*Journal of Sustainability Science and Management 2007 Volume* 2 (2): 64-74

# REMOVAL OF PETROLEUM HYDROCARBONS IN SEAWATER USING A MIXED ADSORBENT OF COCONUT HUSKS AND SHRIMP SHELLS

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**Abstract :** The removal of dissolved petroleum hydrocarbons in seawater was evaluated by using coconut husks and shrimp shells as the adsorbents. The experiments were conducted at a temperature of 30 °C, salinity 30 g/l, pH 8 and dissolved oxygen > 6 ppm using the column experiments. The 10 ppm water-soluble fraction (WSF) of the Malaysian crude oil was used for the study. The adsorption kinetic studies were studied by applying the Freundlich Isotherms Equation. The adsorption kinetics of hydrocarbons by coconuts and shrimp shells followed the first order kinetic with Adsorption Capacity ($K_F$) values of 0.408±0.004, and 0.407±0.006 respectively. The maximum adsorptions of the above adsorbents were 1.81 and 1.57mg hydrocarbons/g respectively. Treatment techniques are attempted to use the above adsorbents for removing hydrocarbon residues in seawater. Both of them possess surprisingly high effectiveness in removing dissolved hydrocarbons in seawater to level below 50 ppb. Both adsorbent exhibits its characteristics and selectivity in adsorbing the aliphatic and aromatic hydrocarbons present in seawater. A combination of coconut husks and shrimp shells is able to reduce the oil in seawater from 10 ppm to 0.0257 ppm. The bioassay study using *P. monodon* post-larvae as test organism supports the success of this treatment technique.

KEYWORDS: Treatment, hydrocarbons, adsorbents, seawater, toxicity.

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## Introduction

Malacca Straits is a major international shipping route in the world. With the increasing vessel traffic, the risk of oil pollution caused by vessel accidents and operational discharges is increasing (Chua et al., 2000). Crude oil especially its water-soluble fraction is highly toxic to marine organisms. A summary of the toxicity of crude oil and its constituents indicate that the 96h$LC_{50}$ value for marine organisms is in the range between 1 and 20 ppm.(UNEP, 1992). The safety level recommended for tropical organisms is below 50 ppb (Law and Hii, 2006). The present level of oil contamination in the Straits of Malacca is between 150 and 300 ppb oil in water and 70-100 ppm in sediment (Law & Hii, 2006). Toxicological studies reveal that this sub-lethal level of oil in seawater has posed some chronic effects on growth and hatching rate of shrimps (Law, 1997).

Fish consumption per capita in Malaysia is forecasted to increase from 39 kg person$^{-1}$yr$^{-1}$ in 1995 to 55 kg person$^{-1}$yr$^{-1}$ by 2010 (Rosly, 2002). The demands for fish and fish products is estimated to be 1.56 million metric tones in 2010, while the present landing is at about 1 million metric tones per year. Statistical analysis shows that the present fish landing from the Malaysian seas has reached the maximum level. We do not anticipate that the increase of landing can meet our nation's fish protein demand. As such, our optimistic hope of meeting the fish protein demand is

from aquaculture especially the marine culture. The success of aquaculture depends on many factors especially on providing the healthy flies for hatchery operation and clean water for culturing (Yap, 2002). Straits of Malacca is vulnerable to oil pollution. The aquaculture activities need a lot of seawater for culturing and for husbandry activities. Technologies are developing for removing the toxic and carcinogenic hydrocarbons in seawater for successful aquaculture operation. The large amount of inorganic salts in seawater has rendered the failure of this technology development.

In our laboratory, we have successfully removed the trace amount of aliphatic and aromatic hydrocarbons in seawater using some of the locally available adsorbents. The oil contaminated seawater after treatment with these adsorbents has been proved safe for organisms using the bioassay technique. The treated seawater will be free from hydrocarbons contamination. More healthy larvae of shrimps will be produced and better growth of shrimps will be expected using this treatment technique for husbandry operation.

