-products and other marine sources, based on three steps: preparation, extraction and recovery.

The preparation involves cleaning, the separation of animal parts, and size reduction by cutting or mincing the samples. Generally, fish are split up in skins, scales, fins and bones, because their collagen composition is different (e.g., mineralization in fish bones and scales). In the case of jellyfish, it is common to separate the oral arms from the umbrella and to then divide the umbrella into the mesoglea, exumbrella and subumbrella [28].

Size reduction of these samples is essential to facilitate subsequent chemical (pre)treatment actions, used to remove noncollagenous proteins, pigments or fats. The common method provides the use of a basic pretreatment with sodium hydroxide (NaOH), which does not cause structural modification to collagen chains, alcohols (namely butyl-alcohol or ethanol), and oxygen peroxide in the removal process of noncollagenous proteins, fats and pigments, respectively [16,18,19,60–62]. Furthermore, to remove noncollagenous proteins from codfish skin, the use of sodium chloride (NaCl) as an alternative to NaOH was also proposed [63].

Moreover, to improve the collagen extraction from bone, cartilage and scales, ethylenediaminetetraacetic acid (EDTA) is recommended for demineralization purposes [15,23,64]. Alternatively, HCl can also be used [65].

For the extraction phase, it is well-known that the solubility of collagen in cold water is poor because of the presence of strong cross-links in its triple helix structure. There are two different conventional methods largely used: extraction of acid-solubilized collagen, and extraction of pepsin-solubilized collagen. Using these two methods, yield, chemical composition, and characteristics of the extracted collagen differ from one another. The whole extraction phase is performed at 4 °C.

When collagen extraction is performed using only acid, the product is referred to as acid-soluble collagen (ASC). For collagen extraction from marine animal tissues, acetic acid is the most used dilute acid (generally, at the final concentration 0.5 M), but also citric acid and lactic acid are utilized. The extraction protocols are generally adapted from methods reported by [23,30].

About 95% of marine invertebrates such as jellyfish consists of water, which affects collagen solubility in acetic acid. Therefore, homogenizing or freeze-drying jellyfish is necessary to improve the collagen solubility in diluted acids and, accordingly, increase the extraction yield.

Recently, Yusoff et al. proposed a new method to extract collagen from aquatic animals, in which the acidic treatment is combined with a sequence of physical and mechanical treatments, including pH adjustments, homogenization, mixing, as well as sonication [66]. By increasing physical intervention in jellyfish, the extraction yield increased significantly compared to the conventional extraction processes [49].

When the enzyme pepsin is added in the extraction process, the extracted collagen is referred to as pepsin-soluble collagen (PSC). This treatment is very useful, since proteases cleave telopeptide cross-linked regions without breaking the integrity of the triple helix, and thus hydrolyze some noncollagenous proteins and increase the purity of collagen [67]. Therefore, in most cases, enzymes are used to obtain specific protein products, high yield and reduced wastes, as well as a decrease in the antigenicity caused by telopeptides [68–70]. However, when a high amount of pepsin is used for long time, PSC yield may be lower because the collagen is likely cleaved, impairing the triple helix's integrity [62].

During the recovery step, collagen is precipitated, generally by adding NaCl to a final concentration 2.3–2.6 M. The resultant precipitate is collected by centrifugation, dissolved in 0.5 M acetic acid, dialyzed and freeze dried [71].

From jellyfish, collagen is generally extracted by a methodology based on solubilization in a 0.5 M acetic acid solution (typically for three days), followed by salting-out by dialysis against a Na_2HPO_4 solution. The precipitated collagen is separated by centrifugation, solubilized in acetic acid, and purified by reprecipitation by adding solid NaCl at a concentration of 0.9 M. ASC can also be digested with pepsin to obtain atelo-collagen [27,72].

The intact collagen fibrils of sea urchins' peristomial membranes are different from other collagens and cannot be extracted by traditional methods of acid solubilization, as this method generally produces it in a hydrolyzed jelly form [73]. Therefore, the minced native tissue is sequentially treated with a hypotonic solution and an SDS-based decellularizing solution to remove both cell debris, skeletal parts and pigments [73,74]. After 3–4 days in the disaggregating β-mercapto-ethanol solution, the collagen fibers obtained are then removed by a filtration step and dialyzed against a 0.5 M EDTA-Na solution. The same protocol is used to extract collagen fibers from starfish aboral arm walls, but the samples are processed with an additional step in 1 mM citric acid between decellularizing and disaggregating solutions to remove the calcium carbonate ossicles present in the fresh tissue [75].

5. Marine Collagen Proceeding

Marine collagen is used in its native fibrillar form as well as after denaturation. During biosynthesis, collagen acquires a number of post-translation modifications that are critical to structure and biological functions of this protein [76]. The extent of these modifications influences not only the collagen extraction, but also the denaturation and consequently, the processing of the protein [12]. In particular, the denaturation temperature increases as a result of an increase in the hydroxyl groups of hydroxyproline and hydroxylysine obtained by these modifications. The content of hydroxyproline and hydroxylysine depends on different marine species and on the water temperature of their native habitat, and the content is lower than vertebrate collagens [77]. Denaturation offers the possibility to fabricate several collagen forms, including sheets, tablets, pellets, and sponges. When the triple helix structure of collagen is broken into single-strand molecules by acid, alkaline or enzymatic hydrolysis, a water-soluble gelatin is obtained. Gelatin can be easily processed using thermoplasticization techniques by applying heat and mechanical stresses in extrusion-based technologies.

Gelatin may be chemically treated to bring significant changes in its physical and chemical properties. Typical reactions include acylation, esterification, deamination, cross-linking and polymerization, as well as simple reactions with acids and bases [78,79].

The formation of thermo-reversible gels is obtained when the aqueous solution of gelatin with a concentration greater than 0.5% is cooled to approximately 35–40 °C. The rigidity or strength of the gel depends upon gelatin concentration, structure and molecular mass, pH, temperature, and presence of any additives [80,81].

Two common technologies are employed to process collagen, gelatin and other general proteins: wet (or solvent) and dry processes. The wet process is based on the dispersion or solubilization of collagen proteins in a solvent medium followed by the solvent removal, which can occur by drying or through a solvent–nonsolvent exchange mechanism. Most of the literature works on the use of collagen and gelatin to prepare films, fibers or sponges are based on wet processes [82]. In the dry process, mainly employed for other kind of proteins, thermal and mechanical energies can be used to disrupt intra and intermolecular interaction of biopolymers by extrusion or mechanical mixing, common plastic processing techniques. A large variety of extrusion-based processes can therefore be employed, including film casting, film blowing, compression molding, extrusion foaming and fiber spinning.

In almost all cases, the manufacturing of protein-based products in both wet and dry processes requires the use of plasticizers that improve both the processing and properties of the materials. Plasticization, often obtained with mixtures of plasticizers, leads to materials with lower glass transition temperatures, lower elastic modulus and higher deformability. Depending on the concentration of plasticizers, it is also possible to control the viscoelastic properties of a melt, which is necessary to optimize the shear or the elongational rheology during dry processes.

5.1. Dry Process

Due to the strong intermolecular and intramolecular hydrogen bonds, native proteins cannot be processed like common thermoplastic polymers. However, in presence of suitable plasticizers, they can melt and flow if treated at higher temperatures (usually 60–160 °C) and under shear. In this condition, proteins are denaturated and the melt is processed in conventional manufacturing technologies employed for thermoplastics, like extrusion, injection, and compression molding, blowing and foaming.

Plasticizers have different roles: they (i) contribute to breaking hydrogen bonds replacing inter-and intra-molecular interactions with protein and plasticizers interactions, (ii) lower the melt temperature below the decomposition temperature of the protein, (iii) reduce the viscosity of the melt. The process of increasing the macromolecular mobility (which leads to materials with lower melt temperature and higher flexibility by using plasticizers) is common in conventional polymers and is known as "plasticization".

In general, plasticizers are low molecular weight molecules compatible with protein, and are therefore usually polar and hydrophilic. In particular, the ability of the plasticizer to interact with protein is fundamental and its efficiency depends on several factors, including its size (molecular weight), shape and functionality (mostly, number of oxygen atoms) [83].

The most common plasticizers for proteins are water, monosaccharides, oligosaccharides, polyols, lipids and derivatives [84]. Glycerol is the most used plasticizer in thermoplastic processing of proteins, e.g., corn gluten meal, wheat gluten, soy protein, zein, and kafirin [85–87].

5.2. Extrusion-Based Processes

Extrusion is a highly efficient and continuous process usually employed for large-scale manufacturing and used for thermoplastic polymers. The materials are continuously introduced into a hopper, conveyed by a screw, and pushed through a die of desired shape. During the conveyance, several operations can be performed: heating, cooling, feeding of solids and liquids, conveying, compressing, shearing, reacting, mixing, melting, homogenizing, cooking, and shaping.

So far, there is no literature available regarding the extrusion process of thermoplastic gelatin, but there are some reports available for plant protein-based films, such as zein and gluten [88,89] that can be used as a point of reference for the development of novel products and processes for marine collagen. Zein sheets plasticized with fatty acids were produced by extruding a moldable, dough-like resin prepared by precipitating zein and oleic acid from aqueous-alcohol solutions [90]. Oliviero et al. showed that it is possible to prepare thermoplastic films from commercial zein/PEG400 mixtures by film blowing technology, as shown in Figure 2 [91]. This gives films a low-enough thicknesses and suitable mechanical properties for packaging applications, making them comparable to those from common synthetic polymers.

Thermoplastic processing of gelatin was first reported in 2007 [92]. Thermoplastic formulations containing glycerol (20, 25 wt%) and lactic acid (20 wt%) were prepared using a twin counter rotating internal mixer at 60 °C, for 6 min at a speed of rotation of 60 min^{-1}. Films with different mechanical properties were then obtained by compression molding. There are not works available in the scientific literature regarding the use of other manufacturing technologies for film production, such as film casting or film blowing.

Thermoplastic gelatin can be successfully foamed by employing a mixture 80/20 of N_2/CO_2 at temperature above its glass transition temperature of 50 °C [92]. As shown in Figure 3, good foams with different cellular morphologies can be obtained in the temperature range of 80–140 °C.

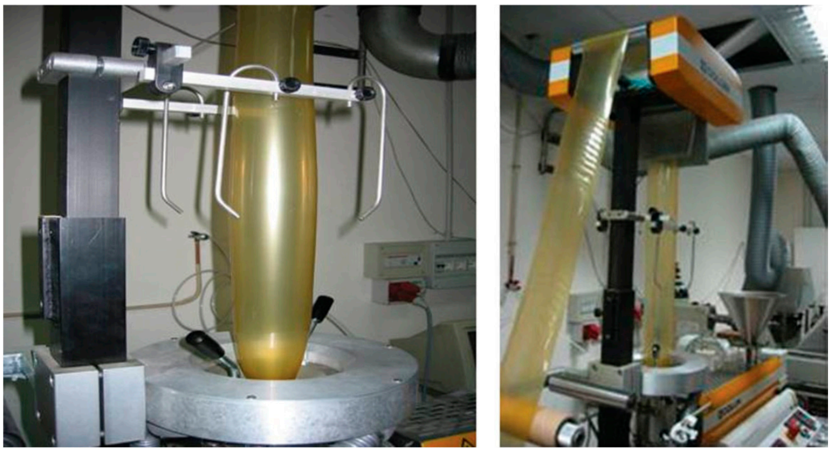

Figure 2. Lab-scale film blowing of thermoplastic zein. Reproduced with permission from [91]. Copyright publisher, 2020. In the figure, the film bubble during the film-blowing process of thermoplastic zein is shown. The zein powder was first plasticized with poly (ethylene glycol) 400 directly in the extruder, without the use of a solvent and of a premixing phase.

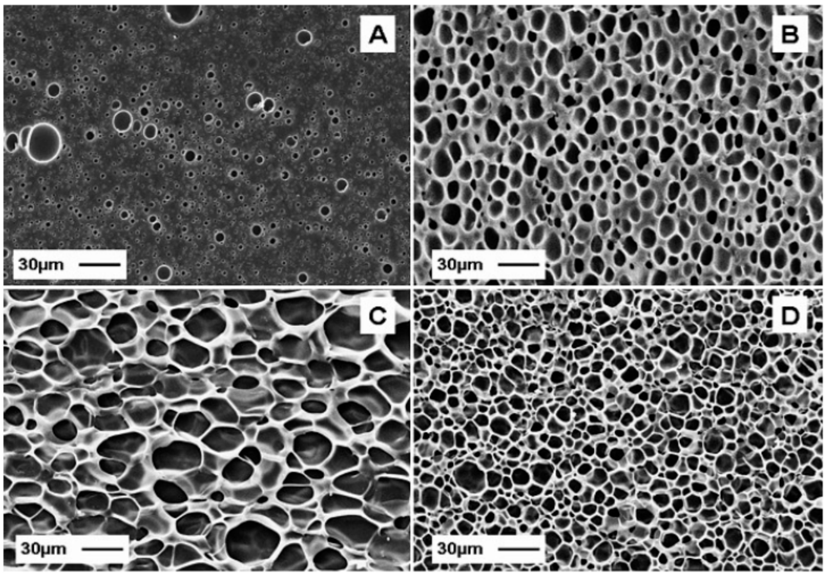

Figure 3. Micrographs of thermoplastic gelatin foams. Scanning electron microscopy (SEM) micrographs of thermoplastic gelatin foamed with N2-CO2 80-20 vol.% at Psat = 180 bar, PDR = 700 bar/s and TF = 44 °C (**A**), 80 °C (**B**), 120 °C (**C**) and 140 °C (**D**). Reproduced with permission from [92]. Copyright publisher, 2020. The gelatin powder was first plasticized with glycerol directly in the mixer.

