Application of Natural Sorbents in Crude Oil Adsorption

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Abstract

In last decades, oil spill pollution has become an important issue of concern due to its serious environmental impacts; therefore, necessary actions should be taken to prevent or reduce these types of pollution and their environmental consequences. Natural organic sorbents are emerging as proper choices for oil spill cleanup due to their availability, eco-friendliness, and low cost. In this study, phragmites australis, sugarcane leaves straw, and sugarcane bagasse were used for crude oil sorption in dry (only oil) systems. The results indicated that sugarcane bagasse had a higher oil sorption capacity compared to the others. Therefore, sugarcane bagasse was selected as the preferred sorbent and the effects of sorbent contact time and its particle size on oil adsorption capacity were evaluated for the systems of dry and crude oil layer on water. The results showed that the maximum adsorption capacity of raw sugarcane bagasse for dry system and crude oil layer system was about 8 and 6.6 gram crude oil per gram sorbent respectively.

1. Introduction

One of the main sources of water pollution is crude oil spill. Oil and petroleum products can pollute sources of water such as seas, oceans, rivers, or underground waters. Oil spill over the oceans and seas requires prompt attentions due to their environmental and economical impacts (Annunciado et al., 2005).

In general, wherever oil is produced, transported, stored, and used, there will be a risk of spillage. Spilled oil has an undesirable taste and odor, affects tourism and economy, and causes severe environmental damages. The spilled oil eventually enters toxicity components into the human food chains and affects our health. Therefore, spilled oil causes enormous environmental problems unless it is removed as quickly as possible (Hussein et al., 2009; Sayed and Zayed, 2006). The most commonly used shoreline cleanup options are listed in Table 1 (Zahed et al., 2005; Zhu et al., 2001; Alade, 2011).

Sorption can be happened in two mechanisms, namely absorption and adsorption. Absorbents allow oil to penetrate into pore spaces in the material they are made of, whereas adsorbents attract oil to their surfaces but do not allow it to penetrate into the material (Karan et al., 2011; Sayed et al., 2003).

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Adsorption is a promising process and cost-effective method to reduce the environmental problems of oil spill and cleanup these types of pollution.

Table 1
Different technologies for oil spill cleanup methods (Zahed et al., 2005; Zhu et al., 2001; Alade, 2011)

Category of Response Option	Example Technology
Natural method	Natural attenuation
Physical method	Booming and skimming
	Wiping with absorbent materials
	Mechanical removal
	Low pressure flushing
	Washing
	Cutting vegetation
	Stripping
Chemical methods	Dispersants
	Demulsifiers
	Gelling agents (solidifiers)
	Surface film chemicals
	In situ burning
Biological methods	Bioremediation
	Phytoremediation

Oil sorbents can be classified into three basic categories, including inorganic mineral products, organic synthetic products, and organic vegetable products (Adebajio et al., 2003; She et al., 2010). Inorganic sorbents include zeolites, silica, perlite, graphite, vermiculites, sorbent clay, diatomite, glass, wool, sand, and volcanic ash; materials such as polypropylene and polyurethane are organic synthetic products. Natural organic sorbents include peat moss, wood fiber, cotton fiber, cellulosic kapok fiber, kenaf, milkweed floss straw, hay, sawdust, ground corncobs, feathers, and other carbon-based products (Annunciado et al., 2005; She et al., 2010).

In the study conducted by Canada Environmental Protection Services, oil sorption capacity per unit weight of sorbent was measured for different sorbents. Table 2 shows the results of this study (Ross, 1991). First column shows different used sorbents and the other columns list the amount of different oil that was adsorbed.

Several natural organic sorbents have been studied for the removal of oil spill, e.g. raw sugarcane bagasse (Hussein et al., 2008; Brandão et al., 2010; Said et al., 2009), raw and fatty-acid grafted sawdust for oil (Banerjee et al., 2006) and other pollutants (Shukla et al., 2002), black and white rice husk ash (Vlaev et al., 2011), barley straw (Hussein et al., 2009), banana trunk fibers (Sathasivam and Haris, 2010), acetylated sugarcane bagasse (Chung et al., 2011; Sun et al., 2003), carbonized peat bagasse (Hussein et al., 2009), peat-based sorbents (Cojocaru et al., 2011), and hydrophobic aerogels for emulsified oil (Wang et al., 2010; Site 2001). Even though several studies have been performed in this area, more research is still required. In the current study, the performance of three natural organic sorbents, namely phragmites australis, sugarcane leaves straw, and sugarcane bagasse in oil sorption was compared.