## Materials and methods

### Methods:

The adsorbents for the experiments were prepared as follows. Coconut husks were cut into small pieces, dried overnight in an oven at 100 °C. The dried substrates were grounded by using a blender and sieved to a size range between 0.3 mm and 0.85 mm using the successive sieving method. The sieved substrates were boiled in distilled water for half an hour to remove the color and then treated with 1.5 N NaOH and then with 2 N $HNO_3$ until the substrates were neutral in pH. Finally, the treated substrates were dried overnight in an oven at 100 °C before use.

The shrimp shells were washed to remove sand and dirt particles. The shrimp shells were grounded to small pieces and the grounded shrimp shells were sieved in a size 0.5 mm using the successive sieving method. The organic content in the shrimp shell were removed and formed the chitin. Shrimp shells were treated with acid (1.25 N HCl) for demineralization or removal of $CaCO_3$ and then with alkali (40% NaOH) to remove the protein. The chitin was deacetylated using hot alkali to form chitosan. Finally the remaining water was drained off and the shrimp shells were dried at 60 °C in an oven for overnight (Infofish, 1991).

The Granular Activated Carbon (GAC) was purchased from a local manufacture company. The water-soluble fraction (WSF) of the Malaysian Tapis Blend Crude Oil was used as the adsorbate for this study. Preparation of WSF oil in seawater followed the method of Law and Shazili (1995). Briefly, 50 ml of the crude oil was mixed gently with 450 ml of seawater (salinity 30 g/L) in a 1-liter conical flask for 20 hours at room temperature (30 °C). Thereafter, oil and water phases were allowed to separate for 1 - 2 hours before the water phase was siphoned off and used immediately for experiment. This gave a stock solution of 100 % WSF solution at salinity of 30 g/L for preparing the desired WSF oil level in seawater for experiments. The actual WSF oil level in the testing solutions was estimated by using the Luminescence Spectrophotometer (Perkin Elmer Model LS 55) at 310 nm excitation and 374 nm emission (Law, 1997). Briefly, 80 ml of the water sample was added to 20 ml of n-hexane in a volumetric flask (Merck). The solution was shaken and its oil concentration was determined based on the crude oil standard curve. The standard used for the calibration was prepared from the same crude oil dissolved in n-hexane. The water-soluble fraction (WSF) of the Malaysian Tapis Blend Crude Oil was prepared fresh prior to the experiment.

**Total petroleum hydrocarbons analysis:**

Total petroleum hydrocarbons in seawater after treatment with absorbent were determined using the Turner Portable Fluorometer (AU 10 Turner) and also the GC-FID techniques. Standardization of the Fluorometer was performed using a series of standard solution prepared from the 100% WSF oil stock solution. The standard solutions used for the standardization were 100, 200, 300, 400 ppb and a control (blank seawater). The oil concentration in water sample was determined directly with the Fluorometer without solvent extraction.

The quantitative and qualitative of petroleum hydrocarbons in water sample before and after treatment with absorbents are also determined using the GC-FID technique after the extraction and purification methods of UNEP (1992). A GC-FID (HP 6890) equipped with a 30-meters of capillary column (5% phenyl methyl silicone) was used for this analysis. Recovery of the spiked surrogate standard (9,10 Dihydroanthracene for PAHs and n-Octadecene for saturated hydrocarbons) was used to correct losses due to extraction and clean-up procedure. The percentage recoveries of these internal standards were 88.7% and 82.5% respectively.

**Kinetic studies:**

The apparent adsorption of WSF oil on adsorbent was determined as follows. Briefly, 3-50 g of adsorbent was mixed with 1 L of freshly prepared (10 ppm) WSF oil seawater in a 1-liter conical flask placed in a rack mounted on a horizontal platform shaker with the shaking speed at 250 rpm. Oil concentration in seawater was determined by using the Turner Portable Fluorometer at 5 min, 15 min, 30 min, 1 hour, 2 hours and so on until the oil level in water reached equilibrium. The maximum capacity adsorption of WSF oil, the adsorption constant, $K_F$ and the order of reaction, n, were determined by using the Freundlich Isotherm Adsorption Equation (Nicholas and Paul, 1993).