As a major drawback, neat thermoplastic gelatin has a strong sensitivity to moisture, which can heavily decrease its barrier as well as its thermomechanical properties. Blending with hydrophobic biodegradable polymers has been a typical approach already employed for other natural occurring polymers such as in the case of thermoplastic starch, or other thermoplastic proteins [93,94]. Blends of thermoplastic gelatin with poly(butylene succinate), a polyester deriving from butanediol and succinic acid have been investigated with the aim to improve not only the resistance to moisture, but also the rheological properties, as well as the diffusivity and solubility of the blowing agent for the foaming technology [95]. Also, in blending with PCL, it is possible to foam the thermoplastic gelatin. In that case, a selective extraction of the water-soluble gelatin phase allowed for the development of porous network pathways characterized by multimodal porosities for biomedical applications [96–98].

6. Biomedical and Pharmaceutical Applications of Collagen

Numerous attempts have recently been made to use marine collagen as a biomaterial. Collagen is the most promising natural biomaterial as scaffold in tissue engineering, as it is abundant, biocompatible, biodegradable, resembles the components present in the extracellular matrix and supports the connective tissue including skin, tendon, bone, cartilage, blood vessel, and ligaments [37]. However, collagen from fish is less crosslinked and its mechanical strength is poorer than collagen extracted from bovine. Therefore, the use of marine collagen as biomaterial in tissue engineering is possible after crosslinking treatment [72,99]. In order to improve the mechanical strength of marine collagen, some kinds of bioceramics with the similar constituent to the intrinsic inorganic components of nature bone are also widely used in collagen scaffolds for bone regeneration. Apart from the enhancement of mechanical properties, they can also improve osteoconductive ability, dimensional stability and increase the surface area for cell attachment on the composite scaffolds [100].

Marine collagen is also widely used in dentistry [12,101], generally as membrane, bone graft materials, an agent for local delivery and a hemostatic agent. In particular, the membranes are used in periodontal and implant therapy to guide soft tissue regeneration and inhibit the rapid regrowth of skin when implanting bone which takes longer to generate. Most collagen membranes on the market are resorbable in a few days.

The collagen used for local drug delivery is generally in the form of membranes. The membrane most used is constituted by two components: chlorhexidine and collagen [102]. Another product used for local drug delivery comprises tetracycline fibers impregnated in collagen fibers. Both systems allow diffusion of the drug as collagen undergoes resorption, releasing the drug from the matrix in a controlled manner [103].

Marine collagen is also used to control bleeding. Different products are commercially available; they have sponge-like structures and are highly absorbent and able to hold many times their own weight of fluid. They may be cut to desired shape and applied to a bleeding surface. The placed product rapidly absorbs the blood, creating an artificial clot-like structure that stop the bleeding at the site. These products resorb completely within 14 to 56 days [104].

The hydrophilic nature and the molecular structure of collagen, characterized by a high content of diaminodicaroxylic amino acids and carbohydrate, provide a surface geometry very suitable for cell adhesion and wound repair in dentistry and surgery. Another factor, which promotes the adhesion of fibrogenic cells on collagen implants, is the presence of a glucoprotein-like fibronectin on cells surface that have a high affinity with particular regions of collagen surface [104]. There are two primary forms of collagen wound dressing: sponges and films. Sponges are used as both temporary and permanent coverings, and the cellular growth depends on the sponge porosity and the presence of fibrous structure. The films are instead produced by casting on methacrylate surfaces, and are crosslinked by using UV radiations in order to improve their handling properties [104].

The use of collagen-based materials in drug delivery involves the study of different aspects, such as in vivo instability, bioavailability, solubility and body tissue absorption with target-specific delivery and tonic effectiveness. To this purpose, nanotechnologies play an important role in order to develop new drug delivery systems for targeting drugs to specific body parts [105].

A collagen skeleton of marine sponges was used to develop new bio-based topical formulations, where the marine collagen acts as bioactive, biomimetic carrier for the loading of L-cysteine hydrochloride, facilitating the wound healing processes due to its glycosaminoglycans [11].

In addition, due to its abilities in skin repair as shown when tested on female volunteers [106], marine collagen has been increasingly utilized for the development of cosmeceutical products containing bioactive ingredients with pharmaceutical benefits. Cosmetic products, based on marine extract collagen, have shown a comparable effect on the skin with that of animal collagen in terms of pH, moisture and sebum. Moreover, marine collagen hydrolysate has shown an effect on the inhibition of photo-aging [107]. The hydrolysis of polypeptides with a small molecular weight, capable of penetrating the skin, could also overcome a major issue related to fish collagen usage, i.e., the low denaturation temperature that is much lower than the temperature of the human body. In particular, we focus our attention on the applications of collagen extracted from fish waste, echinoderms, and jellyfish.

6.1. Collagen and other Collagen-Derived Peptide Bioactivities from Sustainable Marine Sources

Several studies have been performed to define potential biomedical and pharmaceutical applications of marine collagen and collagen-derived peptides as well as gelatin from sustainable sources. Some possible uses are reported below, and the applications are schematized in Figure 1.

6.1.1. Fish Waste

Collagen derived from fish waste and bioactive peptides derived from collagenous sources have been shown to have several bioactivities with possible cosmeceutical and pharmaceutical applications, as well as biomaterial for tissue engineering [12,58]. Collagen extracted from codfish and salmon skins was characterized to evaluate its inclusion as a component in cosmetic formulations [108]. It demonstrated a good capacity to retain water, which shows promise as a suitable candidate for dermal moisturizing applications. In addition, possible skin irritation and inflammation potentially due to the extracted collagen was evaluated by using a human 3D reconstructed epidermal model (In Vitro Epiderm™ Assay Kit, EPI-200, MatTek Corporation) and by measuring inflammatory mediators (i.e., IL-6 and IL-18) by commercially available ELISA kits. Results showed that fish collagen did not have any irritation or inflammatory effects.

A pilot study obtained collagen oligopeptide-rich hydrolysate from codfish skin by using a collagenolytic protease from the deep-sea bacterium *Pseudoalteromonas* sp. SM9913 [109], and bioactivity testing showed that obtained collagen peptides had antioxidant activity, reducing free radicals at 10 mg/mL, higher than those of hyaluronic acid, an ideal material in cosmetics. The obtained hydrolysates (in which collagen peptides accounted for approximately 95%) also had promoting cell-proliferation effects on human dermal fibroblasts and showed no toxicity. Acute toxicity was tested on Kunming mice, while skin irritation was tested on rabbits [109]. The in vivo experiments showed that there was no depression, hair loss, dyspnea, wound formation, significant differences in body weight or pathological abnormalities in various body parts of the mice, and edema, erythema, and rough or thinning skin were not observed in the rabbits.

In vivo studies in the mice showed that salmon skin collagen peptides reduced oxidative damage [110] and acetylcholinesterase (AChE) and increased phosphorylated cAMP-response element binding protein (p-CREB) and brain-derived neurotrophic factor (BDNF) expression [111]. Moreover, collagen from salmon skin was used with hydroxyapatite to produce scaffolds for bone regeneration, based on the biomimetic mineralization principle [112]. The scaffold with interconnected pores allowed human mesenchymal stem cells to adhere and proliferate, providing a good support for osteogenic differentiation.

Subcritical water-hydrolysed fish collagen peptide (SWFCP) from tuna skin shown adipogenic regulatory activity [110,113]. In particular, SWFCP downregulated the expression of key adipogenic target genes (C/EBP and PPAR protein) and transcription factors in 3T3-L1 preadipocytes exposed to dexamethasone and insulin. SWFCP also downregulated the expression of aP2, an adipogenic target gene, hence inhibiting adipogenic differentiation. Furthermore, SWFCP also reduced lipogenesis in hepatocytes and significantly affected other obesity-related factors, e.g., low serum cholesterol, low serum triglyceride, and low-density lipoprotein, and reduced the size of epididymal adipocytes.

Collagen hydrolysates were also obtained from unicorn leatherjacket skin (*Aluterus monoceros*) by using collagenase at three different temperatures 5 °C, 25 °C and 50 °C (collagen peptides named CP-5, CP-25 and CP-50, respectively) [114]. Results showed that CP-5 was more active than the others for anticancer, antidiabetic and wound healing activities, suggesting that collagen extraction and hydrolysis parameters can influence the bioactivity.

Finally, several sharks are landed as secondary catches from the fishing of other species. Various parts of the body have found a plethora of applications on the market. Examples are the meats as food, the cartilage to produce chondroitin sulphate (food supplements for treating osteoporosis and cancer), squalene for skin care, and skin for shoes and handbags. In addition, shark skin is very rich in collagen type I, while shark cartilage is rich in collagen type II. Collagen from shark tissues have been used to prepare a gel matrix for in vivo culturing of fibroblasts as a food supplement to create functional foods, and to also increase the cryoprotection of foods [115]. Moreover, the antioxidant capacity of type II collagens (i.e., type II ASC, CIIA and PSC, CIIP) was also assessed by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging capacity, showing that the reducing power of CIIP was greater than that of CIIA [116].

Collagen type I was extracted from the skin of the common smooth-hound, *Mustelus mustelus* (Linnaeus, 1758) and combined with chitosan to produce a composite film in order to test it as green bioactive film to preserve nutraceutical products [117]. It was found that this combined film had lower tensile strength and higher elongation at break when compared to chitosan film, and lower water solubility and lightness when compared to collagen film. In addition, this collagen-chitosan-based biofilm showed antioxidant activities evaluated by using the DPPH assay, as well as potential UV barrier properties.

Marine collagen from fish and especially marine collagen-based scaffolds have proved to be useful alternatives for several biomedical applications [12]. For example, collagen from chum salmon, *Oncorhynchus keta* (Walbaum, 1792) skin increased serum osteocalcin, size, mineral density, and dry weight of femurs in growing male rats [118]. Oral administration of collagen from skins of Gadiformes fish species controlled cartilage degradation in osteoarthritis-induced rabbit models [119].

Tilapia collagen/bioactive glass (Col/BG) nanofibers, fabricated via electrospinning, were used as wound dressing to protect against infection and to promote wound healing and skin regrowth in both *in vivo and in vitro studies* [120].

Type I collagen from the Nile tilapia, *Oreochromis niloticus* (Linnaeus, 1758) scales promoted rat odontoblast-like cells and accelerated matrix mineralization [121], which indicated that it could be an alternative to type I collagen from mammals in the application for tissue regeneration in oral-maxillofacial area.

Marine collagen was recently studied as a promising biomaterial with great potential in drug delivery applications due to its unique properties. A scaffold-controlled release system for skin tissue engineering, based on poly (D,L-lactide-co-glycolide acid) (PLGA) microspheres and fish collagen, chitosan and chondroitin sulfate scaffolds were obtained by freeze-drying. The developed marine collagen drug delivery system exhibited a tunable protein release rate, depending on the ratio of fish collagen, and it showed good biocompatibility and ability to promote fibroblast cell proliferation and skin tissue regeneration [122].

6.1.2. Echinoderms

There are particular collagens from echinoderms that have been described, such as those from sea urchin and starfish by-catches. They are well-known for their unique connective tissues, named mutable collagenous tissues (MCT), recently proposed as possible inspiration for “smart dynamic biomaterials” for tissue engineering and regenerative medicine applications [74,123]. It can be used to develop collagen barrier-membranes for guided tissue regeneration (GTR) [75].

Echinoderm-derived collagen membranes (EDCMs) are similar to each other in terms of structure and mechanical performances, and are much thinner and mechanically more resistant than the commercial membranes, suggesting that they could be alternative collagen sources for the production of efficient GTR membranes.

Particularly, the sea urchin peristomial membrane, a well-known MCT, is a food industry waste that can be transformed into a highly valuable by-product. It has been suggested as sustainable and eco-friendly source of fibrillar collagen to produce membranes for regenerative medicine applications [24].

6.1.3. Jellyfish

Recently, the jellyfish *R. esculentum* has received some attention as the type I collagen extracted from this species is quite similar to the human type, making it suitable for different applications in the biomedical field [10]. It was cross-linked with 1-Ethyl 3-(3-Dimethylaminoprophyl)-Carbodiimide (EDC) to form collagen-based sponges which showed hemostatic properties as blood clotting after tail amputation in rats, suggesting that it may be a suitable candidate for hemostatic material and wound-dressing applications [31]. Moreover, peptides derived from *R. esculentum* collagen were involved in wound-healing processes in vivo, by increasing the production of chemotactic factors TGF-β1 and β-FGF [124].

The capacity of the collagen to promote cell migration in wounded tissue suggests its possible use in synthetic matrix production for cartilage tissue engineering, mainly fibrous, hydrogel or hybrid materials [125,126]. Several efforts have been focused on collagen-based material colonization with cells of connective tissue such as fibroblasts or endothelial cells and other growth supports, in an attempt to produce a similar biocompatibility and immune response with collagen-based material commercially available. Recently, the type I collagen extracted from the blubber jellyfish, *Catastylus mosaicus* (Quoy and Gaimard, 1824) effectively supported preosteoblast growth [127].

Collagen from the giant Nomura's jellyfish, *Nemopilema nomurai* mesoglea was used to prepare porous collagen scaffolds. This collagen did not show any cytotoxicity and therefore resulted biocompatible with primary human fibroblasts (HFs) and endothelial cells. It showed a better cell viability compared with bovine collagen, glucan, gelatin and hyaluronic acid, while the in vivo implantation produced a similar immune response to commercial bovine-derived collagen [72]. Moreover, *N. nomurai* collagen was used to produce a hybrid collagen/hyaluronic acid 3D highly porous scaffold, which allowed fibroblast proliferation on its wide surface without interfering with cell viability [99].

An in vivo comparative study of jellyfish and bovine sponges as prototype medical devices reported that jellyfish collagen is able to stimulate both transcription and translation, thus enhancing immunoglobulin and cytokine production [50]. Results confirmed an immunological response of jellyfish collagen sponges, comparable to that stimulated by bovine collagen and gelatin [50].

