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Research Article

Assessing Ecofriendly Wastes in Removal of Pyrene as a Model of Oil Spills

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Abstract

Though oil spills have always been present in ocean waters, the amount has greatly increased with global scale oil production. With no two oil spills alike, cleanup provides a difficult and unique challenge to the community. The toxicity of oil spills is related to the presence of Polycyclic Aromatic Hydrocarbons (PAHs). Although the long-term effects on marine life exposed to oil have not been accurately measured, the short term effects are disastrous with mass deaths of animals and plants alike. Current methods of cleanup involve dispersants with research indicating its toxicity may be doing more harm than good. With this problem in mind, green adsorbents are a new low-cost alternative and eco-friendly in regards to the environment. Previous studies have shown their potential in areas such as heavy metal contamination and wastewater treatments. This current study use sugarcane (Saccharumofficinarum) bagasse and, crawfish (Procambarus clarkia) shells Louisiana's major waste products, as potential adsorbents of PAHs. Liquid-Liquid Extractions (LLE) were performed on water samples dosed with pyrene (as individual PAH). Adsorbents were tested under various conditions to determine the optimal settings. These conditions included varying amounts of adsorbents added, varying contact time between water and adsorbent and internal water temperatures. These samples were analyzed using GC-FID and compared to control concentrations. We observed that both adsorbents were able to absorb large amounts of pyrene. Sugarcane bagasse had a much larger efficiency when compared to crawfish in shorter adsorption time and less amount of adsorbent needed. These adsorbents were able to decrease PAH levels to trace amounts in many cases. This study shows the huge potential for using waste products as green adsorbents in oil spills.

Keywords: Craw fish shells, GC-FID, PAHs, pyrene, sugarcane bagasse

Introduction

Petroleum oil contamination is one of the problems causing the largest effect on seawater ecosystem. Often contamination occurs as a result of petroleum spills that became more frequent with increase in oil production, especially in offshore locations. The transportation of petroleum Containing substances also may aggravate the problem [1]. The unfavorable impact of oil spills comes from Polycyclic Aromatic Hydrocarbons (PAHs) [2,3]. These compounds are constituents of crude oil which are known for their carcinogenic and mutagenic effects on living systems [3,4]. Their toxicity include immediate decrease of plankton. Also, reproduction levels of fish decline significantly [4]. The long term consequences of oil spills are even more harmful. Since marine plants enclosed in oil are unable to carry photosynthesis, the amount of oxygen significantly decreases whereas the opposite is observed with carbon dioxide. The resulting mass plant and zooplankton deaths disrupt the food web, which leads to significant decline in animal and bird population observed even 20 years later after the occurred spill [4]. As a result, this problem requires sufficient methods for removing hydrocarbons from water.

At present, one of the ways of cleaning up the spills is spreading dispersants over the water surface. Dispersants are various toxic chemical mixtures that facilitate breaking the floating oil film into suspended droplets [1]. Applying these chemicals prevents the oil patch from reaching shores and reduces the chance

of animals to contact with oil [5-7]. However, studies indicated that oil dispersants can cause more damage than the beneficial effect on marine life [6]. According to some research, the toxicity from the oil mixed with dispersants can be over 50 times higher than that of the crude oil. In addition, toxicity of the oil-dispersant mixture retains its high toxicity level for a long period of time [7]. Another issue of using dispersants is strict regulations imposed by the United States on the application of these chemicals [8]. The mentioned drawbacks urge finding of other ways for treating oil spills. In the 2000s, the new low-cost method was developed. The treatment involved eco-friendly adsorbents and showed promising results when being used with wastewater, radioactive material, heavy metals, dyes, pharmaceuticals, and pesticides [9].These adsorbents sometimes are less effective than commercially produced analogs. However, their low cost and eco-friendly quality makes them highly competitive [9-11]. The absorbents are working by biosorption principle. The biological material absorbs the contaminant [12-15]. And later can be removed from water leaving clean environment. In this research, the effect of two biological adsorbents was studied. The absorbents sugarcane bagasse and crawfish shells were chosen because of their abundance in Louisiana as main biological waste products. The goal of this work is finding the best adsorbent from Louisiana waste bio-products suitable for treating oil spills. The amount of Pyreneans analyzed using the Gas Chromatography with Flame Ionization Detector (GC-FID), following the Unites States recommendations [16].