Table 2
Oil sorption capacities of some typical sorbents (Ross, 1991)

Sorbent	Diesel (gr oil/gr sorbent)	Crude-1 day (gr oil/gr sorbent)	Crude-7 day (gr oil/gr sorbent)	Bunker C (gr oil/gr sorbent)
Alfob	2.51	2.88	3.71	5.84
CCD wood chips	0.54	0.78	1.84	3.65
Clay	-	0.76	1.21	1.59
Cork	4.65	3.78	3.82	2.14
Oclansorb	9.07	6.16	6.76	5.51
Sawdust	4.08	5.29	6.65	9.75
Wool	9.54	14.07	19.80	11.70
Alsorb II	14.56	16.15	18.90	22.15
Eco oil sorbent	13.23	16.98	23.15	12.64
E100	11.04	9.99	16.01	14.73
Foam "X"	5.32	7.48	10.77	14.17
Graboil	18.62	10.17	8.19	6.71
Hazorb	9.52	8.49	7.03	4.36
Malasorb	7.98	9.16	11.91	10.34
Pig slimmer	8.14	4.94	5.93	5.57
S100	8.98	9.9	12.76	9.12

2. Materials and methods

2.1. Sorbents and oil properties

Raw sugarcane bagasse was obtained from Karoun Agro-Industry factory (Iran) and phragmites australis and sugarcane leaves straw were collected from a suitable area in Khuzestan province (Iran). The prepared sorbents were washed several times with tap water and dried in open air. Next, the sorbents were crushed and washed with distillate water and then dried in an oven at 60 °C for 10 hours and were used as sorbents for the systems of dry and crude oil layer. The used crude oil had a specific gravity of 0.86 at 15 °C and was supplied by Abadan's oil refinery (Iran).

2.2. Adsorption experiments

To determine the sorption capacity, the tests were conducted in a batch system according to the following standard procedures:
1. ASTM F 726-99 for sorption experiments (F 726-99);
2. ASTM D 1141-98 to produce saline water (D 1141-98).
Sorption experiments were first carried out for dry systems (Figure 1.A) using phragmites australis, sugarcane leaves straw, and sugarcane bagasse; however, only sugarcane bagasse was used for removing oil from the oil layer system (Figure 1.B) because it showed a higher oil sorption capacity compared to the others in dry system. A dry system contained only crude oil, while there were two phases of oil and water, in a way that the oil formed a layer on water, in an oil layer system.
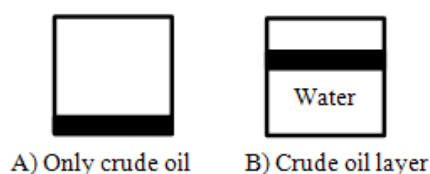
Figure 1
Dry system and oil layer system

For the dry system, 50 ml of crude oil was poured into a 250 ml beaker and then a specific amount of sorbent was added to crude oil. These tests were performed in a static system, without stirring. For crude oil layer sorption, 100 ml of artificial sea water was poured into a 250 ml beaker. Crude oil was added to the breaker to form an oil layer with a specified thickness. Then, the sorbent was spread over the surface. After a certain amount of sorption time, sorbent was removed with a net, which was hanged over the beaker for 5 min to allow the crude oil that was not adsorbed to separate. Each experiment was performed twice and the sorption capacity was calculated using the following equations:

$$Oil\ sorption\ capacity = \frac{weight\ of\ adsorbed\ oil}{weight\ of\ sorbent} \qquad (1)$$

$$Weight\ of\ adsorbed\ oil = weight\ of\ initial\ crude\ oil - weight\ of\ remained\ oil \qquad (2)$$

$$Weight\ of\ remained\ oil = weight\ of\ oil\ layer + weight\ of\ dissolved\ components \qquad (3)$$

Weight of oil layer was determined by collecting the remained oil layer from water surface using a decanter and the weight of components dissolved in water was determined by measuring the chemical oxygen demand (COD) of polluted water.

3. Results and discussion

The oil sorbed and retained inside porous media can be divided into three parts, including (i) the oil part retained by weak capillary forces, which is released under gravitational forces during several minutes, (ii) the oil part retained by capillary forces, which is not released under gravitational field, and (iii) the oil part retained by strong capillary forces and adsorptive forces, which is not released under gravitational and centrifugal field (Cojocaru et al., 2011). In the present work, after oil sorption process, sorbent was hanged over the beaker for at least 5 min so that the oil part retained by weak capillary forces was extracted. In this time, the decrease in the retention capacity is very noticeable. This can be explained by the fact that a part of liquid is weakly retained into macropores by weak capillary forces, and therefore, is easily drained. The other parts (part ii and part iii) of oil contribute to the oil sorbed by the adsorbent.