Furthermore, *R. esculentum* collagen was used for growing human and rat nasal septal chondrocytes, with no cytotoxic effects and good biocompatibility, confirming the marine collagen as a suitable candidate for cartilage bioengineering [128]. Recently, *R. pulmo* type II collagen was used to develop a collagen-based biomaterial. The scaffold was implemented with nanoreservoirs of the growth factor TGF-β3 and human stem cells, building up a new adaptable device for articular cartilage repair [129].

The immunostimulatory effect of *N. nomurai* collagen stimulated the production of immunoglobulin and cytokine, not only in the specific human hybridoma cell line HB4C5, but also in the peripheral blood lymphocytes (PBL). In addition to these effects, the tumor necrosis factor (TNF)-α and the interferon (IFN)-γ levels were increased in PBL [130].

Thrombosis and hypertension are among the main causes of cardiovascular-associated death [131,132], thus the research for new treatments still remains an active field. In this regard, *R. pulmo* collagen was used to fabricate an apta-sensor for the clinical detection of thrombin in the blood. The collagen was cross-linked to the designed amine thrombin aptamer using glutaraldehyde. This hybrid sensor displayed a detection limit of 6.25 nM, largely below the imposed clinical limits, suggesting interesting future implication of collagen as a promising candidate for clinical analysis of thrombin [133].

Recently, Liu et al. described four novel angiotensin-converting enzyme (ACE) inhibitory peptides purified from *R. esculentum* collagen hydrolysate [134]. After the jellyfish collagen peptides (JCP) oral administration, the angiotensin II concentrations in the kidney decreased, leading to a significant decrease in both systolic and diastolic blood pressure [135].

Jellyfish collagen is a source of a great number of antioxidants. Recently, it was demonstrated that peptide fractions from *R. pulmo* collagen were able to prevent oxidative stress in HEKa cells treated with H_2O_2 [136]. Moreover, collagen peptides exhibiting scavenging and antifatigue activities were identified in *R. esculentum* [137,138], as well as collagen hydrolysate with several activities (including superoxide anion-scavenging and melanogenesis-inhibitory activities) based on the capacity of the hydrolysate to chelate copper inhibiting the intracellular tyrosinase activity [139]. Both jellyfish collagen and its hydrolysate were found to operate as UV radiation protectors, proposing their possible utilization in skin care industries [107]. Similarly, it was demonstrated that collagen peptides from *S. meleagris* are an effective tyrosinase inhibitor, acting on glutathione (GSH) levels [140].

7. Other Potential Applications of Marine Collagen: Food Additives and Packaging

Other than in the biomedical and pharmaceutical fields, collagen can find wide application in the food industry, as a food additive or packaging. However, so far, there is no literature available regarding the use of marine collagen in these applications, but there are many reports available for bovine, porcine, ovine and duck feet collagen. In this section, some of these examples are reported as references for the development of novel products and applications of marine collagen.

Currently, collagen has become a necessary ingredient toward the healthy food development. The production of collagen in the body decreases with age and with an unhealthy diet. Therefore, collagen has been added to a variety of foods [2]. Collagens are usually used as food additives to improve the rheological properties and reduce the fat consumption of sausages and frankfurters. Collagens are used also to ensure the presence of adequate amount of animal nutritive fibers [141].

Collagen-based edible films and coatings have already been proposed to protect, maintain and extend the shelf life of different food products. The film or coating acts, in this case, as a barrier layer against the migration of oxygen, moisture and solutes, providing structural integrity and vapor permeability to the food product [142]. Moreover, it prevents fat oxidation, discoloration, microbial growth and preserves the sensory qualities.

If properly treated with solvents, the collagen from the corium layer of food grade beef hides can be used to produce sausage casings (preformed casings) wherein subsequently the meat batter is stuffed [143]. In addition, collagen casings can be also coextruded around sausage meat batter, obtaining a process that is continuous and well-controlled [143]. However, in this coextrusion process, collagen for its complex structure must be first treated in order to obtain a dough or a suspension to be fed to the extruder. Conversely, gelatin, the denatured form of collagen, is easily processed by using thermoplasticization techniques by applying heat and mechanical stresses in extrusion-based technologies. A plasticizer is needed as it acts as an internal lubricant, leading to an increase of molecular mobility, necessary to promote the melt flow. The gelatin-based films obtained in this way are transparent and have excellent barrier properties against oxygen.

However, as a major limitation to widespread use, they have a strong sensitivity to moisture, which is responsible for a drastic reduction in barrier and as thermomechanical properties. One strategy to overcome this weakness is to associate the gelatin based film with a moisture resistant biodegradable polymer through laminating (coextrusion) as is typically done in film packaging, where multilayered structures that consist of distinct layers of moisture and oxygen barriers have been optimized for the specific different package and conditions [144].

A biodegradable three-layer gelatin film was obtained by hot compression of sodium montmorillonite-plasticized gelatin as the inner layer and cross-linked dialdehyde starch and plasticized gelatin films as the outer layers [145]. The multilayer film displayed a compact and uniform microstructure due to the highly compatible individual layers which could interact by strong hydrogen bonding. Lamination reduced moisture absorption compared to the single layers, while maintaining transparency and biodegradability [145]. Films of plasticized gelatin with 30% (*w/w*) glycerol can be also combined with poly (lactic acid) films as outer layers. The obtained multilayer film shows water vapor permeability values of around 1.2×10^{-14} kg m s^{-1} Pa^{-1} m^{-2} [146], which is higher than that obtained from other commercial polymers such as high density polyethylene or poly (vinyl chloride) (2.4×10^{-16} and 0.7–2.4×10^{-16} kg m s^{-1} Pa^{-1} m^{-2}, respectively) [147]. Poly (lactic acid) has been also used for gelatin-based three-layer film manufacturing with the dip-coating technique [148].

Further factors that should be considered when designing a food packaging are chemical nature of food, controlled release mechanisms, food organoleptic characteristics, additive toxicity and storage [149]. Consequently, different types of additives must be used to achieve suitable gelatin-based films or coatings for food packaging. Much research has been conducted to develop active packaging films and coatings, including antimicrobial, antioxidant and other agents which can enhance the biological features of foods. Recently, natural additives without negative effects on human health have been studied in order to reduce the use of synthetic chemical additives in the food industry. These additives can be obtained from different sources, including plants, animals, bacteria, algae, fungi and by-products generated during fruit and vegetable processing. Bioactive peptides, such as lysozyme, can be incorporated into gelatin films for food preservation. In particular, lysozyme incorporated into fish gelatin films did not inhibit the growth of *Escherichia coli*, but is effective against Gram-positive bacteria at very low concentrations [150]. The antibacterial activity of fish skin gelatin films incorporated with various concentrations (10, 20 and 30 wt%) of peppermint and citronella oils were also studied [151]. A growth inhibition of *E. coli* and *Staphylococcus aureus* was achieved with a success of higher than 80% with each oil loaded at 10 wt% [151]. The incorporation of chitosan into gelatin film forming solutions also resulted in active films against relevant food poisoning micro-organisms. These authors observed that mixing gelatin with chitosan was a means to improve water and mechanical resistance of gelatin films, but also to provide gelatin films with antimicrobial activity [152]. Wu et al. developed fish gelatin films incorporated with nanocapsules containing cinnamon essential oil with the purpose of improving and controlling their release rate [153]. The results of antimicrobial test showed a higher inhibition zone for the obtained film with cinnamon essential oil nanoliposomes compared to that of gelatin with cinnamon essential oil, demonstrating an improvement in antimicrobial stability along with a decrease in release rate after storage for one month. Liu et al. investigated the applicability of gelatin-based films packaged with sunflower oil [153]. An improvement in antioxidant activity was demonstrated over a long period of storage (six weeks), as well as the preservation of the functional properties of the new films. Food products such as fish, meat, fruits and vegetables can be coated with gelatin-based films in order to retard degradation processes due to the transport of gases (O_2 and CO_2) and water vapor. However, new methods and formulations for the production of marine gelatin-based films with improved final properties and potential applications require further exploration.

8. Conclusions

Contemporary societies across the world are facing the urgent need to find alternative, sustainable and eco-friendly resources due to the overexploitation of terrestrial resources and the problem of waste disposal. At the present time, humans live longer than their ancestors, which means that they need more support from the pharmaceutical, nutraceutical and biomedical fields to age better. Hence, research has been focusing on marine organisms to find new and alternative sources of natural compounds [154]. In the latest 20 years, more than 28 marine natural products and 175 chemical entities were found, and hundreds of new compounds are still being discovered every year, likely due to the advances in collection and molecular biology techniques [155,156]. To date, there are seven approved marine-derived drugs in clinical use, and about 26 natural products in phase I to phase III clinical trials [154].

Collagen has several applications in different fields, including nutraceuticals, cosmeceuticals, biomedicals, biomaterials and the food industry. Such a large variety of applications means that collagen can be key for the health and well-being of humans. To date, the sources of collagen mainly relied on terrestrial organisms, but they are becoming limited due to the spread of diseases and increasing alternative dietary choices of humans. This review highlights how marine organisms and their wastes can be a sustainable, eco-friendly source of collagen for the applications aforementioned.

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Progress in valorisation of agriculture, aquaculture and shellfish biomass into biochemicals and biomaterials towards sustainable bioeconomy

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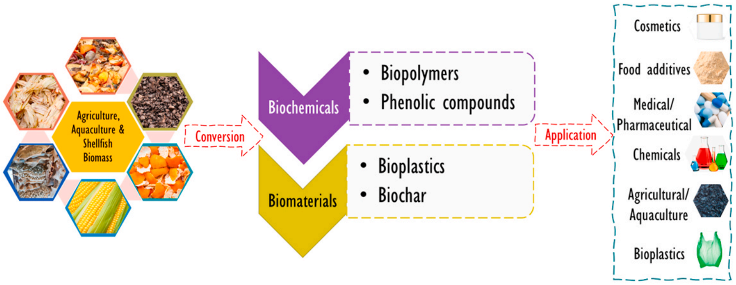
HIGHLIGHTS

- Valorisation of agriculture, aquaculture, shellfish biomass wastes is reviewed.
- Pectin, furfural, vanillin and bioactive compounds can be extracted from biomass.
- The industrial application of phenolic compounds from biomass is discussed.
- Bioplastic from biomass and bacteria is desirable to replace conventional plastic.
- Pyrolysis combined with modification techniques improve biochar properties.

GRAPHICAL ABSTRACT



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ABSTRACT

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The recurrent environmental and economic issues associated with the diminution of fossil fuels are the main impetus towards the conversion of agriculture, aquaculture and shellfish biomass and the wastes into alternative commodities in a sustainable approach. In this review, the recent progress on recovering and processing these biomass and waste feedstocks to produce a variety of value-added products via various valorisation technologies, including hydrolysis, extraction, pyrolysis, and chemical modifications are presented, analysed, and discussed. These technologies have gained widespread attention among researchers, industrialists and decision makers alike to provide markets with bio-based chemicals and materials at viable prices, leading to less emissions of CO_2 and sustainable management of these resources. In order to echo the thriving research, development and innovation, bioresources and biomass from various origins were reviewed including agro-industrial, herbaceous, aquaculture, shellfish bioresources and microorganisms that possess a high content of starch, cellulose, lignin, lipid and chitin. Additionally, a variety of technologies and processes enabling the conversion of such highly available bioresources is thoroughly analysed, with a special focus on recent studies on designing, optimising and even innovating new processes to produce biochemicals and biomaterials. Despite all these efforts, there is still a need to determine the more cost-effective and efficient technologies to produce bio-based commodities.

1. Introduction

For around a century and a half, fossil resources were the indisputable feedstock to produce fuels, chemicals and materials. In the energy sector for instance, over 80% of the energy consumption around the globe are based on fossil fuels (i.e., natural gas, coal and petroleum), and around 10% of the fossil resources are applied in the non-energy sector, such as the chemical industry (IEA, 2020). With the increasing world population and the simultaneous rise of the living standards in many countries worldwide, the shortcomings and unsustainability of the fossil-based linear economic model started to be clearly revealed with the emergence of highly complicated economic, societal, ecological, geopolitical issues around the world (i.e*.,* recurrence economic crises, accentuated disparities and mass migration, climate change and greenhouse gas emissions, armed conflicts around resources, transgressed planetary boundaries, etc.) (Steffen et al., 2015; Sillanpää et al., 2017; Johnsson et al., 2019).

It was not until a few decades ago that governments and large companies, mainly in developed countries, started paying attention to the adverse impact of such issues on sustaining and promoting economic growth, social welfare and environmental protection. As a quick response to such an alarming global context, national and international policies and plans were drafted (Fourie, 2018; Tsani et al., 2020), and more responsible actions were taken by the private sector (Topple et al., 2017; Florini and Pauli, 2018), but with limited impact considering the wide amplitude and complexity of such issue, conflicting objectives between the public and private sectors, and overall the need for a systemic paradigm shift to set course for a genuine sustainable development worldwide.

More recently, sustainable development has become a priority for policymakers and influential stakeholders around the world, with the necessity to gradually shift away from fossil resources as a key endeavour. Such delicate and lengthy enterprise comes with its own set of challenges that need to be faced to make a smooth transition towards low-carbon, resource-efficient societies, and sustainable economic systems. In this context, bioeconomy emerges as an alternative paradigm providing bio-based resources as viable replacements to the fossil-based counterparts to produce biofuels, biochemicals and biomaterials.

Despite numerous studies on the valorisation of biomass, there is a lack of inclusive review on designing and innovating new processes to extract useful compounds for the production of sustainable biochemicals and biomaterials. Thus, in the present review, the focus is on exploring the recent progress, achievements, and multitude of opportunities to valorise biowastes from agriculture, aquaculture, and shellfish processing sectors into value-added bio-based chemicals and materials for various applications in different economic sectors. Further, the ongoing and future challenges towards a sustainable bioeconomy are discussed, as well as the anticipated impacts of its implementation, from both social and environmental perspectives.