The packed column studies were conducted using a polyethylene tube of 6 cm internal diameter and 60 cm height. Cotton wool was placed at the bottom and top of the adsorbent to prevent leakage of the adsorbent. 500 grams of adsorbent alone (or a mixture) was used for each experiment. The packed column was then fed with 1 liter of 10 ppm WSF oil and the effluent was collected after the seawater was filtered through the column at a specific flow rate with a peristaltic pump. The WSF oil level in the pretreated seawater and collected effluent were determined using the portable Turner Fluorometer (U-10 model). The flow rate, which gave the maximum efficiency adsorption of WSF oil in the packed column, was evaluated and used for the rest of the studies.

**Bioassay:**

The bioassay technique of ASEAN-Canada CPMS-II (1993) for tropical acute toxicity tests with fish and invertebrates was followed. A compartmentalized tank was used as the test container (Law, 1997). The compartmentalized tank measured 61 cm x 17.8 cm x 15 cm (length:width:height) housing with 30 compartments measuring 5.1 cm x 5.1 cm x 15.3 cm (length:width:height) each. One post-larva per compartment was used for the experiment. The WSF oil test solutions ranging from 0 to 22 ppm WSF oil were used for the experiments. The test solutions were renewed daily with freshly prepared WSF oil solution. Mortality of the post-larvae was recorded at 12, 24, 48, 72, and 96 h. The lethal concentration (LC) values for mortality were estimated using Probit Analysis (Wardlaw, 1985).

## Results

The kinetics of hydrocarbons adsorption on coconut husks or shrimp shells followed the Freundlich Isotherm Adsorption Equation closely (Figure 1). The Freundlich Isotherm Adsorption Equation fitted well for the experimental data of dissolved hydrocarbons adsorption on coconut husks as well as on shrimp shells under static condition. The basic Freundlich equation is $x/m = K_f C_e^{1/n}$, where x is the amount of dissolved hydrocarbons adsorbed (mg), m is weight of adsorbent (g) and $C_e$ is the equilibrium concentration of hydrocarbons (ppm) in solution. $K_f$ and *n* are the empirical constants (Nicholas and Paul, 1993). Both of the adsorbents followed the first order adsorption of Freundlich equation with $K_f$ values of 0.408 and 0.407 respectively. The maximum adsorption capacity of dissolved hydrocarbons by coconut husks and shrimp shells are $1.81 \pm 0.01$ mg $g^{-1}$ and $1.57 \pm 0.01$ mg $g^{-1}$ respectively. The experimental results revealed that for reducing 1 liter of seawater containing 10 ppm hydrocarbons to 0.05 ppm, 500 grams of coconut husks or shrimp shells is required according to the Freundlich Equation. The optimum flow rate for removing 10 ppm hydrocarbons in seawater using a fixed bed column of 60 cm height and 6 cm in diameter is 20 ml/min.

The amount of each aliphatic hydrocarbon presents in seawater containing 10 ppm hydrocarbons before and after treatment with coconut husks, shrimp shells or a mixture of them are presented in Table 1. While for the aromatic hydrocarbons, the values are given in Table 2. The GC chromatograms of aromatic hydrocarbons in seawater containing 10 ppm oil and its effluent after treatment with a mixture of coconut husks and shrimp shells (9:1 weight ratio) are given in Figure 2. While the aliphatic hydrocarbons portion are presented in Figure 3.

## Discussion

The water-soluble fraction of crude oil especially its aromatic hydrocarbons content is highly toxic to marine organisms especially to their early life stages. Previous studies of the toxicity of oil on marine organisms recommended that the safety level of oil in seawater should be lower than 50 ppb (Law, 1997). The petroleum hydrocarbons concentration in the Strait of Malacca This study is aimed to reduce the oil contamination in seawater down below 50 ppb using some local available adsorbents, which have high ability to adsorb oil in seawater. Hopefully, an effective filtration treatment system could be developed for removing oil contamination in seawater for protecting marine organisms and for aquaculture uses.

A number of local available adsorbents such as coconut husks, shrimp shells, palm press filter, granular activated carbon, marine silt, and sands have been examined for their adsorption efficiency of oil in seawater. Amongst them, coconut husks and shrimp shells possess the high efficiency in adsorption of aliphatic and aromatic hydrocarbons in seawater.