Figure 2 shows the effect of contact time on crude oil sorption in the dry system for three different sorbents of similar particle size. It shows that sugarcane bagasse has the maximum sorption capacity which is about 8 gram oil per gram bagasse. Next, sugar leaves straw has a medium average sorption capacity of 5.5 gram oil per gram sugar leaves straw. The minimum oil sorption capacity belongs to phragmites australis which is about 4.5 gram oil per gram phragmites australis. Sugarcane bagasse has a higher oil capacity compared to the other sorbents due to its higher porosity and lower density. It also indicates that most of the oil is adsorbed at the early stage of the process (within a few minutes) and, afterward, a small amount of oil will be adsorbed.
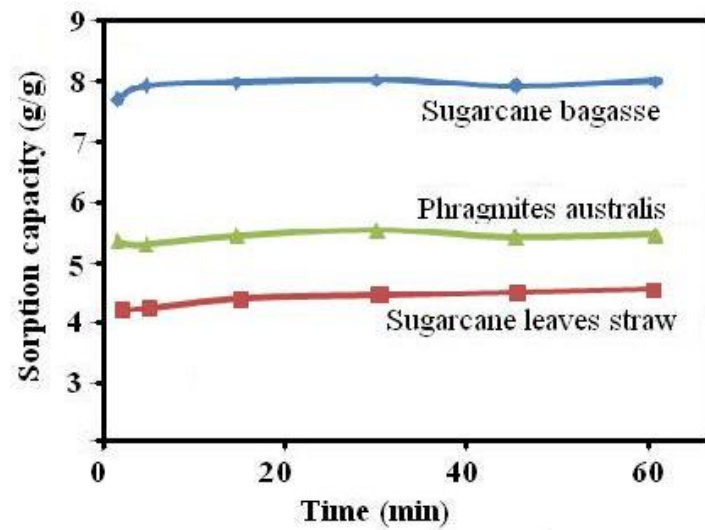
Figure 2
Effect of contact time on oil sorption in the dry system for the three sorbents

Due to its higher oil sorption capacity, sugarcane bagasse was selected as the main sorbent and its properties were determined by using FTIR. The effects of particle size and contact time on sorbent absorption capacity were also evaluated in this investigation.

Figure 3 shows the sizes of the prepared raw bagasse particles by using different sieves. Six mesh numbers of 8, 10, 18, 20, 30, and 60 were used herein. The larger bagasse particles belong to a lower mesh number as can be seen from Figure 3.

Figure 3
Effect of sieve size on the particle size of raw bagasse passing through the sieve

Table 3 tabulates the bulk density and true density of raw sugarcane bagasse at different particle sizes according to ASTM D2854-96 and ASTM D854-02.

Table 3
Bulk and particle densities of investigated raw bagasse at different particle sizes

| Sorbent name: Raw bagasse	Bulk density (g/cm^3)	Particle density (g/cm^3)
Mesh size 10	0.174	0.65
Mesh size 18	0.141	0.68
Mesh size 20	0.108	0.68
Mesh size 30	0.101	0.71
Mesh size 60	0.093	1.06
Microsize	0.083	1.18

The identification of the important bands seen in the FTIR diagram (Figure 4) is according to the previous studies of sugarcane bagasse (Brandão et al., 2010) and banana trunk fibers (Sathasivam and Haris, 2010).

