

MODIFICATION AND PERFORMANCES OF TiO₂ PHOTOCATALYST TOWARDS DEGRADATION OF PARAQUAT DICHLORIDE

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Abstract: Titanium dioxide, TiO₂ nanostructured has been synthesised by microemulsion technique under controlled hydrolysis of titanium butoxide, Ti(O(CH₂)₃)CH₃ in hexadecyltrimethyl ammonium bromide, HTAB in the form of nanodroplets microemulsion. The physical and chemical properties of synthesised TiO₂ have been determined by using SEM, XRD, BET and photocatalytic activity. In order to measure its catalytic performance, the synthesised TiO₂ is used as catalyst to decompose paraquat dichloride when exposed to UV bench lamp 302 nm 230 V~50 Hz. The result indicates that paraquat dichloride is degraded by 70% within 4 hours. The optimum catalytic properties enable to demonstrate TiO₂ nanostructured has good behaviour to photocatalytically degrade paraquat dichloride to relatively safe and tolerable compounds in the environment.

KEYWORDS: TiO₂, microemulsion, photodegradation, paraquat dichloride.

Introduction

Among various oxide semiconductors, TiO₂ has attracted great deal of importance as a photocatalyst due to its novel properties. TiO₂ nanostructure is considered to be one of the most promising materials due to its unique properties, such as excellent physicochemical stability under extreme conditions (Hashimoto and Fujishima, 2005) (Wu and Zhang, 2004), mechanical hardness (Lu *et al.*, 2008), high refraction index (Li *et al.*, 2009) nontoxicity (Wilhelm and Stephan, 2007), ease of preparation in the laboratory (Murugesan *et al.*, 2007) (Pu *et al.*, 2007) and low production costs (Lu *et al.*, 2008) (Pu *et al.*, 2007). Furthermore, it has become more interesting as its absorption spectrum overlaps with the solar spectrum and hence opens up the possibility of using solar energy as the source of irradiation that has greater band gap energy than TiO₂ (approximately 3.2 eV or 320 nm light) (Hong *et al.*, 2005) (Nguyen *et al.*, 2007) (Štengl *et al.*, 2006).

TiO₂ has attracted a great deal of attention due to its wide applications such as solar energy conversion (Yoshida *et al.*, 2008), photovoltaic cells (Grätzel, 2001) (Keshmiri *et al.*, 2004) (Kim and Kim, 2005), antibacterial (Zhang

et al., 2003), and purification of hazardous compounds in polluted water and air (An *et al.*, 2007) (Liu and Chen 2008) (Wu and Zhang, 2004). However, among TiO₂ nanomaterial applications, TiO₂ photocatalyst has attracted most attention of the researchers, because of its utility in the removal of NO_x and gaseous elements (Wu *et al.*, 2008), environmental purification processes, such as water purification and decomposition of pollutant (Liu and Chen, 2008) (Nguyen *et al.*, 2007), catalytic reactions for hydrogen generation (Nowotny *et al.*, 2007) and in making of electrodes for dye-sensitizing solar batteries (Yoshida *et al.*, 2008).

To date, researchers have carried out investigations and have appreciated the photocatalyst process as a great mechanism to degrade several organic pesticides (Burrow *et al.*, 2002) (Zhanqi *et al.*, 2007), surfactants (Zhang *et al.*, 2004), and hazardous gasses (Wu *et al.*, 2008). These studies have proven that photocatalysis is a superior and preferable method to treat environmental pollution rather than absorption, biological treatment and chemical oxidation process. Therefore, TiO₂ photocatalyst has attracted great attention as a promising photocatalyst for photocatalytically

degrading organic pollutants. However, preparation method has great influence on morphology, particle size and specific surface area.

