

## **BENEFITS OF AGRICULTURAL WASTE FROM RICE PLANT 2: COMPARATIVE ABSORPTION OF SPILL OIL FROM FRESH AND MARINE WATER USING RICE STRAW**

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### **ABSTRACT**

Spill oil released to fresh and marine environment through accidental spillage pipes, tankers, ships, offshore platforms. In general wherever oil is produced, transported, stored and used there will be the risk of a spillage. The presence of dissolved crude oil in water aquatic life causes serious damage to the environment and marine life. Treatment of oil spills remains a challenge to environmental scientists and technologists. Nowadays natural sorbents are applied as a single solution for oil spills since this technique is effective, rapid and cost saving for cleaning these pollutions and reduce environmental hazards. This study was carried out to investigate the potential of raw rice straw to remove the spill oil. In this respect an attempt was done to provide an efficient, easily deployable method of cleaning up oil spills and reusing of the oil again. It is important to provide a safe system for oil removal and recovery. The results presented and discussed in this work pointed the efficiencies of different sizes and weights of rice straw in removing of oil spill are very different. Removal of oil spill from polluted water (marine or fresh) using different size of rice straw was observed in the following order: medium > small > very small > long. Removal of oil spill from polluted water (marine or fresh) using different weights of rice straw was observed in the following order: 10.0 g > 8.0 g > 6.0 g > 12.0 g > 4.0 g > 2.0 g. Rice straw at 10.0 g weight achieved a maximum removal of oil spill. It will provide a cheap way of cleaning oily contaminated water and environment, thus safeguarding human health and aquatic life.

**Keywords:** Used oil, Sorption capacity, Sorbent, adsorption, Rice straw.

### **INTRODUCTION**

Water is the main living part of all creatures and has covered 70% of the earth and is being polluted with many activities of human including urban, agricultural and industrial. Water protection must be one of the major topics in our life because we depend on water in our life. According to declaration of World Health Organization (2012), about one billion people in the world do not have access to clean drinking water. Every year, about 800 million people are suffering from many kinds of diseases resulting from drinking polluted water (Behnood *et al.* 2013). Therefore, water pollution problem is very important and appropriate planning and necessary activities should be prepared to avoid and reduce this pollution. One of the main sources of water contamination is oil spills or oily waste waters. Oils and petroleum products polluted all sources of water such as seas, oceans, rivers or underground waters. Currently oil spills are a chief problem in the oceans and seas as a

result of their environmental and economical influence (Annunciado and Sydenstricker 2005). Oil spills may be due to discharge of crude oil or its derived products such as gasoline, diesel or machine oil from tankers, ships, offshore platforms, or heavier fuels used by large ships, or accidents in pipe lines or production process, as well as spills of other oily waste waters such as produced water, and ballast water. Crude oil spilt in the marine environment undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photo-chemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration, etc. (Jordan and Payne, 1980). These physico-chemical changes enhance oil dissolution in seawater (Payne and Phillips, 1985). The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. The main limitations of some of these techniques are their high cost and inefficient trace level adsorption (Wardley-Smith, 1983). Also most of the dispersants are often inflammable and cause health hazards to the operators and potential damage to fowl, fish and marine mammals. They can also lead to fouling of shorelines and contamination of drinking water sources (NRC, 1989). Several methods used in the past to address the problems of oil spillage include: burning the oil with wicking agents; disposing of oil with detergent, graphite, and chalk; and using polymeric foams and other absorbents (Imevbore and Ekundayo 1987; Ebewele and Dzung 1990). Of all these methods, using recycled rubber from scrap tires as an absorbent has shown encouraging promise in terms of oil absorption from water surfaces (Aisien *et al.* 2003). However, these studies have been of limited nature serving only to highlight the potential of the concept. In recent years, a number of natural biodegradable sorbents have been found as one of the most cost-effective and capable means for the oil spill cleanup and a number of works have been studied for utilizing these materials in the removal of oil spill, e.g., barley straw (Husseien *et al.* 2009a), rice husk ash (Vlaev *et al.* 2011), peat-based sorbents (Cojocar *et al.* 2011), fatty acid grafted sawdust (Shashwat, *et al.* 2006), carbonized bagasse (Husseien *et al.* 2009b), and acetylated bagasse (Xiao-Feng *et al.* 2003) which can be excellent sorbents (She *et al.* 2010). The aim of this work is to study the oil sorption from aqueous medium by raw rice straw and not only to provide an environmentally acceptable method of cleaning up oil spill, but also get an applicable technique which allows its recovery.