In Figure 4, the strong signal at about 3412 cm^{-1} is attributed to the stretching vibrations of hydroxyl groups present in cellulose, hemicellulose, and the lignin of sugarcane bagasse. The medium signal, between 1500 cm^{-1} and 1750 cm^{-1}, is ascribed to carboxylic groups present in lignin and hemicellulose. The bands at 2920.26 cm^{-1} and 2850 cm^{-1} corresponds to asymmetric C–H and symmetric C–H stretching of CH$_2$-groups respectively. The band at 1248.38 cm^{-1} is due to C–O stretching in hemicellulose.
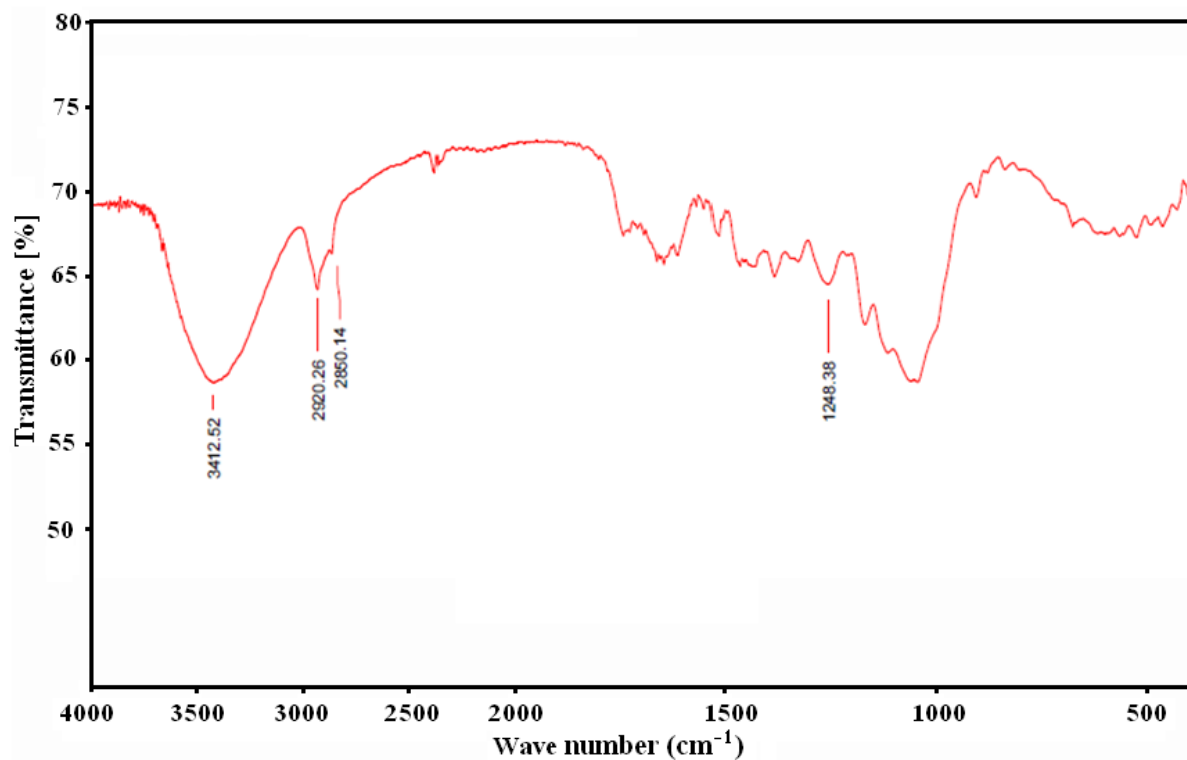
Figure 4
FTIR spectra of raw sugarcane bagasse

Figure 5 shows the effect of sorption time (2-30 min) on crude oil sorption capacity in the dry system for bagasse with different particle sizes. It is obvious from Figure 5 that the sorption capacity of bagasse with different particle sizes increases with time. The time required to reach the maximum sorption capacity depends on the particle size. As the particle size increases, the time required for the maximum sorption rises. The smallest particle size investigated (mesh 30-60) requires only a few minutes, whereas it takes much longer for the largest particle size investigated (mesh 8-10) to reach the maximum sorption. In large particles, the time of oil diffusion into particles becomes an important factor and it takes bagasse particles a long time to become saturated with oil; however, this time is much shorter for small particles.
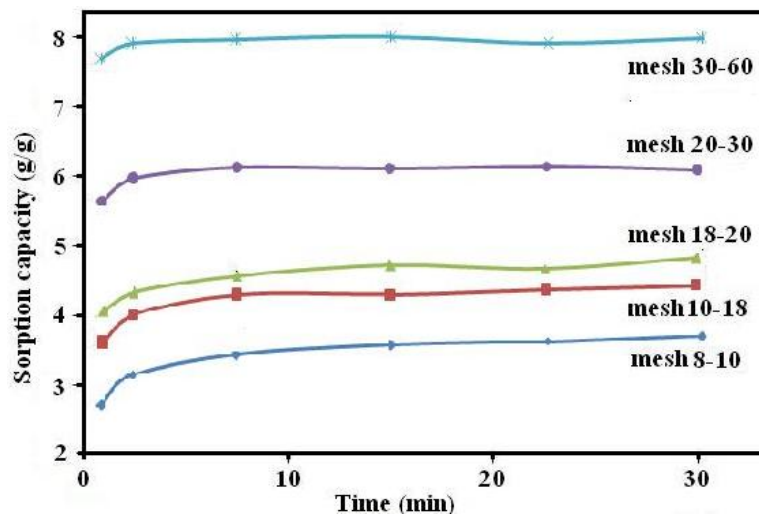
Figure 5
Effect of contact time and particle size on oil sorption by bagasse in the dry system