To date, several researchers have reported numerous specific methods to synthesise TiO₂ including chemical treatment (Kluson *et al.*, 2007) (Yu *et al.*, 2007), sol gel (Chang *et al.*, 2010), chemical vapour deposition, CVD (Kitano *et al.*, 2007) and hydrothermal treatment (Lee *et al.*, 2005a), as most common methods used to synthesise TiO₂. However, these methods suffer several problems namely high-temperature processing, long aging time, grain growth, non-economic favourable and extremely vigorous stirring (Lee *et al.*, 2005b) (Zhang and Gao, 2002). For sol-gel method is rarely used due to high costs as required in the preparation steps (Li Puma *et al.*, 2008). Furthermore, sol-gel processing technique will exhibit high shrinkage of product, even film or monolith during drying and heat treatment (Keshmiri *et al.*, 2004). Whereas, CVD process exposed to a single or multi component volatile precursor in gaseous phase has been oxidized at very high temperatures to prepare nanosized TiO₂ (Mohapatra *et al.*, 2006). In addition, CVD process is also sensitive to flow of suitable gases during the oxidized reaction. Thus, in this method it is more difficult to remove the by-products which are generated during this process.

Therefore, microemulsions method is acceptable as the best method to synthesise crystalline nanosized TiO₂ powder in the last two decades. Microemulsion process has lots of advantages in obtaining nanosized particles and becomes the most favourable method by most researchers (Mohapatra *et al.*, 2006) (Pu *et al.*, 2007). Microemulsion method has been employed to synthesise nanometer-sized particles of a variety of nanoparticle species such as BaCO₃ (Rajput *et al.*, 2009), gold (Li *et al.*, 2005), BaMoO₄ (Pal *et al.*, 2009), Platinum (Deorsola and Valluri, 2009) and TiO₂ (Wu *et al.*, 2002).

Due to the excellent ability of TiO₂ proven to degrade organic compounds, an investigation is carried out in this study to determine the photocatalytic properties and behaviour of

this compound to degrade paraquat dichloride, IUPAC name 1, 1'-dimethyl-4, 4'-bipyridinium dichloride. This pesticide is widely studied as it has been used as one of the herbicides of choice worldwide. It acts by interfering with photosynthesis process through increasing light intensity and humidity at leaf surface. Basically, paraquat dichloride consists of two pyridinium rings, which refers to the cationic form of pyridine such as shown in Figure 1 below.

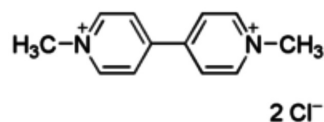


Figure 1: Molecular structure of paraquat dichloride.

Paraquat dichloride is always attributed to active compound for several commercial herbicides, which cause fatal intoxication in both humans and animals. In addition, paraquat dichloride has presented itself as an environment pollutant both in soil and sources of fresh water. Several methods were used to manage the disposal of paraquat dichloride such as adsorption and purification by degrading the chemical compound to simple compounds (Rusmidah and Siti Habsah, 2008).

Therefore, the present study is aimed to synthesise high performance TiO₂ catalysis by using micro-emulsion method. This method has promising properties using nanostructured TiO₂ and may have capacity to decompose paraquat dichloride to several harmless compounds in the environment.

Experimental

Catalysis Preparation

TiO₂ nanoparticles were prepared according to 6:3:1 proportion as carried out in previous studies (Komarneni and Katsuki, 2010). The microemulsions A and B consist of 60 ml cyclohexane (Hamburg Chemical) as oil phase and 30 ml Hexatrimethyl Ammonium Bromide, HTAB (Sigma - Aldrich). As starting material, 10 ml of titanium (IV) butoxide, Ti(O(CH₂)₃)CH₃ (purity 97%, Sigma-Aldrich) was added in microemulsion A, meanwhile 10

ml of ammonium hydroxide solution, NH_4OH (Mallinckrodt) 2 M as reducing agent in reagent B. After 30 minutes of stirring separately, both microemulsions were mixed in a beaker and stirred for 4 hours before vibrated homogeneously in ultrasonicator (JAC Ultrasonic Cleaner, JAC 2010, 240~50Hz/30 A) for 1 hour. This step was carried out to prevent the agglomeration of TiO_2 pigment in water.

Then, 10 ml of 5 M solution of sodium chloride, NaCl (Merck Schuchardt) was added to microemulsions, vibrated in ultrasonicator for another 1 hour to ensure the mixture was completely mixed. The microemulsion, was washed with 30 ml acetone before the product was annealed (Nabertherm, HTC 08/16, 400 V, 50/60 Hz) at 600 °C for 4 hours. The powders obtained were washed with distilled water and acetone to remove the remaining NaCl, followed by drying in oven at *ca.* 90°C overnight to remove excess water.