## **MATERIALS AND METHODS**

### **Sorbent and oil properties**

In this study the raw rice straw was selected as a natural organic sorbent. This sorbent was used in different particle sizes and different contact time of existence in water was studied. Crude oil had a specific gravity of 0.86 at 15°C was obtained from Shell Gas Station El Haram, Giza, Egypt. Raw rice straw was obtained from a roadside Nubareia Research Station (El-Behira Governorate).

### **Rice straw preparation**

The prepared rice straw after being transferred to the laboratory, it was washed for several times with tap water and then dried in open air under sunshine (Behnood *et al.* 2013). This rice straw was crushed with a vegetable crusher to different sizes (1.0 mm, 1.5 mm, 4.0 mm and 4-10 cm). These sorbents was washed again with distillate water and was dried in oven at 60°C for 10 hours, then used as sorbent for crude oil layer Figure (1).

### **Oil sorption Studies**

Sorption experiments were done for marine and fresh water. For crude oil layer sorption, 1000 ml of fresh or artificial sea water (35.0 g Na Cl /1.0 L water) was put in 2 L beaker. Crude oil (425 gm) was added to form an oil layer (250 ml) with a specified thickness (4 cm). Then, rice straw (10 gm) was added in a cotton fiber bag on the surface. After certain sorption times (2, 4, 6, 8, 10, and 12 min) sorbent was removed with a net that was hanged over the beaker for 5 min to provide the falling down of crude oil that was not adsorbed. The remaining oil was separated from the water and its weight was recorded and then returns the remaining oil into the water for sorption experiments again. Hexane was used as the carrier solvent (Husseien *et al.* 2011). The sorption capacity was calculated using this equation (Behnood *et al.* 2013).

Oil sorption capacity = weight of adsorbed oil / weight of sorbent

All tests were triplicate and the average of the three runs was taken for calculation. If the value of any run deviates by more than 15% from the mean of three runs, the results were rejected and the test was repeated with three new specimens.

### **Fourier Transform Infrared Spectroscopy (FTIR)**

The dried rice straw sample was embedded in KBr pellets and analyzed with a Shimadzu FTIR spectrometer (model 8201PC). The spectra were recorded in the absorption band mode, in the 4000-400 cm<sup>-1</sup> range.



**Figure 1: Raw rice straw with different particles size**

## RESULTS AND DISCUSSION

### FTIR Spectra

The FTIR spectrum (Figure 2) of raw rice straw shows strong bands at  $3352\text{ cm}^{-1}$  due to -OH stretching presented in cellulose. The band at  $2904\text{ cm}^{-1}$  corresponds to C-H asymmetric stretching of -CH<sub>2</sub>- groups. The band at  $1645\text{ cm}^{-1}$  is attributed to H-O-H bending and the bands at  $2372\text{ cm}^{-1}$  are attributed to -OH stretching (Nakanishi and Solomon, 1977).