Figure 6 illustrates the effect of bagasse particle size on oil sorption capacity at a constant sorption time of 15 minutes. It shows that decreasing the average particle size increases the oil sorption capacity, and the maximum is reached at an average particle size of 0.2 mm. However, decreasing further the average particle size reduces the oil sorption capacity.
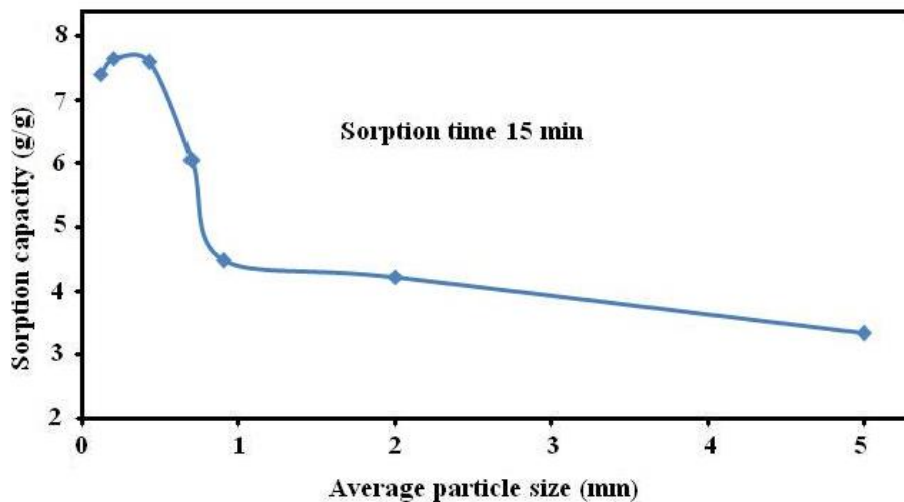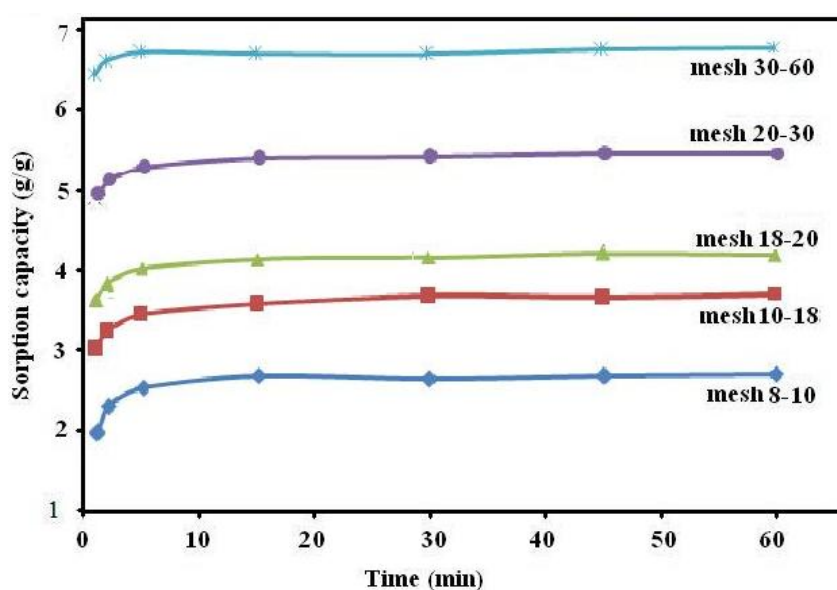

Figure 6
Effect of particle size on the oil sorption at a sorption time of 15 minutes

A decrease in bagasse particle size has a higher effect on oil sorption capacity for smaller particles. This can be attributed to the fibrous form of the sorbent, which causes the particles with different fiber lengths and equal diameter to pass through the sieve. This results in the formation of heterogeneous and non-uniform particles in large sieves and the number of larger particles in the unit of mass is low due to higher bulk density; therefore, the interfacial area (area/volume) becomes smaller. A rise in oil sorption capacity by decreasing the average particle size from 5 mm to 0.2 mm may be ascribed to an increase in interfacial area. For particles smaller than 1 mm, the effect of decreasing size is higher because particles are more homogenous in this size range and the number of particles rises more considerably.