Catalysis Characterisation

The physical properties of the TiO_2 synthesised by varying their HTAB concentration were characterized by Scanning Electron Microscopy, SEM (JEOL JSM-6360 LA). Meanwhile, the obtained TiO_2 powders was determined by X-Ray Diffraction, XRD (Rigaku, Miniflex II Desktop X-Ray Diffractometer). Nitrogen adsorption/desorption isotherms by Brunauer-Emmett-Teller (BET) method was carried out by using Quantasorb (Quantachrome Autosorb Automated Gas Sorption) to determine the specific surface area. The samples were degassed by liquid nitrogen at 150°C for 15 hours.

Catalytic Activity

The general procedures for catalytic activity for synthesised TiO_2 were carried out according to the previous study (Narayanan *et al.*, 2009). The photocatalytic degradation of paraquat dichloride was performed with 100 ml aqueous solution of paraquat dichloride (1.0×10^{-4} mg/l) (Sigma-Aldrich) and 0.1 g of synthesised TiO_2 catalyst. The degradation mixture were stirred magnetically and irradiated by UV-light (302 nm, 230 V~50 Hz) for 1 hour to ensure their optimum thermodynamic stability. Every 5 ml of

the aqueous suspension was collected at each 30 minutes interval during the irradiation and then was filtered on 0.10 μm Milipore syringe filter (Whatman) to remove the catalyst. The samples were exposed for 4 hours under UV-light and analyzed by using UV-Vis spectrophotometer (UV-1601 PC, UV-Visible Spectrophotometer Shidmadzu) for the percentages of degradation determination.

Results and Discussion

Modified Catalyst

In this study, SEM was used to observe the morphology of synthesised TiO_2 photocatalysis prepared by microemulsion method. Synthesised TiO_2 nanoparticles yielded less agglomerate spherical particles with dimensions in the range between 60-100 nm. This physical behaviour of nanoparticles is due to suitability and ideal choice of emulsifier or so called surfactant content in the micro emulsion. The morphological surface of synthesised TiO_2 nanoparticles observed in SEM is shown in Figure 2.

An appropriate emulsifier content is efficiently required to hinder the coalescence of the nanodroplets, thus it allows the formation of small and less aggregate TiO_2 particles during precipitation such as suggested by Deorsola and Vallauri (2009). Thus in this study, 0.5 M of HTAB is considered as an appropriate concentration of surfactant in microemulsion to synthesise TiO_2 nanoparticles as suggested by Wang and his co-workers (2004). On the other hand, an excessive content of surfactant in microemulsion should be avoided as it will show tendency to inhibit the interchange among nanodroplets which is vital in the formation of stable nanoparticles.

The stirring duration of microemulsion is another factor which should be considered in order to yield TiO_2 nanoparticles at an optimum level. It is known that a vigorous mixing favours the formation of droplets with smaller dimensions which leads to produce small sized spheres. In this study, when microemulsion was continuously stirred at constant rate (100 rpm) 4 hours, the morphology of nanoparticles gradually became spherical shaped as shown in Figure 2B.

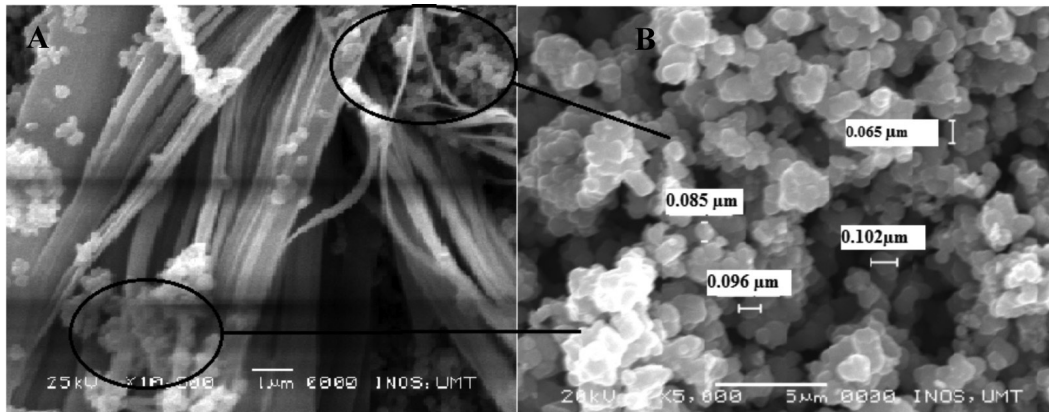


Figure 2: SEM micrographs of synthesised TiO₂ prepared by microemulsion method under controlled hydrolysis of titanium butoxide, calcined at 600° C.