The protocol of treatment of oil in seawater for this study was as follows. A polyethylene column of 6 cm diameter and 60 cm height was packed with 500 grams of adsorbent (coconut husks or shrimp shells). It was then fed with 1 liter of seawater containing salinity of 30 g $l^{-1}$, pH 8, temperature 30°C and 10 ppm WSF oil at a flow rate of 20 ml $min^{-1}$ with a peristaltic pump. The quantitative and qualitative of each aliphatic and aromatic hydrocarbons in the seawater before and after treatment with the packed column were determined using the GC-FID technique. The total petroleum hydrocarbon in seawater sample was determined during the experiment directly with the Turner portable fluorometer without solvent extraction.

The results revealed that oil residue in seawater after treatment with coconut husks was 0.04 ppm, while the oil residue left behind after treatment with shrimp shells was 0.045 ppm. It is surprising to find that granular activated carbon is not a good adsorbent for removing oil in seawater. The oil residue in seawater after treatment with granular activated carbon was 5.65 ppm, which was

much higher than that of the coconut husks or shrimp shells treatment. This implies that activated carbon is unable to remove most of the hydrocarbons in seawater.

The aliphatic and aromatic hydrocarbon concentrations present in the 10 ppm oil seawater before and after treatment with coconut husks or shrimp shells are given in Table 1 and 2 respectively. The results demonstrate that coconut husks can adsorb 99.58% aromatic hydrocarbons and 99.83% aliphatic hydrocarbons in seawater. While shrimp shells can remove 99.54% aromatic hydrocarbons and 99.79% aliphatic hydrocarbons respectively. Therefore, both the coconut husks and shrimp shells possess high efficiency in adsorption of petroleum hydrocarbons in seawater despite of the fact that there is a large amount of cations and anions in the seawater.

The results revealed that coconut husks can adsorb most of the aromatic hydrocarbons presented in seawater except there was a trace amount of Naphthalene (9.47±0.43 ppb), Phenanthrene (13.46±0.85 ppb), and Benzo(a)anthracene (12.46±0.36 ppb) that left behind (Table 2). The initial concentration of these aromatic hydrocarbons in the 10 ppm oil seawater was 996.92±3.49 ppb, 834.92±3.67 ppb, and 373.85±4.07 ppb respectively. This indicates that the coconut husks have adsorbed 99.05%, 98.39%, and 96.67% of these aromatic hydrocarbons respectively from the oil-contaminated seawater. For aliphatic hydrocarbons, after treatment with coconut husks, the trace amounts of aliphatic hydrocarbons left behind were n-Nonadecane (1.75±0.24 ppb), n-Eicosane (1.75±0.20 ppb) and n-Docosane (1.50±0.23 ppb). The initial concentration of these aliphatic hydrocarbons in the 10 ppm WSF oil seawater was 311.54±2.56 ppb, 286.62+1.78 ppb, and 249.23±0.95 ppb respectively. The amount of aliphatic hydrocarbons adsorbed by coconut husks was 99.44%, 99.39% and 99.40% respectively. Similarly for shrimp shells treatment, there was a trace amount of aromatic hydrocarbons such as Napthalene (9.97±0.36 ppb), Phenanthrene (15.45±0.34 ppb), Indeno(1,2,3-cd)pyrene (7.48±0.32 ppb) and Dibenzo(ah)anthracene (6.23±0.31 ppb) left behind in seawater (Table 1). While the aliphatic hydrocarbons left behind were n-Docosane (2.49±0.28 ppb), n-Tricosane (2.49±0.14 ppb) and n-Tetracosane (1.00±0.16 ppb) respectively.

The trace amount of aromatic and aliphatic hydrocarbons left behind in seawater after treatment with coconut husks or shrimp shells could be further reduced by increasing the amount of adsorbent, however this may lead to higher treatment cost. Another possible way of overcoming this problem is to have a right combination of the weight of coconut husks and shrimp shells for removing the targeted aromatic hydrocarbons such as Benzo(a)anthracene, Indeno(1,2,3-cd)pyrene and Dibenzo(ah)anthracene in the seawater. Coconut husks has a high efficiency in removing Indeno(1,2,3-cd)pyrene and Dibenzo(ah)anthracene, while shrimp shells are capable to remove Benzo(a)anthracene (Table 1 & 2). All these aromatic hydrocarbons are known to be carcinogenic to human and toxic to organisms.