Materials and Methods

Sample Collection and Purification

The two adsorbents collected were sugarcane bagasse and crawfish shells. The adsorbents were obtained from waste, the bagasse from a Sugar Mill in New Iberia, Louisiana, and the crawfish shells from fisheries, Lafayette, LA. Adsorbents were purified to prevent any interference with analysis. The crawfish shells were placed in tubs of acetone with a change of acetone every day. This was done until the color of the shells changed from red to white. After removing all pigmentation, the crawfish shells were dried in the oven. They were then crushed in a grinder and sieved to obtain different particle sizes. The process of purifying the sugarcane bagasse focused on removing any sugar residue. The sugarcane was rinsed several times with water for one week, and then dried in oven. This was followed by grinding and sieving to ensure same particle size. The water samples salinity 15%were dosed with a known concentration of pyrene (Restek1, 000 µg/mL in methanol, 1 mL/ampoule), and were treated with either sugarcane bagasse or crawfish shells to examine their efficiency as adsorbents in removing oil pollutants.

Effect of Time of Exposure to Adsorbent

A constant amount of adsorbent was added with a varying amount of contact time between the adsorbent and water. In the case of pyrene and sugarcane bagasse, half a gram of adsorbent was added to several amber glass vessels containing 400 mL of dosed pyrene solution, salinity 15%. Containers were then shookat250 R/M and the concentration of pyrene was determined after different periods of times (half an hour, one hour, two hours, one day and four days). The water samples were filtered to remove the adsorbent before extraction. The same procedure was followed using one gram of ground crawfish shells, under the same conditions as sugarcane bagasse with different time intervals of 12 hours, one day, four days and seven days.

Effect of Amount of Adsorbent

The experiment was performed under constant time of exposure for each adsorbent with the sample, with a varying amount of sugarcane bagasse or crawfish shells. Different amounts of sugarcane bagasse (0.1, 0.2, 0.3, 0.4 and 0.5 grams) were added to containers with 400 mL of dosed pyrene solution. Containers were shaken, as mentioned above, and the concentration of pyrene was determined after one day for each sample. The water samples were filtered to remove the sugarcane bagasse before extraction. In the case of crawfish shells, the amounts (0.5, 2, 3, and 4 grams) were added to dosed pyrene solution. The same procedure as with the sugarcane was followed but pyrene was extracted after two days.

Effect of Temperature

After considering contact time and amount, these variables were kept constant with a different range of temperatures. The amount of sugarcane bagasse used was 0.5 grams added to each sample and one gram in case of crawfish shells. The first temperature considered was 3°C. The sample of dosed pyrene was kept in the shaker/incubator in a tub of dry ice that kept the temperature constant. For three hours the sample was shaken at 3°C before being removed and filtered. This process was repeated at temperatures of 25°Cand 50°C which the shaker/incubator was able to maintain. The internal water temperature was measured and confirmed in the samples before filtration in each case.

Extraction

A volume of 400 mL of pyrene dosed water samples were extracted using Liquid-Liquid Extraction (LLE). The amber bottle containing the dose sample was rinsed with each portion of DCM before extraction. Ten µL of 4-Terphenyl-D14 (2000 µg/mL in ethylene chloride (1 mL/ample) - SUPELCO) was added as internal standard. Five portions of 80 mL of Dichloromethane (DCM) were used as the extraction solvent. After all the DCM portions were added, anhydrous sodium sulfate was then used to absorb any water present in the organic extract. The DCM extracts were collected and evaporated using a rotary evaporator at room temperature. The pyrene residue was then dissolved in hexane. The original container was rinsed several times with hexane to recover all the extracted pyrene. All the hexane rinses were concentrated in a vial to a volume of 1.00 mL by blowing nitrogen down into the vial. A constant aliquot of the extracted samples was manually

injected immediately into the Gas Chromatography-Flame Ionization Detector (GC-FID) or were kept in the freezer until further GC-FID analysis the next day. A minimum of four replicates we analyzed for each experiment.