2. Conversion of biomass into biochemicals

Table 1 summarises the conversion of biomass into biochemicals via various valorisation techniques. Biochemicals can be produced from biopolymers derived from biomass materials. For example, pectin can be extracted from fruit waste for use in the pharmaceutical and cosmetic industries. Agricultural residues are made of hemicellulose, cellulose and lignin. Hemicellulose can be synthesised into furfural, cellulose can be converted into sugar alcohols or sorbitol, whilst lignin can be converted into vanillin. Shellfish and aquaculture wastes consist of bioactive compounds such as chitin, chitosan and protein that can be used in many applications.

2.1. Biochemicals from biopolymers

2.1.1. Food wastes

The agro-industry generates large quantities of food waste such as skin, damaged fruits and vegetables (e.g., citrus peel, banana peel, potato, apple pomace), seed wastes (e.g., grape, carob, pumpkin, date, mango), coffee waste, husk and nuts shell. These food wastes contain a considerable amount of organic matter, such as proteins, fatty acids, phenolic compounds, polysaccharides and dietary fibers (Di Donato et al., 2014). In general, global per capita food waste increased from 287 kcal/cap/day in 1992 to 473 kcal/cap/day in 2013 and is projected to increase to 812 kcal/cap/day in 2050 (Barrera and Hertel, 2021). This translates to approximately 1.6 billion tonnes of food wastage, of which the edible portion accounted for 1.3 billion tonnes (FAO, 2013). Several million metric tons of citrus (3.4 Million tons) and apple (89.3 million tons) are produced each year (Wang et al., 2014). Approximately 10–20% of these fruits are used to produce juice at industrial-scale, hence generating approximately 25–50% of waste containing 10–25% of pectin (Wang et al., 2014). Likewise, banana peel waste (10.9 million tons) and coffee husk compose 21.7 and 12.4% of pectin, respectively (Sanchez-Vazquez et al., 2013). Pectin has a high economic value with 1 billion USD of the market size in 2019 and is projected to reach 1.5 billion USD in 2025 (Petkowicz and Williams, 2020).

Pectin is a natural polysaccharide constituted by repeated homogalacturonans region (HGs) of α-(1–4)-D-GalA*p* and heteropolymeric region of rhamnogalacturonans (RGs) and arabinogalactans. Depending on the degree of methyl esterification (DM), HGs can be divided into two groups low methyl-esterified HGs (DM <50%) or high methyl-esterified HGs (DM >50%) (Müller-Maatsch et al., 2016). Pectin has several industrial applications in the pharmaceutical, food and cosmetic field (Minzanova et al., 2018). It is an important ingredient with interesting functional proprieties such as being a stabilizer, emulsifier, thickener and gelling agent (Mellinas et al., 2020).

Pectin modification could be an interesting way to obtain derivatives with new functional properties. Several methods have been used for obtaining pectin derivatives such as chemical substitution (e.g., oxidation, thiolation, quaternization, amidation, sulfation, alkylation, etc.), grafting and cross-linking (Chen et al., 2015). These modifications are able to enhance the water solubility gel strength, emulsifying proprieties, or antibacterial activity of pectin (Liu et al., 2017; Ciriminna et al., 2020). In addition, the depolymerisation of pectin using chemical, physical, or enzymatic degradation has also been used to obtain pectin oligosaccharides with enhanced biological activities (Ogutu and Mu, 2017). In fact, pectic-oligosaccharides degraded with free radical depolymerisation or ultrasonication showed enhanced antioxidant, antiglycation and prebiotic proprieties, which can be used as a biomaterial for tissue and bone engineering (Chaouch et al., 2015; Gómez et al., 2016).

2.1.2. *Agricultural residues*

The valorisation of agricultural residues becomes an interesting trend owing to the existence of bioactive compounds that allow the development of several industrial sectors (Ullah et al., 2015; Bhuyan et al., 2020). Agricultural residues generated during cultivation, harvesting, and post-harvesting from different crops such as maize, rice, and wheat contain a high amount of lignocellulosic polymers *viz.* cellulose, hemicellulose, and lignin. An estimated 3287 Mt of agricultural residue (fresh weight) of the primary global crops was produced annually in several countries or regions, including Argentina, Canada, Brazil, China, India, United States of America, and EU27 (Tripathi et al., 2019). Among the various crops, cereals remain the primary contributor to global agricultural residue production (Centore et al., 2014).

Cellulose is the most plentiful polymer worldwide. It consists of glucan chains linked by β-1,4-glycosidic bonds with different degrees of polymerization (DP). Cellulose possesses a high economic value with a global market size of 211.6 billion USD in 2019 and is projected to reach 235 billion USD in 2026 (Trache et al., 2017). Cellulose and its derivatives have a large, wide spectrum of functions in various fields (Li et al., 2018). This biopolymer demonstrates versatility in many industrial applications such as textile, cosmetic, medical, and pharmaceutical. For instance, cellulose nanocrystalline mixed with other polymers have been used to prepare edible films for food application (Trache et al., 2017), whilst cellulose nanofibers have been used to prepare aerogel for biomedical applications (Shaghaleh et al., 2018; Abdul Khalil et al., 2020). Likewise, sorbitol or sugar alcohols could be produced via chemo-catalytic transformations of glucose obtained from cellulose (Li et al., 2013).

Lignin is the second most abundant polymer in the world, which contains phenolic polymer with randomly cross-linked C_9 units (Wang et al., 2018). It has been reported that lignin from biomass such as wood and sugar beet pulp can be synthesised into vanillin (Aarabi et al., 2017). Vanillin is usually extracted from vanilla beans or petrochemical materials (e.g., guaiacol) to be applied as a flavouring additive in the cosmetics and food industries (Wang et al., 2018). Nevertheless, the demand for vanillin has surpassed the supply of vanilla beans, whilst the cost of petrochemical products has been increasing due to high competition with other products (e.g., plastics, solvents, drugs). Lignin can be extracted from various types of biomasses and converted into vanillin via various recovery methods such as chemical oxidation and enzymatic hydrolysis, thus making it a sustainable resource to produce vanillin.

In contrast to cellulose, mainly composed of glucose, hemicellulose is a heteropolysaccharide that contains xylose, glucose, galactose, mannose, arabinose, and galacturonic acid (Machmudah et al., 2017). Hemicellulose can be synthesised into furfural that can be used as chemicals in the agrochemicals and pharmaceutical industries (Luo et al., 2019). It has been reported that global production of furfural in 2019 was 551 million USD, and it is estimated to value more than 700 million USD by 2024 (Montaña et al., 2020). There are various valorisation technologies such as pyrolysis, solvolysis and hydrolysis to convert hemicellulose into furfural. Hui et al. (2019) reported that hydrolysis of hemicellulose (derived from corn cob) using superacid SO_4H-functionalized ionic liquids improved the yield of furfural up to 95%, as compared to conventional solvents such as toluene (67%) and acetone (44%). In another study, Fan et al. (2019) investigated the pyrolysis of corn cob using sulphuric acid as a catalyst. Nevertheless, the yield of furfural (19 wt%) was lower than the hydrolysis of corn cob, as reported by Hui et al. (2019).

2.1.3. *Shellfish and aquaculture wastes*

In 2018, total global capture fisheries and aquaculture productions were 96.4 and 114.5 million tons, respectively, with a total farm gate sale value of 263.6 billion USD for aquaculture production (FAO, 2018).

Table 1
Conversion of biomasses into biochemicals via various valorisation technologies.

Source of biomass	Valorisation technologies	Product	Yield of product	Remarks	Refences
Citrus	Alkylation	Pectin	–	Alkylation improves the molecular characterization, conformation and gel properties of pectin.	Liu et al. (2017)
Sweet potato	Ultrasonic treatment	Pectin	–	Sonication improves galacturonic acid content and the antioxidant activity of pectin.	Ogutu and Mu (2017)
Cellulose	Simultaneous hydrolysis and hydrogenation	Sorbitol	95%	The yield of sorbitol is influenced by the reaction condition such as temperature, catalyst, the composition of molten salt hydrate and hydrogen partial pressure.	Li et al. (2013)
Tomato peels	Acid hydrolysis	Cellulose	10–13%	Acidified sodium chlorite/potassium hydroxide removed lignin and hemicellulose from tomato peels to produce a higher yield of cellulose (13%) as compared to chlorine-free sodium hydroxide/hydrogen peroxide, which produce 10–11% of cellulose.	Jiang and Hsieh (2015)
Wood	Alkaline nitrobenzene oxidation	Vanillin	12–13%	The interunit linkages (β-*O*-4) in lignin highly influence the yield of vanillin.	Wang et al. (2018)
Sugar beet pulp	Lignin oxidation	Vanillin	–	Vanillin yield is greatly influenced by oxygen pressure, temperature, reaction time, and concentration of catalyst.	Aarabi et al. (2017)
Corn cob	Hydrolysis using superacid SO_4H-functionalized ionic liquids	Furfural	95%	Strong acid strength improves the conversion of hemicellulose into furfural.	Hui et al. (2019)
Corn cob	Pyrolysis using sulphuric acid as catalyst	Furfural	19 wt%	Sulphuric acid can be used as a catalyst to enhance dehydration of hemicellulose to increase the yield of furfural.	Fan et al. (2019)
Shrimp shell	Classical deacetylated chitosan (CDC) and ultrasound-assisted deacetylated chitosan (UDC)	Chitosan	17%	UDC is more effective in producing chitosan with a high degree of deacetylation and better antioxidant activity compared to CDC. The chitosan shows potential to be used as an antimicrobial agent.	Hafsa et al. (2016)
Litchi fruit pericarp (LFP)	Extraction	Phenolic	0.17 mg/g	LFP contains high total phenolic content, which is comparable to synthetic antioxidants such as butylated hydroxyl toluene (BHT). LFP extract shows the potential to be used as antioxidants and food additives.	Das et al. (2016)

(–) data are not available.

Approximately 25% of shellfish part is edible, while the remaining inedible parts (i.e., heads, shells, skeletons) lead to the inevitable accumulation of shellfish waste (Özogul et al., 2019). Interestingly, many studies have reported the useful bioactive compounds (e.g., chitin, astaxanthin, protein) that can be extracted from shellfish waste (Vázquez et al., 2013; Özogul et al., 2019). Instead of discarding the shellfish waste in the ocean, landfill or incinerator, several techniques are developed to transform shellfish waste into biologically active polysaccharides that can be utilised in many applications.

Chitosan is a linear polysaccharide and the main component of shellfish shells. It consists of D-glucosamine chains linked by β-1,4-glycosidic bonds and also a natural biopolymer produced by deacetylating chitin in an alkali solution (Younes and Rinaudo, 2015). Chitosan and its derivatives have been exploited for many years by the industry due to their abundance, renewable sources, biodegradability and non-toxicity (Özogul et al., 2019). Likewise, chitosan is widely used in food to make edible and biodegradable films and in the preservation of food against microbial deterioration due to its antimicrobial property (Hafsa et al., 2016, 2021). In the recent decade, chitosan derivatives obtained through chemical modification (i.e., acylation, carboxylation, thiolation, phosphorylation, quaternization) and cross-linking have been widely used in several fields such as pharmaceuticals and wastewater treatment (Negm et al., 2020). In fact, chitosan derivatives exhibited enhanced new features such as reactivity and water solubility. Furthermore, they are investigated in several fields such as food quality, wound healing, drug delivery and tissue engineering (Zhou et al., 2021). In addition, the depolymerisation of chitosan using chemical, physical, or enzymatic degradation have been used to obtain chitosan oligosaccharides with enhanced antimicrobial activity, immunostimulant and anticancer properties (Zou et al., 2016).

2.2. *Biomass-derived phenolic compounds*

Phenolic compounds are a class of secondary metabolites implicated in several biological processes during all plant growth and development (Ben Mrid et al., 2021). Phenolic compounds comprise phenolic acids, flavonoids, coumarins, lignans and tannins, that are naturally found in the different parts of the plants and fruits. The wide range of these chemical compounds confers to their different activities and potential applications in the pharmaceutical and food processing industries (Albuquerque et al., 2021).

2.2.1. *Application of phenolic compounds in food processing industry*

In the food processing sector, phenolic compounds are mainly used for food preservation as a food additive and/or active packaging (Das et al., 2016; Zeng et al., 2019). In fact, the potential benefit of phenolic compounds as bio-preservatives lies in their ability to extend the shelf life of perishable products with the ability to delay or prevent oxidation and microorganism's growth (Bouarab Chibane et al., 2019). These phenolic compounds could be generated by the food industry itself. Indeed, in the food industry, the fruit processing industry generates an enormous quantity of wastes (e.g., peels, seeds, pulp); thus, the large amounts of phenolic compounds that are present in these wastes could constitute natural sources of antioxidants and could therefore be used for food preservation.

Indeed, different hydroxybenzoic and hydroxycinnamic acids, flavonoids, and hydrolysable tannins were reported to be highly present in various fruit wastes such as citrus, apple, mango, and pomegranates (Kessy et al., 2018). The antioxidant ability of these groups of natural molecules has been proven in multiple studies and attempts to apply these molecules have already been started. In this regard, phenolic compounds can be extracted from Litchi pericarp (*Litchi chinensis* Sonn), which showed potent inhibition of the lipid peroxidation in sheep meat nuggets. This inhibition was similar to the synthetic antioxidant butylated hydroxyl toluene (BHT) (Kessy et al., 2018).

In another study, Caleja et al. (2016) measured the antioxidant activity by DPPH (2,2-diphenyl-1-picrylhydrazyl) scavenging assay in yogurt fortified by phenolic compounds from *Foeniculum vulgare* Mill. In fact, the plant extract showed an EC50 of 94 mg mL^{-1} compared to the potassium sorbate that showed an EC50 of 111 mg mL^{-1} (Caleja et al., 2016). Phenolic compounds have also been used to increase the functional properties of food. For instance, *C. sinensis* phenolic compounds have enhanced the bioactive profile of bread and cheese (Rashidinejad et al., 2014; Pasrija et al., 2015).