Finally, a packed column with a mixture of 450 grams of coconut husks and 50 grams of shrimp shells as adsorbents was used for treatment of 10 ppm oil seawater. The resulfs showed that there was an improved reduction of oil residue in the effluent. The oil residue in the effluent was 25.68 ppb, which contained only 7.98±0.14 ppb of Napthalene, 12.96±0.34 ppb of Phenanthrene, and 4.74±0.10 ppb of n-Docosane. All others aromatic hydrocarbons were removed. The success of this treatment can be seen from the GC chromatogram given in Figure 3, which reveals that the oil residues in seawater is reduced to a very low level.

The acceptability of the oil contaminated seawater after treatment with the above mixture of adsorbents for marine organisms is further validated by bioassay test with post-larvae of *P. monodon*. The value of 96h$LC_{50}$ of WSF oil for PL(30) *P. monodon* for the present study is 12.246 ppm which agrees with the previous reported of 12.25 ppm (Law, 1997). The 96 hours accumulated mortality of PL(30) *P. monodon* in the untreated seawater containing 10 ppm oil and treated seawater with the mixture of adsorbents containing of 0.0257 ppm oil are 35% and 0% respectively. This indicates that the treatment is successful and the treated water is safe for post-larvae of *P. monodon*.

The present level of oil pollution in the Straits of Malacca is around 300 ppb. By using the above combination of coconut husks and shrimp shells for treatment, one ton of the mixed adsorbents can treat 6530 tons of seawater for hatchery use. The cost of preparation for the adsorbents is low (below USD 150/ton) and the adsorbents are environmental friendly.

**Acknowledgements.** The authors would like to thank the Ministry of Science, Technology, and Environment Malaysia (MOSTE) for supporting this project through IRPA.

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**Table 1.** Aliphatic hydrocarbon species and concentration in the 10 ppm WSF solution and in the effluents after treatment with adsorbents.

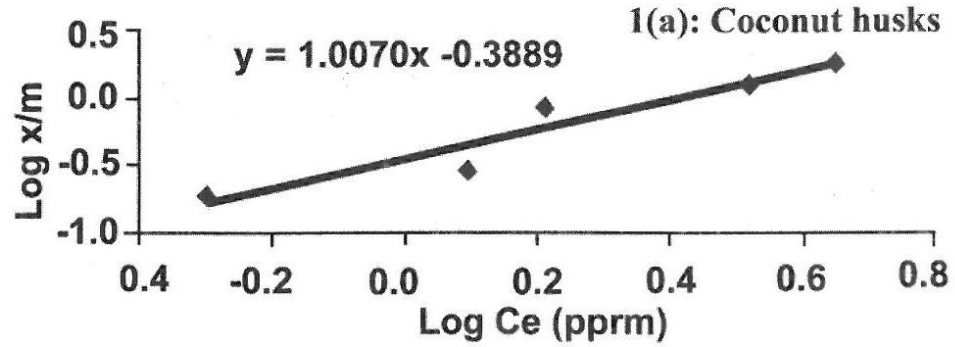
| Aliphatic Hydrocarbons Species | Concentration in untreated WSF oil solution (ppb) | Concentration remained in water after treatment with adsorbent (ppb) | | |
|---|---|---|---|---|
| | | Coconut Husk | Shrimp Shell | Coconut Husk + Shrimp Shell |
| **n-Dodecane** | 186.923 ± 0.320[1] | ~ | ~ | ~ |
| **n-Tetradecane** | 398.769 ± 1.387 | ~ | ~ | ~ |
| **n-Hexadecane** | 286.615 ± 2.294 | ~ | ~ | ~ |
| **n-Octadecane** | 373.846 ± 2.354 | ~ | ~ | ~ |
| **n-Nonadecane** | 311.538 ± 2.559 | 1.745 ± 0.244 | ~ | ~ |
| **n-Eicosane** | 286.615 ± 1.775 | 1.745 ± 0.197 | ~ | ~ |
| **n-Docosane** | 249.231 ± 0.948 | 1.495 ± 0.228 | 2.492 ± 0.280 | 4.735 ± 0.092 |
| **n-Tricosane** | 186.923 ± 1.989 | ~ | 2.492 ± 0.135 | ~ |
| **n-Tetracosane** | 162.000 ± 2.114 | ~ | 0.997 ± 0.161 | ~ |
| **n-Pentacosane** | 137.077 ± 1.368 | ~ | ~ | ~ |
| **n-Hexacosane** | 99.692 ± 3.581 | ~ | ~ | ~ |
| **n-Octacosane** | 74.769 ± 2.391 | ~ | ~ | ~ |
| **n-Triacontane** | 37.385 ± 2.364 | ~ | ~ | ~ |
| **n-Dotriacontane** | 37.385 ± 0.951 | ~ | ~ | ~ |
| **n-Tetratriacontane** | 24.923 ± 2.219 | ~ | ~ | ~ |
| **Σ AH (ppb)** | 2853.689 ± 1.088 | 4.985 ± 0.068 | 5.982 ± 0.103 | 4.735 ± 0.092 |