Analysis

Pyrene concentration was then quantified using gas chromatography with a GC-FID. An aliquot of the organic extract was injected into an Agilent technologies 7820 A GC System, under the following conditions: the injector and detector temperatures were set at 250°C and 300°C, respectively; helium was used as the carrier gas; samples were injected in the split less mode; the oven temperature was programmed to increase from an initial temperature of 60°C to 300°C at a rate of 5°C/min and was then maintained at final temperature of 290°C for 15 min. The non-polar stationary phase5% biphenyl/95% diethyl polysiloxane (30 m x 0.25 mm x 0.25 µm Agilent Capillary GC Columns) was installed and operated with a constant flow of helium at 2.5 mL/menthe PAHs peak areas were computed by Agilent software and converted to concentrations using standard calibration curve, the Limit of detection was determined to be 0.1 µg/L. Statistical analysis were done using Student's t test. Values are expressed as a mean ±SEM, with a value of $P < 0.05$ considered statistically significant. Statistical evaluation was performed by ANOVA. All analyses were made with the statistical software Microcal Origin (Microcal Software, Inc., Northampton, MA).

Results and Discussion

Treatments of Pyrene with Sugarcane Bagasse in all treatments, the concentration of dosed pyrene (450µg/L) was compared to the control concentration of 430 ± 7.3µg/L, water dosed with pyrene standard (95.6 % recovery). In the first treatment, the relationship between adsorbent and contact time was examined. Results indicated that as contact time with sugarcane bagasse increased, the detected pyrene concentration was decreasing. By day one, only traces of pyrene were detected, a concentration of16.0 ± 1.2µg/L, that is about 26 times less than the control. Sugarcane bagasse as an adsorbent was extremely efficient in removing pyrene from water samples in a short period of time (Figure 1).

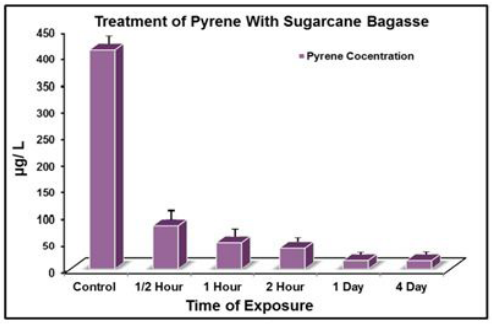

Figure 1: Concentrations of pyrene after treatment with sugarcane bagasse at different intervals of time

Determination of Adsorption Capacity

The adsorption capacity was determined by using the following equation, taking into account the concentration difference of the solution at the beginning and at equilibrium:

$$q_e = \frac{(C_o - C_e)\,V}{m}$$

where qe is the amount of pyrene adsorbed at equilibrium (µg/g adsorbent), Co and Ce are the pyrene concentration (µg/L) at time t = 0 and at equilibrium, respectively, V is the solution volume (L) and m is the amount of adsorbent used (g).The removal percentage can be calculated as: (Table 1) is showing the adsorption capacity and Removal % in case of time of exposure with sugarcane bagasse Co = 430 µg/L

$$\text{Removal \%} = \frac{(C_o - C_e)}{C_o} \text{ x100 \%}$$

Time of Exposure	Concentration of pyrene C_e (µg/L)	Amount of pyrene adsorbed	Removal %
0.5 hour	85.57	275.54	80.10 %
1.0hour	52.09	302.33	87.89 %
2.0hour	41.31	310.95	90.39 %
1.0 day	16.84	330.53	96.08 %
4.0 day	16.61	334.135	96.18 %

Table 1: Adsorption capacity and Removal % for time of exposure with sugarcane bagasse

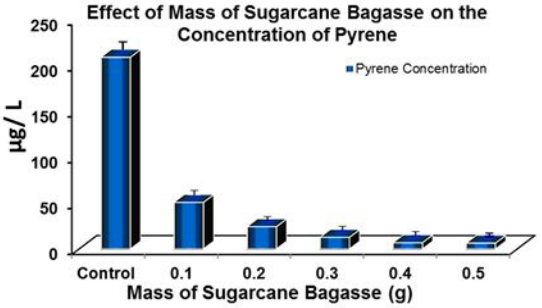

Figure 2: Concentrations of pyrene after treatment with different amounts of sugarcane bagasse