2.2.2. *Application of phenolic compounds in pharmaceutical field*

Due to their antioxidant capacities, phenolic compounds from agricultural food wastes have generated a lot of interest in the pharmaceutical field as well. For instance, phenolic compounds from citrus wastes were evaluated for their antiglycation activity as well as their ability to inhibit digestive enzymes such as lipase, α-glucosidase, and α-amylase. The polyphenol fraction showed high inhibition of the AGEs and potent inhibitory activity against pancreatic lipase and α-glucosidase (Fernandes et al., 2020). In another study, consumption of 800 mg/day of resveratrol increased the blood antioxidant capacity and decreased blood pressure in diabetic subjects (Seyyedebrahimi et al., 2018).

In a recent study, phenolic compounds have been found to minimise the risk of aging-related diseases, including metabolic syndromes (e.g., diabetes, obesity) and neurodegenerative diseases (e.g., Huntington's disease) (Arruda et al., 2020). Phenolic compounds such as rutin and curcumin can improve motor and memory performance by modulating signalling pathways engaged in oxidative damage, inflammation and autophagy, such as reducing neurons degeneration and oxidative stress. Ferulic acid, gallic acid and curcumin can be used to prevent obesity by reducing adipogenesis and adipose inflammation, which results in the reduction of fat accumulation and body weight (Luna-Vital et al., 2020). Nevertheless, the antagonistic and synergistic effects of both phenolic compounds and other food components (e.g., carbohydrates, proteins) should be further investigated to improve the understanding and stability of phenolic compounds as a dietary supplement.

3. **Conversion of biomass into biomaterials**

Other than biochemicals, biomass can be treated via various biological, chemical and thermochemical techniques to produce biomaterials. Biomass can be used to replace fossil-based materials in manufacturing various types of products. This includes the production of bioplastic from biopolymers derived from biomass sources to replace conventional plastics. The production of biochar from biomass using emerging thermochemical technologies has gained significant attention in order to replace the constant use of fossil-based products such as coal and tar, which is discussed in the subsequent section.

3.1. *Bioplastics*

Plastics are essentially organic materials made up of polymers. Their plasticity and other desirable physical properties such as lightweight, durable, low density and inexpensive make plastics the preferred material for use in a wide range of applications across various industries (Bagheri et al., 2017; Narancic et al., 2020). However, the recycling process of plastics, especially the conventional petroleum-based plastics, is difficult due to the complications with various mixtures of plastic types (e.g., differences in processing conditions, not compatible due to immiscibility with different types of plastics) and the reduction in quality after the recycling process of reheating (Hopewell et al., 2009; Gutowski et al., 2013). To date, approximately 90% of plastics are still produced from fossil feedstocks, and their production accounts for 4–8% of global oil consumption (Narancic et al., 2020). Their prevalent usage in almost every industry, coupled with the extremely slow degradation rate (e.g., 10–20 years or 500–1000 years) of conventional plastics in environmental conditions (Ward et al., 2019; Chamas et al., 2020), have led to serious environmental problems, including the formation of meso-, micro-and nanoplastics that could accumulate in all ecosystems and are biologically hazardous to almost all trophic levels of the food chain (Mattsson et al., 2015; Botterell et al., 2019; Wang et al., 2021).

Unlike conventional plastics, bioplastics are bio-based plastics, i.e., made up of renewable sources such as biomass by the action of living organisms, with or without biodegradable characteristics (Batori et al., 2018). Similar to their petroleum-based counterparts, bioplastics are recyclable or incinerable. Although bioplastics can potentially serve as better options due to their lesser greenhouse gas emission, reduction in the reliance on fossil fuels, reclamation of by-products, and the diversification of local resources, the production of bioplastics remain low (approximately 1% of the global plastic production) (Narancic et al., 2020; Coppola et al., 2021). This is due to the high production cost of bioplastic, such as the expensive energy source used for microbial fermentation (Wan Mahari et al., 2022a). In addition, a large amount of raw materials (e.g., carbon sources, chemicals, microorganisms) are needed to generate a high yield of bioplastics. Contrary to conventional plastic production that depends solely on the chemical processing of fossil fuel, the source and production of bioplastics are diverse.

3.1.1. Bioplastics production from biomass extraction

3.1.1.1. Polysaccharide-based. Bioplastics produced from biological treatments are made up of agro-polymers, either plant-, animal- or

Table 2
Sources and method of bioplastic synthesis.

Source of bioplastics	Type of bioplastics	Method of bioplastic synthesis	Main findings	References
1. Polysaccharide-based	Starch-based Thermoplastic starch Starch-based film	- Cross-linking, esterification, pregelatinization - Nano-SiO$_2$ combined with potato starch film	- Starch-based polymer is abundantly available and cheap but needs a plasticiser and water to be used as a deformable thermoplastic material.	(Khan et al., 2017; Zhang et al., 2018)
	Cellulose-based Cellulose aleuritate Cellulose acetate Cellulose-based films	- Acylation via a mixed anhydride system - Acetylation process - Delignified banana stem fibers via an ionic liquid	- Cellulose-based polymer is less affected by acids compared to polystyrene and polypropylene. - Suitable to be applied in the pharmaceutical and food industries.	(Heredia-Guerrero et al., 2017; Mostafa et al., 2018; Ai et al., 2021)
	Carrageenan-based Carrageenan-based film	- Polymer casting - Plasticiser	- Carrageenan-based film derived from seaweed exhibits excellent physical and mechanical properties that are desirable to be used as bioplastic film, especially in non-food and food packaging. - Further studies are needed to evaluate the commercial potential and economic feasibility of this bioplastic film.	(Sudhakar et al., 2020)
	Alginate-based Alginate-based film	- Solvent casting or extrusion technique	- Alginate-based film can inhibit the growth of microorganisms, reduce the evaporation of water, and improve the shelf life of food products. - Further studies are needed to upscale and commercialise the bioplastic film.	(Senturk Parreidt et al., 2018)
	Chitin and Chitosan Crab Shells (*Portunus pelagicus*)	- Solvent casting	- Chitin-based film shows greater ultimate tensile strength compared to the commercial plastic film. - Further studies are needed to optimise the extraction and synthesis process for commercialisation.	(Fernando et al., 2016)
2. Protein- and lipid-based	Protein-based Fish gelatin (animal) Zein (plant) Kafirin (plant) Wheat gluten (plant)	- Plasticised, casting, mixing, extrusion. - Zein-based films blended with oleic acid and xanthan gum - Extraction, physical and chemical modification	- Nano-curcumin fish gelatin film has better mechanical properties and shelf life compared to fish gelatin film. - Zein-based films blended with oleic acid and xanthan gum have higher water solubility, opacity and tensile strength compared to zein-oleic acid film. - Kafirin-derived film possesses desirable bioplastic properties but needs to compete with the other products produced from sorghum, especially food.	(Serna and Filho, 2015; Taylor and Taylor, 2018; Matche et al., 2020)
	Lipid-based Castor oil Soybean oil	- Chemical treatment - Organoclay nanocomposites, epoxidation	- Maleated castor oil foams are cost-effective, smoother and stronger with comparable compressive stress at 25% strain as commercial polyurethane foams. - Incorporation of organoclay nanocomposite on the epoxidised soybean oil has improved the mechanical strength properties (e,g. tensile toughness, tensile strength) of the bioplastics.	(Wang et al., 2008; Tanrattanakul and Saithai, 2009)
3. Microbe-origin	Pullulan (fungus) FucoPol (bacteria) Polyhydroxyalkanoate (PHA)	- Enzymatic hydrolysis and fermentation	- Pullulan has distinctive functional features (e.g., inhibit bacteria growth, extend shelf-life) and is proclaimed as safe for use in food packaging. Future studies are needed to apply pullulan on the food market and industrial scale. - FucoPol possesses flocculating and emulsion stabilising capacity and membrane forming capacity, which can be applied in a multilayer packaging material. - PHA has tissue biocompatibility in animals and humans, thus can be used in the medical industry. PHA can replace conventional plastic due to its biodegradability, but it requires a high cost for raw materials during microbial fermentation.	(Ferreira et al., 2014; Singh et al., 2019)
4. Petrochemical-based	Polybutyrate adipate terephthalate (PBAT) Polybutylene succinate (PBS)	- Polyester manufacturing technology - Copolymerisation	- PBAT is produced from polycondensation of adipic acid, butanediol and terephthalic acid. It is biodegradable and can be used to replace fossil-based plastic. - PBS has good thermo-mechanical properties and is biodegradable. The application of PBS in the biomedicine industry is attracting attention.	(Gigli et al., 2016; Jian et al., 2020)

microbe-based (Table 2). Being regarded as the most abundant macromolecules in the biosphere, polysaccharides are complex carbohydrates that support the structural constituent of plants and animals or serve as energy storage material (Ferreira et al., 2016). In addition to polysaccharides, proteins and lipids of plants such as soy and gluten and animals such as casein, whey and collagen are also being harnessed as raw materials for bioplastic production (Felix et al., 2017).

Starch-based bioplastics derived from plants are preferred and consist of 20% of the global bioplastic production due to their abundance and stable thermoplastic behaviour (Ferreira et al., 2016; Jiang et al., 2020). They are easily available as starch can be obtained easily from common agricultural crops and various plant parts, including cereals (Xu et al., 2010; Marichelvam et al., 2019), grains and nuts (Santana et al., 2018; Tsang et al., 2019). Starch granules are made up of amylose (linear microstructure) and amylopectin (branched microstructure), both of which depend on amylose/amylopectin ratio, granule size, plant source and other physicochemical properties such as pH (van Soest and Essers, 1997; Seung, 2020). These influential properties, in turn, determine the quality of the bioplastics produced.

The general concept of converting starch into bioplastic film involves two essential steps of thermal treatment: starch gelatinisation to destroy the starch granules' crystalline structures via heated water and solution casting or annealing to allow the re-crystallisation or retrogradation of the gelatinised starch (Seung, 2020). One of the most common techniques used during gelatinisation is extrusion. The extrusion process involves melting and solidification. When water temperature above the gelatinisation temperature is applied, hydrogen bonding within starch granules would be disrupted, allowing the integration of water molecules with starch molecules and consequently resulting in the swelling and dissolution of crystallites (Lim et al., 2000). The amylose/amylopectin ratio influences the mechanical properties of the bioplastics produced, with the amylose content positively correlating with tensile strength, whereas higher amylopectin content corresponds to higher strain (Tanetrungroj and Prachayawarakorn, 2015). As most starch-based biofilms have inadequate mechanical properties (e.g., hard and brittle), glycerol is often added to retard the swelling and gelatinisation of starch to achieve bioplastic with high mechanical stability (Santana et al., 2018).

Being the main constituent of plant cell walls, cellulose is earth's most abundant organic polymer and is composed of linear β-D-glucose units. The regular structure and abundance of hydroxyl groups in cellulose result in strong hydrogen-bonded crystalline fibers with high mechanical strength. Coupled with other characteristics such as low cost, durability, biocompatibility, chemical stability and renewability, cellulose is a prime candidate for producing bioplastic (Wang et al., 2013). Commonly used raw material source for bioplastic production includes pulps, sugarcane bagasse fibre, cocoa pod husk and wood fibre (Wang et al., 2013; Azmin et al., 2020; Kamau-Devers and Miller, 2020). Although there are various commercialised derivatives, common industrial cellulosic materials include cellulose acetate, cellulose esters and regenerated cellulose. Cellulose-based bioplastic is commonly produced using thermo-chemical treatment methods. Plant ingredient needs to be delignified using sodium hydroxide and purified using sodium hypochlorite during cellulose extraction. Subsequent gelatinisation could involve the addition and heating of starch to allow thorough mixing before air dying on casts. Often, in addition to chemical modification to improve the thermoplastic properties of cellulose, the inclusion of plasticisers and blending with other polymers are incorporated to alter and enhance the mechanical and chemical properties of the final cellulose product (Ferreira et al., 2016). By incorporating hot-pressing to the cellulose hydrogel, Wang et al. (2013) developed a new class of cellulose bioplastic with superior tensile and flexural characteristics, good thermal stability and exhibited low thermal expansion in comparison with conventional plastics and regenerated cellulose biofilms (Wang et al., 2013).

Carrageenan is a linear polysaccharide obtained from red seaweeds (family Rhodophyceae). It is widely used as a food thickener and emulsifier and is often found in meat products and yogurt (Mena-Casanova and Totosaus, 2011). Due to their good mechanical properties and edible characteristic, carrageenan is commonly used to produce edible biofilms and coatings (Bico et al., 2009). The addition of plasticiser polyethylene glycol (PEG) was shown to enhance the tensile strength of carrageenan-based biofilm (Sudhakar et al., 2020). Alginate is another natural polysaccharide derived from algae, specifically brown seaweeds (e.g., genura *Laminaria* and *Ascophyllum*). In addition, alginate can be produced by two bacterial genera, i.e., *Pseudomonas* and *Azotobacter* (Hay et al., 2013). Alginate is soluble in water and suitable for the production of biofilm due to characteristics such as non-toxic, biodegradable, biocompatible and low cost. The linear structure found in alginate entails a strong membrane structure of alginate-based biofilms. On top of that, as a polyuronide, alginate is a natural ion exchanger and, in its charged state, could lead to gel formation (Senturk Parreidt et al., 2018). The process of converting carrageenan into bioplastic is straightforward; carrageenan and alginate are subjected to thermal treatment for proper mixing, followed by the solvent casting method. Various additives, such as plasticisers (El Miri et al., 2018), surfactants (Albadran et al., 2018), antimicrobials (Raybaudi-Massilia et al., 2008), antioxidant and antibrowning agents (Robles-Sánchez et al., 2013), and nutritional additives (Bazargani-Gilani, 2018) have been tested and incorporated onto alginate-based coatings or biofilms to enhance their functionality.