[1]: Mean ±SD. (n=6)

**Table 2.** Aromatic hydrocarbon species and concentration in 10 ppm WSF solution and in the effluents after treatment with adsorbents.

| Aliphatic Hydrocarbons Species | Concentration in untreated WSF oil solution (ppb) | Concentration remained in water after treatment with adsorbent (ppb) | | |
|---|---|---|---|---|
| | | Coconut Husk | Shrimp Shell | Coconut Husk + Shrimp Shell |
| **Napthalene** | 996.922 ± 3.488[1] | 9.471 ± 0.429 | 9.969 ± 0.354 | 7.975 ± 0.139 |
| **Acenapthylene** | 373.846 ± 3.095 | ~ | ~ | ~ |
| **Acenaphthene** | 473.538 ± 7.194 | ~ | ~ | ~ |
| **Fluorene** | 747.692 ± 11.433 | ~ | ~ | ~ |
| **Phenanthrene** | 834.922 ±3.699 | 13.458 ± 0.850 | 15.452 ± 0.339 | 12.960 ± 0.357 |
| **Anthracene** | 872.307 ±2.781 | ~ | ~ | ~ |
| **Fluoranthene** | 473.538 ±2.057 | ~ | ~ | ~ |
| **Pyrene** | 436.153 ±2.712 | ~ | ~ | ~ |
| **Benzo(a)anthracene** | 373.846 ±3.099 | ~ | ~ | ~ |
| **Chrysene** | 398.769 ±5.280 | 12.462 ± 0.364 | ~ | ~ |
| **Benzo(b)fluranthene** | 373.846 ±4.074 | ~ | ~ | ~ |
| **Benzo(k)fluoranthene** | 448.615 ±4.257 | ~ | ~ | ~ |
| **Benzo(a)pyrene** | 560.769 ±4.183 | ~ | ~ | ~ |
| **Indeno(1,2,3-cd)pyrene** | 361.384 ±3.352 | ~ | ~ | ~ |
| **Dibenzo(ah)anthracene** | 461.076 ±2.749 | ~ | 7.477 ± 0.315 | ~ |
| **Benzo(ghi)perylene** | 311.538 ±5.726 | ~ | 6.231 ± 0.137 | ~ |
| **ΣAH (ppb)** | 8498.761 ± 3.918 | 35.391 | 39.129 ± 0.312 | 20.935 ± 0.232 |

[1]: Mean ±SD. (n=6)



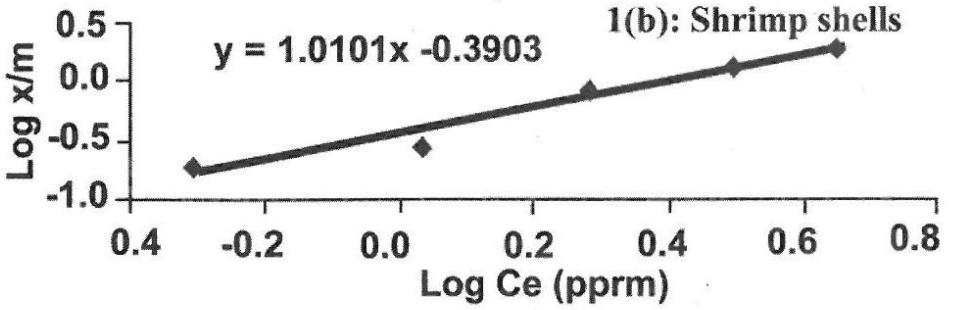




**Figure 1.**The Freundlich Isotherm Adsorption Equation fitting the experimental data of the adsorbents : 1(a) for coconut husks, and 1(b) for shrimp shells