In case of varying amounts of adsorbent was added to samples to find the optimum quantity. The concentration of pyrene control, 208.8 µg/L, was doused with pyrene (240 µg/L) and containing no adsorbent, which is 87.0% recovery. In all trials, the pyrene concentration was decreasing with increasing masses of sugarcane bagasse. The concentration with 0.5 g was found to be 6.0 ±2.3 µg/L, an amount 34 times less than that of the control. Figure 2 shows that sugarcane bagasse showed strong efficiency in adsorbing pyrene from water samples. (Table 2) is showing the adsorption capacity and Removal % in case of different masses of sugarcane bagasse Co = 208.8 µg/L

Mass of sugar-cane bagasse (g)	Concentration of pyrene C_e (µg/L)	Amount of pyrene ad-sorbed	Removal %
0.1	50.67	63.27	75.67 %
0.2	24.08	73.88	88.47 %
0.3	12.45	78.54	94.04 %
0.4	6.64	80.86	96.82 %
0.5	6.14	81.06	97.06 %

Table 2: Adsorption capacity and Removal % related to different masses of sugarcane bagasse

Another examined variable was how the internal temperature of the water would affect adsorption as a model that mimics oil spills into ocean waters at different places in the world. Very cold, hot, and average temperatures were tested: 3°C, 25°C, and 50°C. At 25°C the concentration detected was nearly 21 times less than the control. Overall, at every temperature trace amounts of pyrene were detected in waters, however all the pyrene was gone at 50°C, either by adsorption or degradation? (Figure 3).

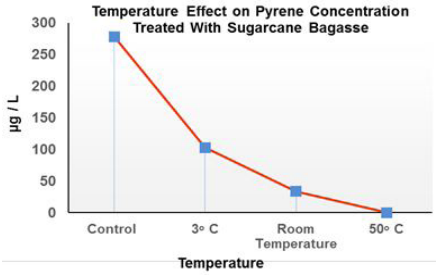

Figure 3: Concentrations of pyrene after treatment with bagasse at different temperatures

Treatments of Pyrene with Crawfish Shells

The same parameters were examined using the second adsorbent, grind crawfish shells. When looking at varying time of exposure to crawfish shells, it was found that as the time increased the concentration of detected pyrene was decreasing. By day for the concentration of pyrene was found to be 62 ± 2.7 µg/L, 7 times less the level of pyrene in the control. However, in case of crawfish shells at day 7 the concentration of pyrene was found to be 66 ± 3.6 µg/L, a slight increase from the day 4 concentration. This is an indication that day four is the optimum time for best adsorption of pyrene. After day 4, crawfish shells, starts to release the adsorbed pyrene back into the water (Figure 4).

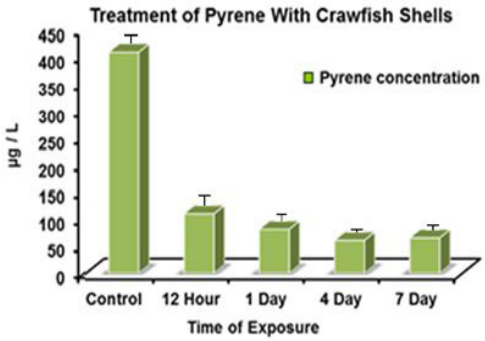

Figure 4: Concentrations of pyrene after treatment with crawfish shells at different intervals of time

(Table 3) is showing the adsorption capacity and Removal % in case of time of exposure with sugarcane bagasse Co = 430 µg/L

Time of Expo-sure	Concentration of pyrene C_e (µg/L)	Amount of pyrene ad-sorbed	Removal %
0.5 day	116.88	125.25	72.82 %
1.0 day	86.52	137.39	79.88 %
4.0 day	64.54	146.18	84.99 %
7.0 day	69.64	144.14	83.80 %

Table 3: Adsorption capacity and Removal % for time of exposure with crawfish shells

It is critical to find the most effective amount of crawfish shells as an adsorbent. With a constant contact time, increasing amounts of adsorbent was added to the pyrene solution. This was compared to the extracted control which had a concentration of 205±3.8 µg/L. After calculations, it was found that pyrene concentration did decrease with increasing masses of crawfish shells added. The concentration in the presence of 3 g was found to be 20±1.6 µg/L, which is 10 times less than the control. Upon using 4 g of crawfish shells, no pyrene was detected, showing that crawfish had adsorbed nearly all the pyrene in the sample (Figure 5).