Being the primary element that provides structural support in the exoskeleton of arthropod crustaceans, chitin is now being harvested from shell waste of crustaceans (e.g., shrimps, prawns and crabs), aquaculture, and fishery. Although chitin only makes up approximately 20% of the exoskeletal wastes, the global annual production of chitin was estimated to be at 362,000,000 MT (Fernando et al., 2016). In general, chitin is easily extracted using either biological or chemical extraction. Both extraction methods isolate, demineralise and deproteinise chitin. However, the chemical extraction method is known to produce chitin of higher purity (Younes and Rinaudo, 2015; Fernando et al., 2016). Following chitin extraction, polymer film formation is done by mixing chitin with dissolution solvent and moulded into film via cold-pressing (Fernando et al., 2016). An important derivative of chitin that is also used in the production of bioplastic is chitosan; a polysaccharide derived from the partial deacetylation (about 50%) of chitin (Shamshina et al., 2020). Similar to chitin, chitosan biofilms are also biodegradable, edible and renewable (Fernandez and Ingber, 2014). Owing to its soluble properties, chitosan is used in various forms, including solutions, gels, films and fibres. Chitosan film production is relatively straightforward – purification (dissolve in acid and filter through membranes), chemical adjustment (alter pH to about 7.5), washing and drying (Rinaudo, 2006).

3.1.1.2. Protein- and lipid-based. In addition to plant-based sources, another potential source of bioplastic production is protein and lipid obtainable from livestock and biomass (e.g., agricultural residue). One such example is the extraction of casein and whey proteins from cheese production and expired dairy products (Wagh et al., 2014). Casein and whey proteins exhibit superior film-forming characteristics, including flavourless, elastic, transparent, high nutritional value, and have been used to produce food packaging material (Wagh et al., 2014; Chalermthai et al., 2019). The process of biofilm production from casein and whey involves denaturation in heated aqueous solution (above 75 °C), adjusting pH to 5.6 using NaOH, adding plasticizer (*e.g.,* glycerol and sorbitol) and final casting (Wagh et al., 2014).

Another potential renewable and easily available biopolymer source is collagen and gelatin. The main source of collagen and gelatin is from the leather industry and with minimal contribution from the animal slaughtering and processing industry (Matche et al., 2020). Leather solid wastes, specifically during fleshing and shaving phases, contain raw collagen that could be synthesised into collagen hydrolysate (CH) after enzymatic hydrolysis (Haroun, 2010). Haroun (2010) successfully developed a biodegradable thermoplastic film by blending modified polyethylene (MPE) with CH (Haroun, 2010). The author also reported the production of biopolymer with 20% of CH that can achieve 63% biodegradation in 24 days. Gelatin is produced from chemically treated collagen, and its properties are influenced by the features of input collagen and the extraction parameters (Nur Hanani et al., 2014; Ramos et al., 2016). Although gelatin is widely used in food, packaging, pharmaceutical and photographic industries, it is still limited by the low thermal stability and mechanical properties (Ramos et al., 2016). Matche et al. (2020) recently developed biodegradable films from fish gelatin for the packaging of fish fillets (Matche et al., 2020). The addition of carrageenan and laminarin improved the properties, whereas the incorporation of curcumin added antimicrobial features to the developed film (Matche et al., 2020). Compared to other biopolymers, gelatin is superior in terms of exhibiting excellent oxygen barrier and heat sealability (Nur Hanani et al., 2014).

Zein, kafirin and gluten are proteins found in maize, sorghum and wheat, respectively. Gluten has high thermoplastic and viscoelastic properties and is capable of withstanding various chemical modifications. However, its gliadin and glutenin proteins may confer celiac toxicity and wheat allergies to some people, thus rendering it unsuitable to be used in food-related and biomedical sectors (Taylor et al., 2013). There are limited records of allergic cases with zein, but kafirin is an excellent nontoxic choice for celiac sufferers (Pontieri et al., 2013). Chemical treatment or thermo-mechanical treatments can be used in the production of gluten films. Wheat gluten can be either mixed with acetic acid, Na_2SO_4 and glycerol before spreading and drying at 60 °C, or mechanically mixed with glycerol using a mortar and subsequently subjected the mixture to heating press at 150 bar (Domenek et al., 2004). Zein is normally extracted using chemicals such as 70% ethanol, whereas kafirin is derived using thermal (warm water) and the addition of a reducing agent (Schober et al., 2011). Serna and Filho (2015) developed a zein-oleic acid blend film with greater water solubility and opacity by adding xanthan gum during the mechanical mixing process (Serna and Filho, 2015).

Apart from being protein-based, bioplastic could also be made from lipids (triglycerides). Due to their economic values, soybean oil, castor oil and linseed oil are readily available. Soybean oil was epoxidised with acetic acid and hydrogen peroxide before transforming into bioplastic via curing process using methyl-tetrahydrophthalic anhydride and 1-methylimidazole (Tanrattanakul and Saithai, 2009). Castor oil needs to be maleated using maleic anhydride before being synthesised into plastic sheets via copolymerisation reaction that is initiated by styrene (Wang et al., 2008). Vaicekauskaite et al. (2019) developed cross-linked polymer composites using epoxidised linseed oil and 1-hydroxyethane-1,1-diphosphonic acid, with organic industrial wastes (e.g., pine bark, grain and weeds) as fillers (Vaicekauskaite et al., 2019). Low-temperature curing (20–25 °C) is sufficient in forming the composite films.

3.1.2. Bioplastics synthesised from microorganisms

Several types of microorganisms, including yeast, fungus and bacteria, are able to produce polysaccharides that can be synthesised into biofilms (Ferreira et al., 2016) (Table 2). Pullulan is synthesised via the fermentation process of liquefied starch under specific conditions using non-genetically modified, non-toxigenic and non-pathogenic *Aureobasidium pullulans*, a type of black yeast-like fungus (Prajapati et al., 2013). In addition to being biodegradable and impermeable to oxygen, pullulan has great mechanical strength, is highly-water soluble and is not easily digested by our guts' digestive enzymes, making it a preferred choice in the pharmaceutical and food industries (Singh et al., 2019). Various carbon sources, such as starch, soybean oil, beet molasses and other agro-industrial waste, could be used as the fermentation target for the production of pullulan (Cheng et al., 2011; Prajapati et al., 2013). Pullulan has been commercially produced via fermentation, and optimal yield (more than 70%) of pullulan is expected within 100 h. The recovery process of pullulan includes removal of *A. pullulans* via filtration, removal of melanin via activated charcoal treatment, and subsequent precipitation and purification using organic solvents (Singh et al., 2019).

Xanthan gum is produced similarly to pullulan via fermentation process by bacteria such as *Xanthomonas campestris* (Palaniraj and Jayaraman, 2011). On the industrial scale, xanthan can be produced via batch or continuous operation using a wide variety of substrates and nutrients. The production of xanthan is relatively easy to manipulate and carried out as *X. campestris* grows optimally under 28–30 °C and neutral pH (Gumus et al., 2010; Palaniraj and Jayaraman, 2011). FucoPol is a microbial polysaccharide produced by *Enterobacter* A47. Unlike pullulan and xanthan, the production of FucoPol relies on using glycerol as its carbon source, and a yield of 7.8 g/l was reported after 4-day production using bioreactor (Ferreira et al., 2014)

Another important biopolymer produced by microorganisms is polyhydroxyalkanoates (PHAs) that can be synthesised by a wide variety of bacteria (Anjum et al., 2016). PHAs are gaining attention due to their resemblance to commonly used petrochemical polymers, i.e., polypropylene and polystyrene (Sudesh et al., 2000). PHAs can be synthesised via the fermentation process, and their characteristics are dependent on carbon source, choice of bacteria, and fermentation conditions (Khatami et al., 2021). Bacteria hosts involved in PHA synthesis can be divided into two types – those that require excess carbon source and stress conditions (e.g., *Pseudomonas oleovorans*), and those that do not need to be subjected to nutrient starvation (e.g., *Azotobacter vinelandii* and *Escherichia coli*).

3.1.3. Bioplastics synthesised from petrochemicals

To address the issue of biodegradability, researchers have also dwelled on the potential of producing biodegradable products of petrochemical origin. Among them, aliphatic-aromatic co-polyesters, particularly the Polybutyrate adipate terephthalate (PBAT), show great biodegradable ability due to their soft-chain ester bonds that are sensitive to hydrolysis (Mochizuki and Hirami, 1997). PBAT is not only biodegradable but, owing to the presence of aromatic unit in its molecule chain, also exhibits strong mechanical properties such as flexibility, good thermal stability and moderate crystallinity (Cranston et al., 2003; Jian et al., 2020). PBAT is produced via the poly-condensation process (pre-mixing, pre-polymerisation, and final-polymerisation) of three essential ingredients, namely butanediol (BDO), adipic acid (AA) and terephthalic acid (PTA). During the poly-condensation process, which often involves high vacuum and temperature (>190 °C), and a long reaction period, zinc-, tin-, and titanium-based organometallic elements may be used as catalysts. An in-depth review of the commercially available PBAT was reported by Jian et al. (2020) (Jian et al., 2020). In an attempt to further reduce the reliance on fossil fuel, bio-based BDO produced via biological fermentation is being tested as a replacement to petrochemical-derived BDO (De Bari et al., 2020). Similarly, sebacic acid derived from Castrol oil is also in the trial as a potential substitute for AA (Jian et al., 2020).

Similar to PBAT, Polybutylene succinate (PBS) is an aliphatic polyester and is well known for its thermal stability, great mechanical properties, biodegradability and acceptable production costs. Since 1993, PBS has been commercially available in the form of biodegradable mulching films, bags, textiles and foams (Xu and Guo, 2010; Gigli et al., 2016). The production of PBS involves two fossil-based monomers, succinic acid (SA) and BDO. The production process of PBS is similar to that of PBAT, involving polycondensation that can be further detailed out in two stages, esterification process and the removal of either water or methanol, and subsequent removal of BDO at high temperature and reduced pressure to yield PBS of high molecular weight (Gigli et al., 2012). Currently, increasing studies have shown that SA and BDO can be produced via fermentation, and an acceptable yield has been obtained (Bechthold et al., 2008; Forte et al., 2016). This implies that full bio-based PBAT and PBS are achievable and would reduce dependency on petrochemical (fossil fuel) in the near future.

3.2. Biochar

Biochar is a carbonaceous material produced from biomass *via* thermochemical conversion technologies (e.g., pyrolysis, gasification, torrefaction). The biochar is categorised as biomaterials due to its origin from biomass and desirable properties that shows potential to be used in multi applications such as absorbent, catalyst, solid fuel, and fertiliser (Wan Mahari et al., 2020b; Ren et al., 2021; Yan et al., 2022).

Table 3 summarises the recent studies on biochar recovery via thermochemical conversion technologies of biomass materials. The thermochemical technologies are distinguished based on the operating temperatures, heating source, reaction condition (purged by N_2, O_2, or CO_2). Pyrolysis is an emerging thermochemical technology that decomposes biomass under an inert environment in a temperature range of 300–900 °C to convert biomass into value-added biochar (Parvez et al., 2019; Wan Mahari et al., 2020a). Pyrolysis can be classified into conventional and advanced pyrolysis techniques. In conventional pyrolysis, the furnace is commonly used as the heating source, while the heating rate of the pyrolysis process determines the type of pyrolysis process, which can be slow, fast or flash pyrolysis (Azwar et al., 2022). In advanced pyrolysis techniques, modifications are performed to the pyrolysis system to improve the thermal cracking performance and quality of the biochar. For example, pyrolysis is incorporated with microwave

Table 3

Previous studies on biochar production via various valorisation technologies.