Figure 7 shows the effect of sorption time on oil sorption at different sorbent particle sizes for a crude oil layer on the surface of artificial sea water. Seven (7) grams of crude oil was added to 150 ml water to form an oil layer with an approximate thickness of 2.4 mm and then 1 gram sorbent was spread over the oil surface. As can be inferred from Figure 7, the maximum sorption capacity is reached after about 5 min, which indicates that the sorption phenomenon is fast. Comparing the sorption capacity of bagasse in the dry system (Figure 5) with that of bagasse in the oil layer system (Figure 7) shows that the dry system (only oil) has a higher capacity compared to the oil layer system. This may be related to some water sorption by bagasse; the bagasse is slightly water-philic.
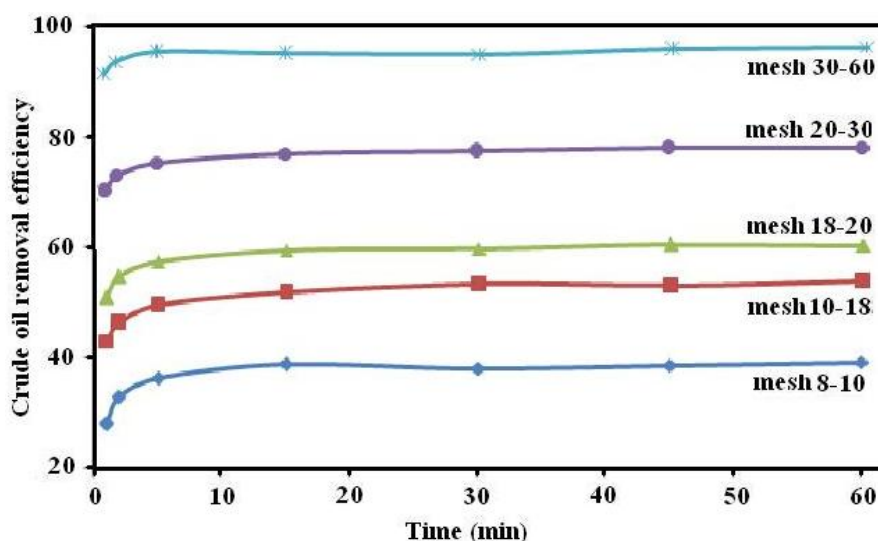

Figure 7
Effects of particle size and sorption time on the oil sorption for a crude oil layer with a thickness of 2.4 mm

The effects of sorption time and particle size on the oil removal efficiency by raw bagasse are shown in Figure 8. Reducing the particle size of raw bagasse increases the oil removal efficiency, which can be attributed to the higher interfacial area of smaller particles. The raw bagasse with a mesh size of 60 has the sorption efficiency of 96% for the crude oil layer over the saline water surface. As the sorption process time rises, the oil removal also increases. However, the efficiency of oil removal is much higher at the early stages of the sorption.

Figure 8
Effects of particle size and sorption time on oil removal efficiency

4. Conclusions

The present study compared the oil sorption capacity of phragmites australis, sugarcane leaves straw, and sugarcane bagasse in the dry system and sugarcane bagasse was then used in different particle sizes to remove a crude oil layer dispersed over artificial seawater. The following conclusions can be drawn from the results obtained:

1- The maximum adsorption capacity of phragmites australis for the dry system was equal to about 4.4 gram crude oil per gram sorbent;
2- The maximum adsorption capacity of sugarcane leaves straw for the dry system was about 5.5 gram crude oil per gram sorbent;
3- The maximum adsorption capacity of raw bagasse for the dry system was obtained to be about 8 gram crude oil per gram sorbent;
4- The bagasse can be applied to effectively remove crude oil in crude oil layer pollution from marine environments;
5- Particle size effect was also evaluated and it was shown that the sorption capacity improved with decreasing particle size due to increasing the surface area;
6- The maximum adsorption capacity of raw bagasse for crude oil layer was equal to about 6.6 gram crude oil per gram sorbent. Optimal sorption time was observed at about 5 minutes.

Acknowledgements

Nomenclature

APS	: Average particle size
BTEX	: Benzene toluene ethylbenzene xylene
CCD	: Central composite design
COD	: Chemical oxygen demand
FTIR	: Fourier-transform infrared
MTBE	: Methyl tert-butyl ether
RSB	: Raw sugarcane bagasse

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