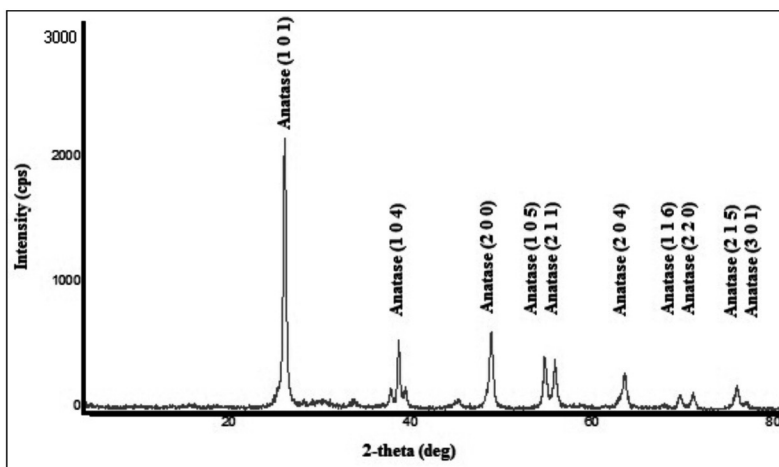


Figure 3: XRD spectrum of synthesised TiO₂ nanoparticles by microemulsion method at pH 9 and calcined at 600°C for 4 hours.

This finding is supported by a previous study, which stated that stirring at constant rate had led to well-dispersed and smaller crystals. The obtained sample is characterised by using XRD spectroscopy as well as in order to investigate crystallite study in further details.

Crystal Structure

In this study, XRD spectrum of synthesised TiO₂ sample has shown good crystallinity. The characteristic peaks at 25.3, 37.8, 48.1, 53.9 and 55.1 (two-theta) degrees were recognized, corresponding to the *hkl* Miller indices (101), (004), (200), (105) and (211) respectively. The

resulted XRD pattern of the synthesised TiO₂ is shown in Figure 3.

From the observation, these peaks of synthesised TiO₂ nanostructures are attributed to the crystalline phase anatase-TiO₂ (PDF Card No: 00-021-1272). The diffraction peaks of synthesised TiO₂ observed are sharp and narrower which indicate an increase of the crystallinity. Meanwhile, the average particles size of synthesised TiO₂ was determined by Scherrer equation (Yu *et al.*, 2006), which is $d=0.89\lambda/B(2\theta)\cos \theta$, where $B(2\theta)$ is the width of the XRD peak at half peak-height in radians, λ is the wavelength of the X-ray in nanometers

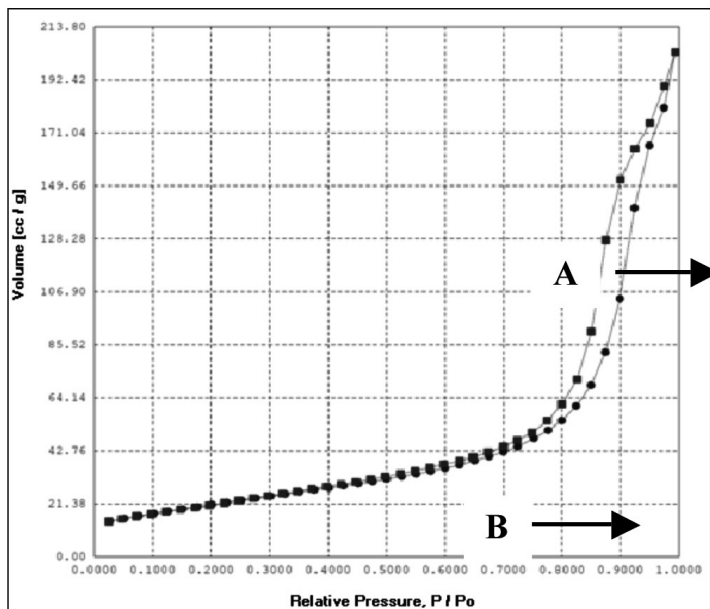


Figure 4: Nitrogen adsorption/desorption isotherms of TiO₂ nanostructures synthesised via microemulsion method and calcined at 600°C.