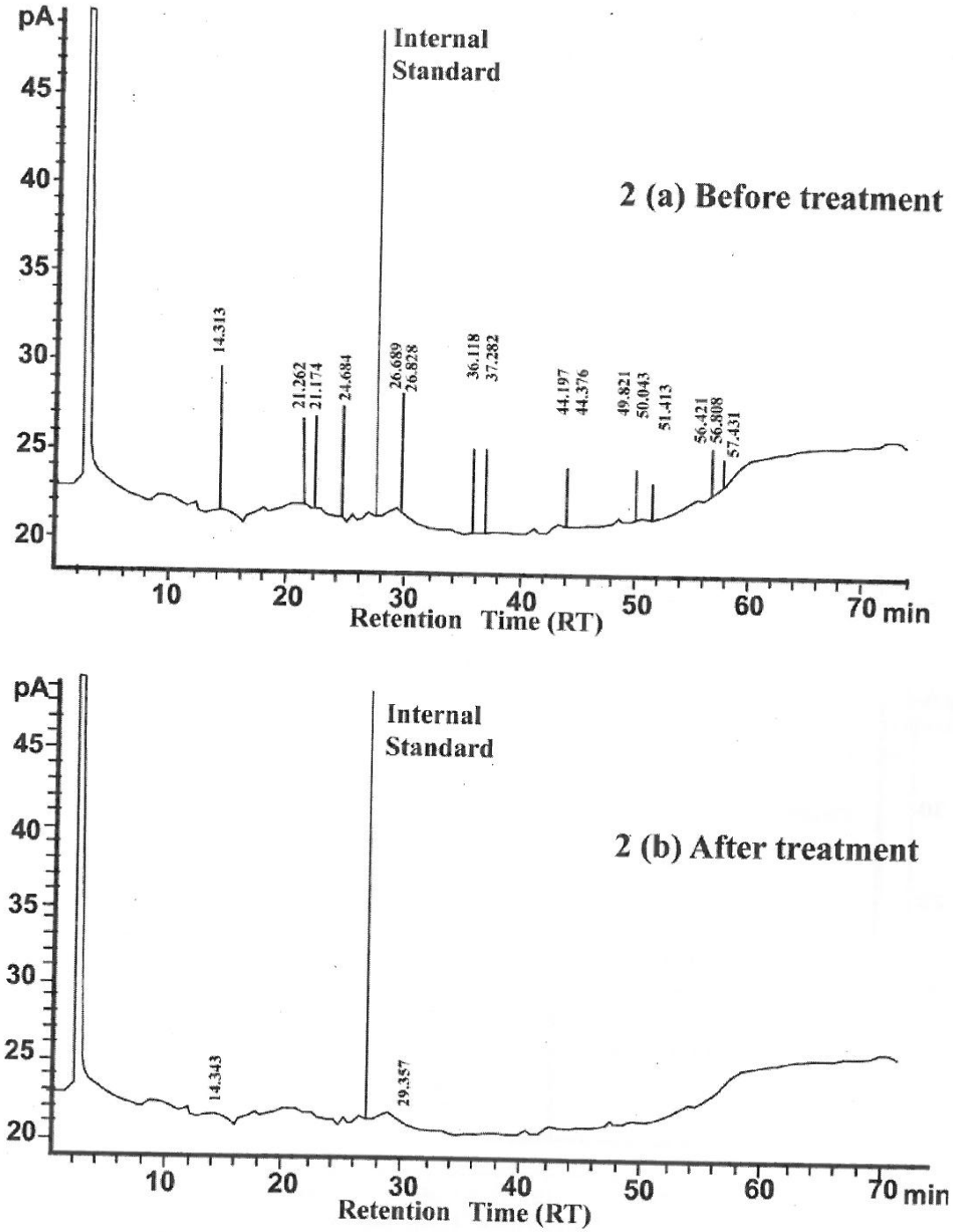



**Figure 2.** The Polyaromatic Hydrocarbons (PAHs) species and concentration in WSF oil solution before (2a) and after (2b) treatment with a mixture of coconut husks and shrimp shells (9:1).