Source of biomass	Valorisation technologies	Yield of biochar	Properties of biochar	Main findings	References
Coffee husk briquettes	Slow pyrolysis	35–40%	C: 70–74%, H: 2–4%, N: 3–4%, O: 20–23%, S: 0.1–0.2% Calorific value: 27 MJ/kg	- Low heating rates allowed better heat transfer between the particles, thus increasing the yield of biochar. - However, the high temperature was needed to improve the yield and quality of bio-oil.	Setter et al. (2020)
Reed	Fast pyrolysis	–	C: 89%, H: 3% Surface area: 1545 m^2/g Adsorption capacity: 1019 mg/g	- Fast pyrolysis improved the porosity properties of carbon products, leading to their high adsorption capacity. - Carbon products can be used as gas storage material or adsorbent.	Rahbar-Shamskar et al. (2020)
Spruce wood chips	Pyrolysis and gasification	–	C: 87 wt%, H: 0.6 wt%, S: <0.1 wt% Surface area: 1253 m^2/g Adsorption capacity: 67 mg/g	- Lower temperature increased the adsorption capacity of biochar. - Require high carbon conversion efficiency to produce biochar with high surface area and adsorption capacity.	Ravenni et al. (2019)
Peat	Hydrothermal carbonisation and torrefaction	70–80%	C: 59–65 wt%, H: 5 wt%, O: 23–28 wt% Calorific value: 23–26 MJ/kg Surface area: 2 m^2/g	- Carbonisation increased the surface area of biochar in contrast to torrefaction. - Torrefied biochar possessed higher energy yield but lower calorific value compared to carbonised biochar.	Krysanova et al. (2019)
Microalgae	Torrefaction and chemical treatment	55–75%	C: 54–68 wt% H: 7–13 wt% O: 17–32 wt% Calorific value: 21–31 MJ/kg	- Wet torrefaction increased the calorific value of biochar for use as solid fuel. - Acid hydrolysis pretreatment improved the active sites and sorption capacity of biochar that can potentially be used as adsorbent.	Yu et al. (2020)
Orange peel waste	Microwave pyrolysis and gas activation	31–44 wt%	C: 63–78 wt%, H: 2–5 wt%, O: 19–32 wt% Surface area: 159–305 m^2/g Adsorption capacity: 96–159 mg/g	- CO_2 activation developed more micropores in contrast to steam activation that developed more mesopores. - Microwave pyrolysis combined with gas activation is a desirable approach to produce activated carbon with high adsorption capacity for the removal of dye from wastewater.	Yek et al. (2020)
Switchgrass	Microwave activation and catalytic pyrolysis	–	C: 26–36 wt%, H: 1–2 wt%, O: 11–17 wt% Surface areas: 38–76 m^2/g Micropore specific surface area: 329–402 m^2/g	- Microwave activation and catalytic pyrolysis increased surface area and cation exchange capacity of biochar. - Biochar boosted plant growth and lowered the concentration of heavy metals in contaminated soil. - Field studies should include the influence of abiotic and from the environment.	Mohamed et al. (2021)
Waste palm shell	Pyrolysis and microwave activation	45 wt%	C: 82%, H: 4%, O: 14% Surface area: 540 m^2/g Micropore surface area: 679.22 m^2/g Adsorption capacity: 595 mg/g	- Pyrolysis combined with microwave activation increased heating rate, reduced operating time, and improved the yield of biochar. - The biochar possessed desirable quality as an adsorbent to treat landfill leachate.	Lam et al. (2020a)
Coconut shell	Pyrolysis and chemical modification	–	C: 72 wt%, O: 21 wt% Surface area: 304 m^2/g Specific electrosorption capacity: 33.9–68.4 mg/g	- Incorporation of MnO_2 nanocomposites into activated biochar has improved the properties of biochar as an electrochemical material for desalination or energy storage. - This technology is energy-efficient, high recovery of effluent, ecologically friendly, and could prevent fouling problems.	Adorna et al. (2020)
Wakame (Seaweed)	Pyrolysis and chemical modification	–	C: 42%, H: 1%, O: 16% Surface area: 744.15 m^2/g Adsorption capacity: 480 mg/g	- Biochar impregnated with magnetic nickel exhibited high adsorption capacity for methylene blue, thus showing excellent potential to be used in wastewater treatment.	Yao et al. (2020)

C: carbon N: nitrogen H: hydrogen S: sulphur O: oxygen.

(–) data are not available.

activation or chemical coating to enhance the heating rate, biochar yield and biochar quality (Adorna et al., 2020; Wan Mahari et al., 2022b) (see Table 3).

3.2.1. Conventional pyrolysis

Setter et al. (2020) investigated the influence of slow pyrolysis temperature (350–450 °C at a heating rate of 0.5 °C/min) of coffee husk briquettes on the pyrolysis product distributions and quality (Setter et al., 2020). It was reported that the biochar yield decreased from 40 wt % to 34 wt%, whereas the fixed carbon content and the distribution of the pores increased over increasing temperature. These findings can be explained by the increase of the devolatilisation of the organic material at higher temperature ranges (Parvez et al., 2019). To date, slow pyrolysis has been incorporated with microwave heating (termed microwave pyrolysis) as an alternative to conventional heating. Through volumetric and internal heating, microwave radiation could increase the chemical reaction rate of biomass at lower temperatures, and in turn provide shorter residence time and high energy consumption efficiency (Mahari et al., 2021a). Parvez et al. (2019) applied pyrolysis of gumwood under different pyrolysis temperatures (600–800 °C) using conventional (e.g., heated by the furnace) and microwave heating (Parvez et al., 2019). They reported that microwave pyrolysis has better performance owing to the 13.5% higher energy efficiency and more biochar and gas yield (about 4 wt%) than conventional pyrolysis. This can be explained by the enhanced heterogeneous reactions between the gases, char and secondary cracking of oil vapours into incondensable gaseous fractions.

On the contrary, fast pyrolysis is performed at higher operating temperature ranges from 550 to 1000 °C and heating rate (≥200 °C/min) but shorter residence time (several seconds) than the slow pyrolysis. Rahbar-Shamskar et al. (2020) carried out fast pyrolysis of reed followed by activation of the produced biochar to improve the biochar properties and its application feasibility, especially for gasoline vapor recovery application (Rahbar-Shamskar et al., 2020). The study revealed that the biochar produced by fast pyrolysis followed by the zinc chloride or ammonium phosphate activation possessed micro/mesoporous structures while the phosphoric acid activation had produced microporous structures with high surface areas (497–1545 m^2/g) compared to the biochar (4 m^2/g) derived from activation-free fast pyrolysis. The micro/mesoporous structures of $ZnCl_2$ activated biochar resulted in a higher adsorption capacity of 1019 mg/g, which was 10 times higher than that shown by commercially activated carbon.

Flash pyrolysis involves heating and pyrolysis of biomass at a high-temperature range of 600–1200 °C, extremely high heating rate (>1000 °C/s), and short vapour residence time (<0.5 s), producing a small amount of biochar product (5–15 wt%) (Chen et al., 2020; Foong et al., 2020). Theoretically, the high temperature achieved within a short time allows the promotion of volatile production and secondary cracking of volatiles while hindering the volatiles re-condensation/combination with biochar, which subsequently results in the production of a high amount of gaseous product compared to biochar (Foong et al., 2020). Nonetheless, it is difficult to govern and optimise the reaction processes as flash pyrolysis is more likely to experience limited mass transfer due to inhomogeneous heat transfers (Jiang and Wei, 2019; Palumbo et al., 2019). Previous studies had reported that the particle temperatures and heating rates during flash pyrolysis were uneven and not well operated in a wire mesh reactor, leading to the discrepancy between the experimental data and model predictions for the reactor (Dufour et al., 2011), thus would bring inaccurate estimations of the simplified solid-state kinetic model of flash pyrolysis.

3.2.2. Pyrolysis combined with gas activation

Biochar could be activated by gaseous agents (e.g., air, carbon dioxide, water vapor and steam) at 700–1100 °C to improve its properties. This, in turn, removes the incomplete combustion products and other impurities from biochar while improving its porosity, surface area, surface reactivity and nutrient retention (Kazemi Shariat Panahi et al., 2020). Despite the various benefits, gas activation has difficulty in reaction temperature control along with nonuniform activation and local overheating (Kumar et al., 2020). Moreover, the gas activation reduces certain functional groups' abundance like carboxyl and phenolic groups on biochar surface. The carboxyl group (-COOH) that functions as a binding site for heavy metals could be washed out during gas activation, resulting in less oxidised biochar and ineffective metal remediation application. Similarly, the phenolic group is also prone to this process, resulting in the formation of less polar biochar (Kazemi Shariat Panahi et al., 2020).

Yek et al. (2020) produced activated orange peel biochar using CO_2 and steam activation at 700 °C (Yek et al., 2020). The steam-activated biochar showed higher surface area (305.1 m^2/g) and adsorption efficiency (136 mg/g) for Congo Red compared to CO_2-activated biochar (158.5 m^2/g, 91 mg/g) and pristine biochar (95.6 m^2/g, 0 mg/g). In another study, Kwak et al. (2019) determined the effects of feedstock type (wheat straw, canola, sawdust, and manure pellet) and steam activation on lead (II) adsorption capacity to demonstrate the potential use of biochar for heavy metal removal in water treatment (Kwak et al., 2019). The steam activation was reported to have increased the surface area (up to 1–356 m^2/g) and lead (II) adsorption capacity (41–195 mg/g) compared to pristine biochar (0.8–302 m2/g, 43–109 mg/g). The canola straw biochar was found to be the most efficient biochar for lead (II) adsorption (195 mg/g), while both steam activated sawdust biochar (41 mg/g) and non-activated sawdust biochar were less efficient for metal adsorption due to their low lead (II) adsorption capacity attributed to the low pH of the biochar.

3.2.3. Pyrolysis combined with microwave activation

Biochar can be activated using microwave irradiation operated at frequencies of 0.03–300 GHz and wavelength of 0.01–1 m and under low process temperature between 200 and 300 °C. During microwave activation, the biochar particles experience a polarization such as a dipole orientation, where the electrons that surround the atoms are displaced trillion times per second. The friction between the rotating molecules will produce thermal energy during microwave radiation (Kazemi Shariat Panahi et al., 2020). Uniform thermal energy could be internally transferred within the biomass, activating biochar and in turn providing larger surface area and more functional groups compared to non-activated biochar. These features give benefits for its application in environmental management since microwave-activated biochar could improve contaminated soil and cation exchange capacity (Mohamed et al., 2021). Mohamed et al. (2021) reported that biochar produced from microwave pyrolysis of switchgrass possessed high surface area and cation exchange capacity (Mohamed et al., 2021). As a result, the biochar not only reduced heavy metals in soil but also supplied nutrients that boosted the growth of the wheat plant. Although microwave activation is regarded as a fast and efficient heating approach (Jung et al., 2019), it is limited by the ability of biomass to absorb microwave radiation (Mahari et al., 2021b). Therefore, microwave absorbent is needed to rectify the limitation of certain biomass to absorb microwave radiation.

Lam et al. (2020a,b) developed a single-step microwave steam activation for producing biochar from waste palm shell (WPS) for application as biosorbent in hazardous landfill leachate treatment (Lam et al., 2020b). This method exhibited a high heating rate (70 °C/min), producing 45 wt% of highly microporous biochar with a surface area of 679 m^2/g. In contrast, the conventional heating approach only produced ≤12–17 wt% of biochar. They also reported that the activated biochar showed high adsorption capacity (595 mg/g), which led to 65% removal of chemical oxygen demand from landfill leachate. The finding was nearly comparable with commercial coconut shell activated carbon which has an adsorption capacity of 663 mg/g and 70% removal of chemical oxygen demand.

3.2.4. Pyrolysis combined with chemical modification

Chemical modification is a common method of chemical treatment to improve the properties and porous structure of biochar. Adorna et al. (2020) synthesised an activated biochar nanocomposite using coconut shell-derived biochar and α-MnO_2 nanocomposite via indirect co-precipitation methods (Adorna et al., 2020). During indirect co-precipitation, the biochar was firstly mixed with HNO_3 and $Mn(NO_3)_2{\cdot}4H_2O$ for 24 h, followed by mixing with $KMnO_4$ for another 24 h. The α-MnO_2 is commonly known for its excellent ion intercalation ability, thus improving the properties of as-prepared composite with a high specific surface area of 304 m^2/g, mesopore volume ratio, capacitance retention, good hydrophilicity and making it an excellent electrode material for capacitive deionization application. It was also reported that the specific capacitance (410–523 F/g) of the MnO_2--biochar nanocomposite at 5 mV s^{-1} was higher than pristine biochar (42 F/g), activated biochar (146 F/g), commercial MnO_2 (57 F/g) and lab-prepared MnO_2 (342 F/g), leading to the higher specific electrosorption capacity of 33.9–68.4 mg/g compared to MoS_2/g-C_3N_4 (24.16 mg/g), 3-D graphene (21.58 mg/g), and MnO_2/activated carbon (9.26 mg/g) (Adorna et al., 2020).

In addition, the biochar can be coated chemically with functional nanoparticles to introduce additional features to the biochar surface, improving the feasibility of biochar for various applications. For example, Hu et al. (2019) prepared a functional chitosan/biochar-nanosilver composite for improving the antibacterial purposes in drinking water purification via coating with $AgNO_3$ solution and carbonization (Hu et al., 2019). Firstly, a carbon-silver complex was prepared by dipping the corn straw in $AgNO_3$ solution for 24 h, followed by carbonization over 300–1000 °C for 1 h. Then, it was mixed with a chitosan-polyvinyl pyrrolidone solution to produce a chitosan/biochar-nanosilver composite. The introduction of chitosan could strengthen the weak bond between carbon and silver while having the ability to adsorb metal ions and inhibit the growth and reproduction of fungi, bacteria, and viruses during water treatment.

3.2.5. Gasification

Biochar can also be produced through gasification performed at high temperatures (700–900 °C) in the presence of various gaseous media, including nitrogen, air, oxygen, steam, or carbon dioxide (Kim et al., 2020). However, the gasified biochar is usually discarded from the gasification plants considering that the syngas is always the main product of interest from gasification (Ravenni et al., 2019). During gasification, the feedstock undergoes several operating steps; starting from drying, pyrolysis (e.g. char production), heterogeneous char gasification followed by homogeneous reactions (e.g. pyrolysis volatiles are subjected to reforming, cracking, and Water Gas Shift reactions) (Cortazar et al., 2020). The char gasification reactivity can be improved by increasing the heating rate and lowering the char production temperature (e.g., during the pyrolysis step). Specifically, the low temperature of the pyrolysis step at around 400 °C and char gasification of less than 1000 °C may result in optimal gasification reactivity (Tian et al., 2020).

The gasified biochar contains inorganics (e.g. alkali and alkaline earth metals originating from the feedstock) and has a higher energy yield than pyrolysed biochar, depending on the feedstock (e.g. feedstock with low O/C ratio) and operating conditions of the gasifier (Ravenni et al., 2019; Kim et al., 2020). The carbon atoms of biochar endured during the whole gasification reactions are arranged in the most stable structures and physically activated into a microporous surface with a high specific surface area. Ravenni et al. (2019) compared the properties and adsorption capacity for naphthalene between gasified biochar and steam-activated pyrolysed biochar (Ravenni et al., 2019). They found that gasified biochar had a better surface area (1253 m^2/g) and naphthalene adsorption capacity (66.7 mg/g) compared to steam-activated pyrolysed biochar (553 m^2/g, 60.5 g/g).