($\lambda=0.154$), θ is the angle between the incident and diffracted beam in degrees and d is the average particles size of the obtained TiO₂ sample in nanometers. Thus, the calculated crystallite size of TiO₂ nanoparticles synthesised via microemulsion method is 24.25 nm. This result indicates the nano scale formation of TiO₂ successfully synthesised via microemulsion method under controlled of pH value at 9 and calcined at 600 °C for 4 hours.

Surface Area Study

The specific surface area of the obtained TiO₂ was measured using the BET method by N₂ adsorption and desorption at 77.3 K. In this study, the specific surface area of synthesised TiO₂ is measured at 76.6 m²g⁻¹. The measurement of the amount of adsorbed nitrogen gas over a range of partial pressures at a single temperature is presented in a graph known as an adsorption isotherm. Figure 4 shows the nitrogen adsorption/desorption isotherms of synthesised TiO₂ nanostructures.

According to the IUPAC classification for adsorption isotherm, Brunauer, Deming, Deming and Teller (BDDT), the synthesised TiO₂ adsorption isotherm is type IV which has two hysteresis loops. Both of hysteresis loops indicated by **A** and **B** above show that desorption occurred in the bimodal pore size distribution in the mesoporous (2-50 nm) region. In this study, adsorption is believed to take place in the high relative pressure regions which are approximately at 0.8 and 0.9 P/Po. This hysteresis loop occurs because most of the structures have larger pore cavities in diameter. As a result, this finding agrees with pore size of synthesised TiO₂ which recorded at 164 Å, whereas the pore volume is 0.3 cm³g⁻¹. This result, we strongly believe, is due to the main reason of paraquat dichloride was not degrading completely in this study. Thus, the limited specific surface area plays significant role to act as adsorption surface to reduce molecular oxygen on the Ti (III) sites to the superoxide radical anion in order to decompose paraquat dichloride (Lu *et al.*, 2008) (Murugesan *et al.*, 2007).

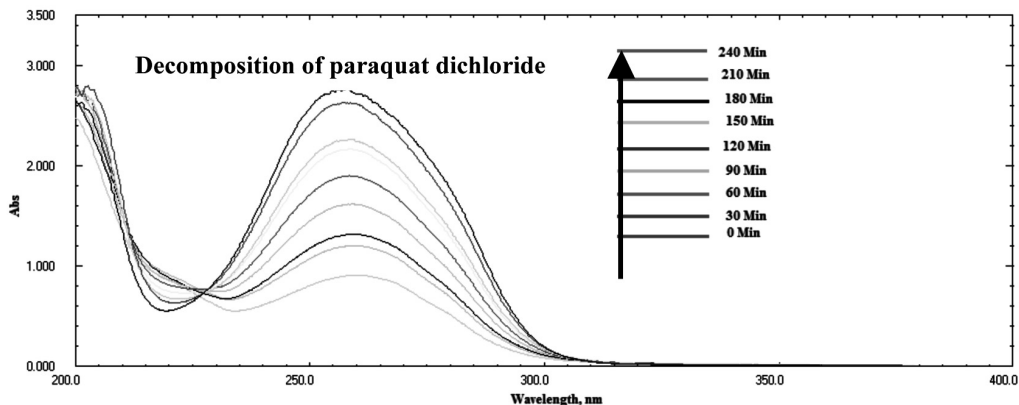


Figure 5: UV-visible spectra of 1.0 x10⁻⁴ mg/paraquat dichloride treated with photocatalytic degradation for 240 minutes and exposed with UV-light (302 nm, 230 V~50 Hz).

Catalytic Activity

The photocatalytic activity of synthesised TiO₂ was determined by measuring the decomposition of prepared 1.0 x10⁻⁴ mg/l of paraquat dichloride. This photocatalytic reaction was carried out in a glass reactor and exposed to UV-lamp for 4 hours in the presence of the synthesised TiO₂. The absorption peak for paraquat dichloride in this study was found to be similar with previous study, which is at λ=258 nm (Górska *et al.*, 2008). The black arrow in Figure 5 indicates the increasing of decomposition of paraquat dichloride with the increasing time of UV-light exposure.