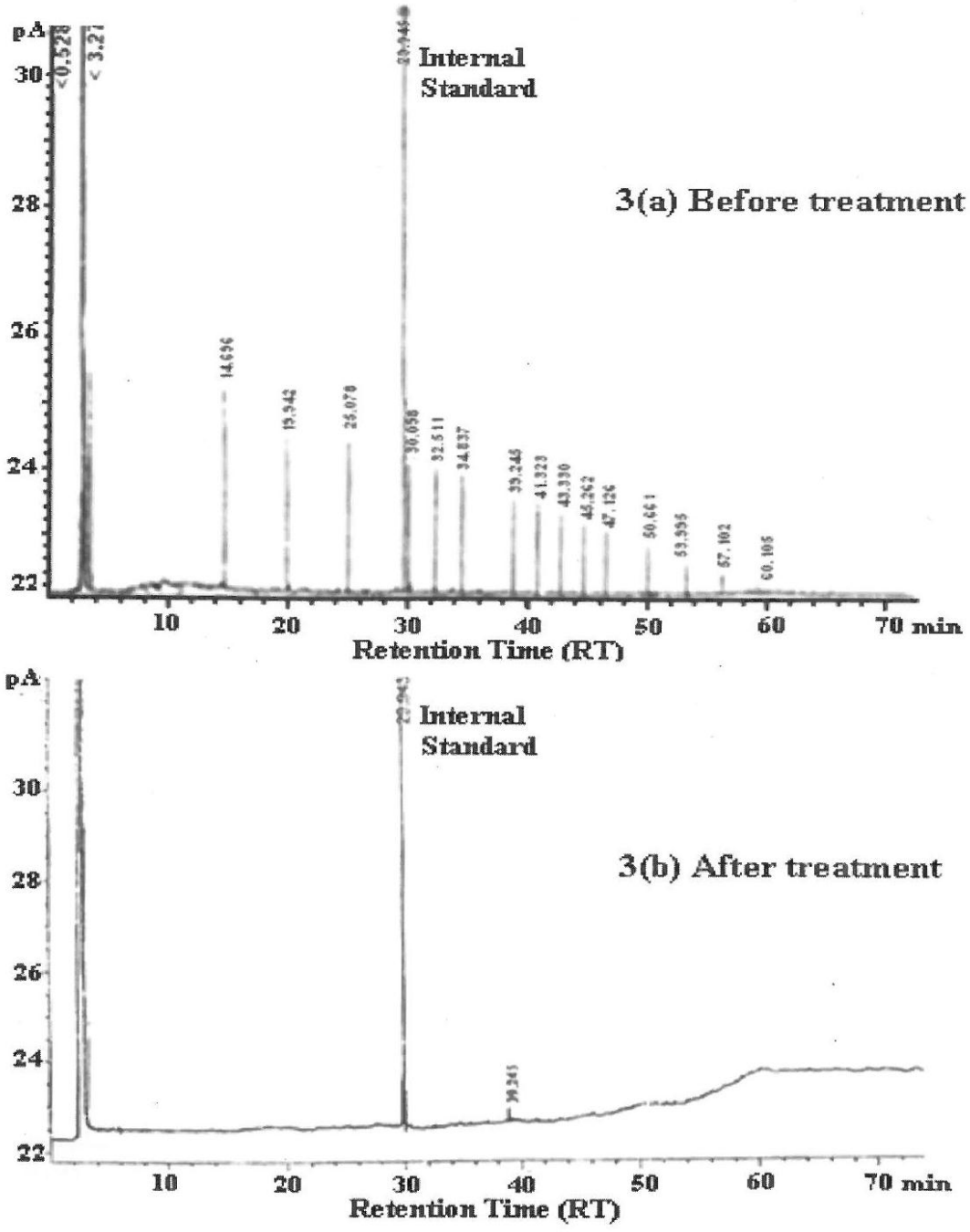



**Figure 3.** The aliphatic hydrocarbons in 10 ppm WSF oil Seawater before (3a) and after (3b) treatment with the mixture of adsorbents.