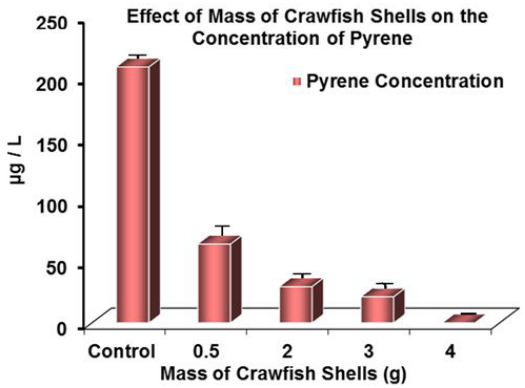

Figure 5: Concentrations of pyrene after treatment with different amounts of crawfish shell

(Table 4) is showing the adsorption capacity and Removal % in case of different masses of sugarcane bagasse Co = 208.8 µg/L

Mass of crawfish shells (g)	Concentration of pyrene C_e (µg/L)	Amount of pyrene adsorbed	Removal %
0.5	64.18	57.84	69.26 %
2.0	29.80	71.89	79.88 %
3.0	21.62	74.87	85.73 %
4.0	0.00	83.52	100.00 %

Table 4: Adsorption capacity and Removal % related to different masses of crawfish shells

As before, with pyrene and sugarcane bagasse, the effect of temperature was studied in relation to the adsorbent's efficiency. The results varied from the previous example. At 25°C adsorption of pyrene was the least, with much lower concentrations of pyrene at 3°C, and 50°C. When exposed to the hot temperature, pyrene adsorption was highest at nearly nine times less than the original concentration. At 3°C, it had a concentration twice as less than the control. Crawfish shells have the potential to adsorb pyrene in a wide range of temperatures (Figure 6).The temperature had no effect on the control without any adsorbent at 3°C and 25°C. However, at 50°C the concentration of pyrene deceased by 25 ± 7.8µg/L, most probably due to degradation at high temperature.

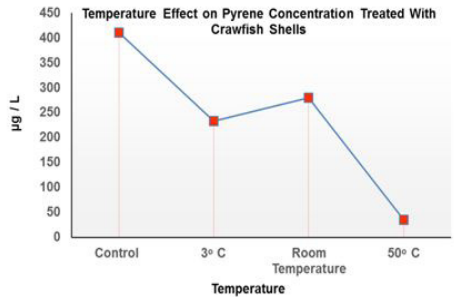

Figure 6: Concentrations of pyrene after treatment with crawfish shells at different temperatures

The effect of particles size was also tested (60, 70 and 80 meshes). It did not have that much effect in case of crawfish shells. However, for sugarcane bagasse the best results were obtained with 60 meshes.

Conclusion

When examining both eco-friendly adsorbents, it was apparent that the sugarcane bagasse and crawfish shells had the ability to absorb pyrene, though not equally. Bagasse was a far more superior adsorbent, which was obvious after one day using half a gram bagasse. Though crawfish as an adsorbent was also successful, it took nearly four days with two grams to remove pyrene or four grams if left for two days. It requires a much longer contact time or a larger amount of adsorbent added in comparison to bagasse. Although some of the adsorbed pyrene was found to be released in case of crawfish shells, the amount was still significantly lower than the original PAH concentration. With hugely different temperatures from 3°C- 50°C sugarcane bagasse proved that it could greatly reduce pyrene amounts. There is a great potential for sugarcane bagasse and crawfish shells to be used in environmental cleanups, namely oil spills, in Louisiana and other places. These adsorbents are waste products, disposed in enormous amounts that can be used in reducing PAH levels in water.

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