Nevertheless, most of the industrialized gasification technology is operated at harsh conditions (at elevated temperatures of up to 1400 °C) using entrained bed gasifier that requires high capital and operation cost (Prajitno et al., 2020). Catalytic gasification is thus opted to improve the process efficiency of conventional gasification (Kim et al., 2020). Furthermore, gasification of biomass with steam is also another attraction as it is capable of converting low-grade solid fuels into high economic value and cleaner fuel products at a higher reaction rate (2–5 times) than using conventional CO_2 while effectively removing the condensable volatiles (tar) during the pyrolysis stage, preventing tar slagging from the reactor (Tian et al., 2020).

3.2.6. Torrefaction

Torrefaction is a pyrolysis method to improve the fuel characteristics of biomass at mild temperatures ranging between 200 and 300 °C (Krysanova et al., 2019; Chen et al., 2020). During torrefaction, the biomass would undergo several chemical reactions such as dehydration, condensation, de-carbonylation, de-methoxylation, decarboxylation, aromatization and intermolecular re-arrangement (Krysanova et al., 2019). Compared to pyrolyzed biochar, torrefied biochar is richer in oxygen-containing functional groups due to the use of lower operating temperatures (Li et al., 2019). It has also been reported to have a higher energy yield (90%) compared to hydrochar (80%) (Krysanova et al., 2019).

Nonetheless, the surface morphology of torrefied biochar still needs further improvements. Krysanova et al. (2019) studied the surface morphology between torrefied biochar and carbonised biochar (Krysanova et al., 2019). It was reported that the torrefied biochar was lack of dispersed structure and tended to agglomerate with other particles compared to carbonised biochar, which contained a highly dispersed structure with microspheres. Such a structure is desirable to prevent agglomeration. This may be explained by the intensification of dehydration and decarboxylation reactions of torrefaction which strongly destroys the structural parts of biomass, hence triggering a more disassembled material structure. In addition, the carbonised biochar possessed a more dispersed structure due to the aromatisation and polymerisation of material caused by the increase in temperature and duration of hydrothermal carbonisation (Krysanova et al., 2019).

Several modifications on torrefaction have been investigated to improve the features of torrified biochar, such as the incorporation of acid hydrolysis with torrefaction. Yu et al. (2020) successfully improved the features of microalgae biochar via torrefaction incorporating with sulphuric acid (Yu et al., 2020). They found that the addition of sulphuric acid could initiate hydrolysis that could facilitate the carbohydrate and protein decomposition of microalgae at relatively low torrefaction operating temperature (160–180 °C). The obtained biochar surface has higher porosity and loopholes that could serve as binding sites for bio-adsorbent applications. In addition to porosity features, Li et al. (2019) focused on the modification of the surface complexion of biochar using oxidative torrefaction (Li et al., 2019). They investigated the corn stover-derived biochar properties produced at different thermochemical conversion technologies between conventional torrefaction (performed at 250 °C under inert condition), oxidative torrefaction (performed at 250 °C under air environment) and pyrolysis (performed at 500 °C under inert condition). It was revealed that biochar produced from oxidative torrefaction had higher oxygen content and oxygen-containing group compared to conventional torrefaction and pyrolysis. This led to the improvement of biochar properties such as surface complexion, chemisorption and uranium adsorption capacity (111.52 mg/g) compared to biochar obtained from conventional torrefaction (101.57 mg/g) and pyrolysis (56.21 mg/g).

4. Techno-economic and environmental perspectives of agriculture, aquaculture and shellfish biomass recovery

Techno-economic analysis is conducted to evaluate the economic growth and bioeconomy of the biochemicals and biomaterials production from biomasses. Capital cost, plant capacity, operational cost and raw materials are the main factors that influence the production cost of biomaterials and biochemicals. Economic indicators such as net present value (NPV), internal rate of return (IRR) and payback period are crucial to determine the economic performance and feasibility of the valorisation process to produce biochemicals and biomaterials. Table 4 summarises the techno-economic analysis of biochemicals and biomaterials production from the biomasses.

Arora et al. (2018) evaluated the techno-economic assessment of mango processing waste biorefinery. There are four stages of the pectin extraction process from mango waste, which are dissolution of proto-pectin, purification of the extract, separation of pectin from the liquid *via* precipitation, and drying of the pectin extract. It was revealed that the NPV for recovery of pectin and seed oil (41 million USD) is higher than the recovery of pectin only (14.2 million USD). NPV represents the difference between the current value of cash inflows and the present value of cash outflow (Viganó et al., 2022). The sensitivity analysis revealed that the capacity of the plant, operation time, and composition of raw materials (e.g. mango seed, mango peel) are the key aspects that influence the production cost and feasibility of the biorefinery approach to producing value-added products.

Khwanjaisakun et al. (2020) performed techno-economic assessment of vanillin production from Kraft lignin via the oxidation process. The energy consumption to produce lignin-based vanillin is higher than petroleum-based vanillin due to the high quantity of raw materials (e.g., feedstocks, solvents) needed to extract and generate lignin-based vanillin, which requires high energy to process the raw materials and remove the impurities of lignin. Hence, further studies should investigate the improved separation and purification techniques that consume a lower amount of raw materials (e.g., solvents) and energy during lignin-based vanillin production. Despite the high energy consumption to produce lignin-based vanillin, the cost of Kraft lignin is significantly cheaper than raw materials to produce petroleum-based vanillin, such as glyoxylic acid and guaiacol. Therefore, the production of lignin-based vanillin is more economical as compared to petroleum-based vanillin.

Thompson et al. (2021) compared the techno-economic assessment of furfural production from sugar beet pulp using pyrolysis and hydrolysis techniques. It was found that the production cost of furfural using pyrolysis (846 USD/metric ton) is lower than that obtained using hydrolysis (980 USD/metric ton). This is due to the high operational cost of hydrolysis, which consumes a large volume of water and high energy/electricity to heat the water. The production of furfural using pyrolysis has significantly lower environmental impacts by releasing lower greenhouse gas (267 kg CO_2 eq./metric ton) compared to hydrolysis (1095 kg CO_2 eq./metric ton). This study also suggests that portable pyrolysis operations close to biomass collection sites can significantly reduce the operating and variable costs as well as greenhouse gas emissions, which lead to sustainable furfural production.

In the shellfish and aquaculture industries, Gómez-Ríos et al. (2017) investigated the techno-economic assessment of chitosan production from the shrimp shell. There were two approaches used in the study, which are the physical-chemical method combined with chemical deacetylation (PC-CDA) and the fermentative physical-chemical method combined with chemical deacetylation (FPC-CDA). It was found that FPC-CDA requires lower energy consumption, water usage and chemicals (e.g., sodium hydroxide) compared to the PC-CDA process. Nevertheless, FPC-CDA demands bigger space which contributes to the increase of investment in fixed assets up to 15% compared to the PC-CDA process. Interestingly, the NPV and IRR values for chitosan

Table 4
Techno-economic assessment for biochemicals and biomaterials production from biomasses using various valorisation technologies.

Source of biomass	Valorisation technologies	Product	Capacity	Remarks	References
Mango	Extraction	Pectin	10 tons/h	Capital cost: 23.2 USD Operational cost: 6.99 million USD Net present value: 14.2 USD Internal rate of return: 20% Payback period: 4.2 years	Arora et al. (2018)
Kraft lignin	Oxidation, Extraction	Vanillin	30–120 g/L	Highest yield of vanillin: 9.25% Payback period: 6.19 years Internal rate of return: 22.6%. Greenhouse gas emission: 134–155 kg CO_2/hr	Khwanjaisakun et al. (2020)
Sugar beet pulp	Pyrolysis	Furfural	4592 ton/year	Production cost: 846 USD/ton Greenhouse gas emission: 267 kg CO_2 eq.	Thompson et al. (2021)
Sugar beet pulp	Hydrolysis	Furfural	6560 ton/year	Production cost: 980 USD/ton Greenhouse gas emission: 1095 kg CO_2 eq.	Thompson et al. (2021)
Shrimp waste	PC-CDA	Chitosan	–	Capital cost: 0.7865 million USD Net present value: 0.4977 million USD Internal rate of return: 26.6% Payback period: 5 years Gross margin: 68%	Gómez-Ríos et al. (2017)
Shrimp waste	FPC-CDA	Chitosan	–	Capital cost: 0.9166 million USD Net present value: 0.4789 million USD Internal rate of return: 24.4% Payback period: 6 years Gross margin: 71%	Gómez-Ríos et al. (2017)
Acai by-products	Pressurised liquid extraction	Phenolic	500 L	Gross margin: 84% Return of investment: 145% Net present value at 7% interest: 175 USD x 10^6 Internal rate of return: 325% Revenues: 41 USD/year x 10^6	Viganó et al. (2022)
Orchard waste	Pyrolysis	Biochar	–	Total fixed and variable costs: 1542.16 USD Production cost: 449 to 1845 USD/Mg of biochar	Nematian et al. (2021)
Oil palm empty fruit bunch	Pyrolysis	Biochar	4800 ton/year	Greenhouse gas emission: 0.046 kg CO_2 eq./year Production cost: 524 USD/year Net present value: 123 USD Payback period: 10 years Internal rate of return: 8.96%	Harsono et al. (2013)

PC-CDA: Physical-chemical method and chemical deacetylation.
FPC-CDA: Fermentative physical-chemical method and chemical deacetylation.
(−) data are not available.

production by the PC-CDA process are higher than the FPC-CDA process, thus more economically feasible. This study also revealed that the cost of raw materials, processing time and investments for assets greatly influence the quality and production cost of chitosan. There are several factors that affect the quality of chitosan, such as water solubility, deacetylation degree, and mineral and protein content.

Andreasi Bassi et al. (2021) studied the economic feasibility and environmental impacts of PHA production from food waste and sewage sludge. It was found that PHA produced from urban biowaste has lower environmental impacts and production costs compared to the PHA produced from first-generation biomass (e.g., maize, sugarcane) and polyurethane. Nevertheless, the production cost of PHA is significantly higher than petroleum-based polymers (conventional plastics) due to the use of expensive raw materials as carbon substrate and chemicals during the extraction process. Recently, Wan Mahari et al. (2022a) reported that liquid oil derived from microwave co-pyrolysis of plastic waste and used cooking oil can be used as carbon substrate to generate bioplastics. The use of wastes during microbial fermentation could replace the use of expensive raw materials as carbon substrate, which may reduce the production cost of PHA. However, more research on optimisation and techno-economic assessment should be done to validate the feasibility of this approach.

In Brazil, Viganó et al. (2022) evaluated the techno-economic analysis of phenolic compounds extraction from acai (*Euterpe oleracea*) by-products (i.e., seed and fibers). Extraction vessels with different capacities such as 50 L, 200 L and 500 L were used in the assessment. Long extraction time increased the cost of manufacturing due to the high consumption of solvents and raw materials. Interestingly, the use of a larger capacity extraction vessel (500 L) shows a higher value of gross margin, return of investment, net present value, internal rate of return and revenue compared to a smaller capacity extraction vessel (50 L), thus showing the profitability and potential of this technique to be upscaled. The payback period of the 500 L extraction vessel is also shorter compared to the 50 L extraction vessel, which indicates faster recovery of the initial investment cost. This techno-economic evaluation from this study suggests that large-scale pressurised liquid extraction of acai seed and fibers could reduce the cost of manufacturing and produce high profit, thus can be applied in biorefinery plants to produce phenolic compounds with antioxidant properties.

In the United States of America, there are several financial incentives to encourage the production of biochar, such as non-financial policy support, loans, as well as research and innovation fund. Nematian et al. (2021) reported techno-economic assessment of biochar production from orchard waste using pyrolysis in California. The total fixed and variable costs are approximately 1542 USD, which includes the cost of processing equipment, machinery, storage facility, raw materials (e.g., lubricants, fuels), labour and miscellaneous (e.g., disposal of waste). The estimated production cost to produce biochar ranges from 449 to 1845 USD/Mg of biochar, which is economically feasible due to the low cost of biomass waste. In another study, Harsono et al. (2013) reported a high and positive NPV, which indicates biochar production from oil palm waste is economically profitable. The techno-economic assessment from this study provides essential information to minimise risks associated with biochar production from agricultural biomass. This finding also encourages the circular bioeconomy concept that recovers useful biomaterials from agricultural waste.

5. Conclusion and outlooks

Biomass is an abundant source of renewable energy and sustainable material production. This review reveals that agriculture, aquaculture, and shellfish biomass possess unique and desirable properties which make them suitable to be converted into value-added products (e.g., biochemicals and biomaterials) *via* various valorisation techniques. The following conclusions and outlooks could be drawn from this review:

1. Biorefinery of biomass and biowaste is a reliable approach to reduce the volume of waste while sustaining the production of new products with high added value.
2. Polysaccharides are the main compound present in biomass and biowaste, including food wastes, agricultural residues, and marine aquaculture by-products. Biomasses contain polysaccharides that can be converted into biopolymer (e.g., pectin, furfural, vanillin) for use in many applications (e.g., pharmaceuticals, cosmetics, agricultural).
3. Bioactive compounds such as phenolic can be extracted from food waste and agricultural residues for use in the pharmaceutical and food processing industries.
4. Biomasses can be converted into bioplastics *via* chemical treatment (e.g., chemical coating) and biological treatment (e.g., fermentation).
5. Bioplastics synthesised by biomass is cheaper than that synthesised by microorganisms. The bioplastics synthesised from biomass could reduce dependency on petrochemicals as plastic sources.
6. Pyrolysis can be mixed with various modification techniques such as gas activation, microwave activation and chemical coating to enhance the pyrolysis performance and properties of biochar.
7. Newly developed microwave steam activation and gasification show great promise to produce biochar with high surface area and adsorption capacity compared to other valorisation techniques.
8. The production of biochemicals and biomaterials from biomass sources is economically feasible due to the low cost of raw materials.
9. The challenge is to maintain or improve the performance of the valorisation technologies to ensure a better quality of biochemicals and biomaterials production as compared to fossil-based products.
10. The biomass sources must be adequate and sustainable to manage the demand to produce bioproducts to be applied in many sectors.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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