Table 1 shows the values of degradation measured by UV-Spectroscopy after 240 minutes. These values show the decreasing of absorbance with time when paraquat solution was exposed to the UV-light increased with the presence of synthesised TiO₂. In this study, distilled water was used as blank solution as comparison during the perform of UV-spectroscopy analysis.

In order to determine the percentage of paraquat dichloride degradation, the samples were analysed by mathematical equation as expressed by equation 1.0 below:

Percentages of degradation (%)
 = (A₀/A_t) x 100 % (equation 1.0)

Where:

A₀ = Initial absorption

A_t = Absorption at t time

Table 1: Degradation results of paraquat dichloride measured by UV-spectroscopy after 240 min in the presence of synthesised TiO₂.

Samples No.	Time exposed to UV-light, min	Wavelength, nm	Absorbance, abs
1	Blank	257.8	2.7075
2	30	257.8	2.6243
3	60	257.8	2.2531
4	90	257.8	2.1589
5	120	257.8	1.8981
6	150	257.8	1.6143
7	180	257.8	1.3141
8	210	257.8	1.1995
9	240	257.8	0.9031

The percentage of photocatalytic degradation of paraquat dichloride in the presence of synthesised TiO₂ nanostructures is shown in Figure 6. In this study, 70 % of paraquat was successfully decomposed by synthesised TiO₂. This synthesised TiO₂ nanostructures has enhanced the performance of paraquat dichloride degradation due to the fact that, preparation method of this photocatalyst via microemulsion method has effectively helped to obtain pure anatase crystal structure, with high active surface area. Indeed, anatase phase produces high performance of degradation as reported by previous researchers (Chen *et al.*, 2003) (Lu *et al.*, 2008). In addition, the TiO₂ nanostructures prepared by microemulsion method have perfect

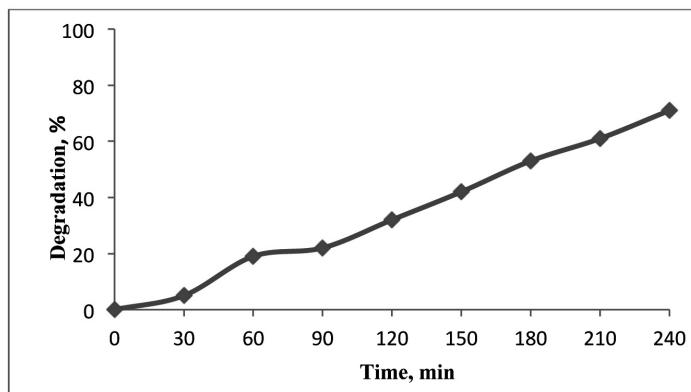


Figure 6: Percentages of photocatalytic degradation of 1.0×10^{-4} mg/l of paraquat dichloride for 4 hours exposed with UV-light (302 nm, 230 V~50 Hz).

Table 2: Physical properties and catalytic activities of synthesised of TiO_2 synthesised by microemulsion method and calcined at 600°C .

Samples	Particles size (nm)	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (\AA)	Crystallite phase	Degradation (%)
TiO_2	24.25	76.66	0.3	164	Anatase	70

crystal lattice that can be assigned as planes of anatase respectively. Thus, this give great influence on their photocatalytic activity.

Furthermore, photocatalytic activity is improved and enhanced by considering the concentration of surfactant (Awitor *et al.*, 2008) (Dhoudi and Adhoum, 2009), pH of microemulsion solution (Zhou *et al.*, 2008) and calcination temperature (Jahromi *et al.*, 2009). Hence, the physical properties and photocatalytic activity of modified TiO_2 nanostructures towards paraquat dichloride is summarised in Table 2.

Conclusion

The microemulsion method is a promising method to synthesise high performance TiO_2 photocatalyst which yields the size of particles up to 24.5 nm. The synthesised TiO_2 nanostructures are efficiently exhibited by pure anatase crystal structure with perfect crystal lattice and less agglomeration which serves as active sites for photocatalytic activity. The highly active surface area including pore volume and pore size has

contributed to the great performance to degrade 70% of paraquat dichloride. This promising result will trigger further studies to develop improved methods to reduce it hazards in the environment, in respect of the determination of molecules that are formed during the degradation process aided by TiO_2 prepared via microemulsion method.

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