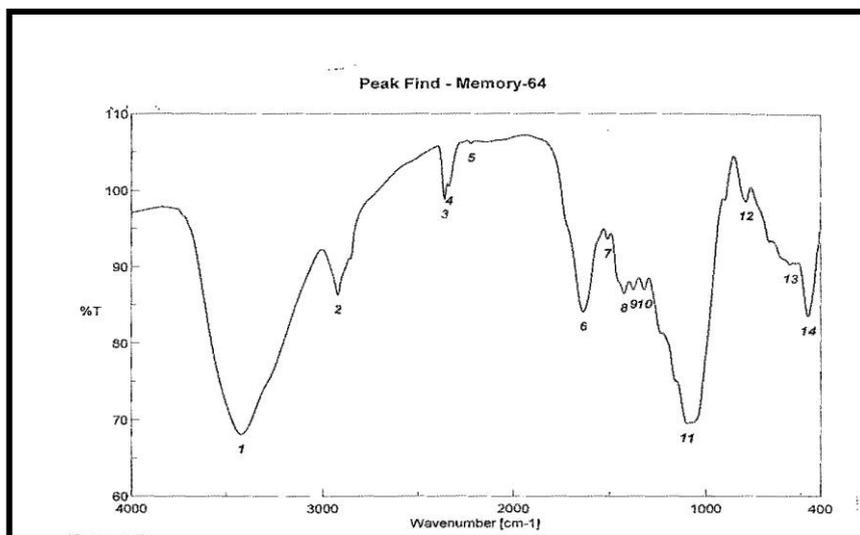


Figure 2: Raw rice straw FTIR

### Effect of different sizes of rice straw on sorption of crude oil from marine water

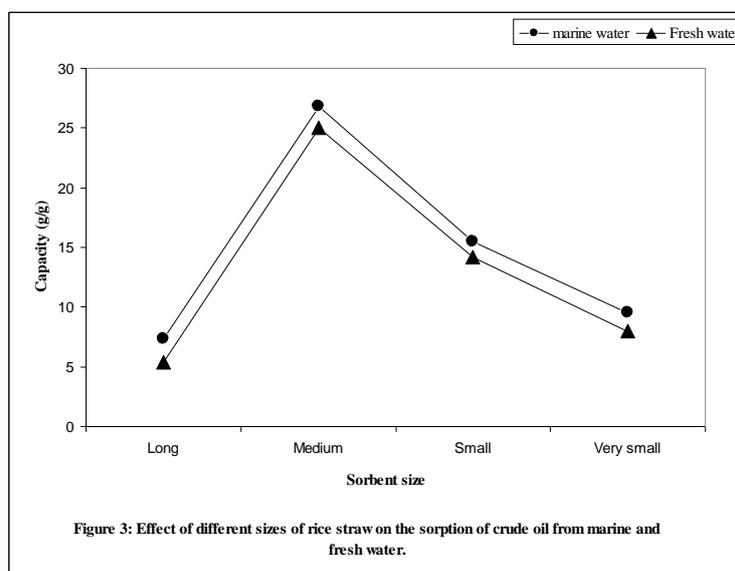
Data of the effect of different sizes (1.0 mm, 1.5 mm, 4.0 mm and 4-10 cm) of rice straw on sorption of crude oil from marine water are presented in Table 1. Data show that all sizes under investigation (1.0 mm, 1.5 mm, 4.0 mm and 4-10 cm) decreased oil film thickness from fresh water. Maximum decline of oil film thickness was recorded when the size of rice straw was at a medium size. Percentage of residual oil at different sizes (long, medium, small, and very small) reached 82.9, 36.9, 63.5, and 77.65%, respectively. At the same treatment, the percentage of oil removed at different sizes (long, medium, small, and very small) reached 17.2, 63.1, 36.5, and 22.4%, respectively. The highest removal for oil was observed at medium size. The same results were also observed with the sorption capacity. Figure 3 showed that the sorption capacity of oil from marine water. The maximum value was observed at medium size. The increasing of sorption capacity at different sizes was in the following order: medium > small > very small > long.

**Effect of different sizes of rice straw on sorption of crude oil from fresh water**

Applying different sizes from rice straw to removal oil from polluted fresh water are presented in Table 1. Percentage of residual oil at different sizes (long, medium, small, and very small) reached 87.1, 41.2, 66.6, and 81.2%, respectively. At the same treatment, the percentage of oil removed at different sizes (long, medium, small, and very small) reached 12.9, 58.4, 33.4, and 18.8%, respectively. The highest removal for oil was observed at medium size also. Figure 3 showed that the sorption capacity of oil from fresh water. The maximum value of sorption capacity was recorded at a medium size. The increasing of sorption capacity at different sizes was in the following order: medium > small > very small > long.

**Table 1: Effect of different sizes of rice straw on sorption of crude oil from marine and fresh water**

Sorbent size	Sorbent weight (g)	Weight of oil (g)	Sorbent weight after (g)	Amount of removal (g)	Residual (g)	Removal %
Marine water						
Long	10	425	83.6	73.6	351.4	17.2
Medium			278.2	268.2	156.8	63.1
Small			165.0	155.0	270.0	36.5
Very small			105.0	95.0	330.0	22.4
Fresh water						
Long	10	425	64.8	54.8	370.2	12.9
Medium			260.0	250.0	175.0	58.8
Small			152.0	142.0	283.0	33.4
Very small			90.0	80.0	345.0	18.8



**Effect of different weights of rice straw on sorption of crude oil from marine water**

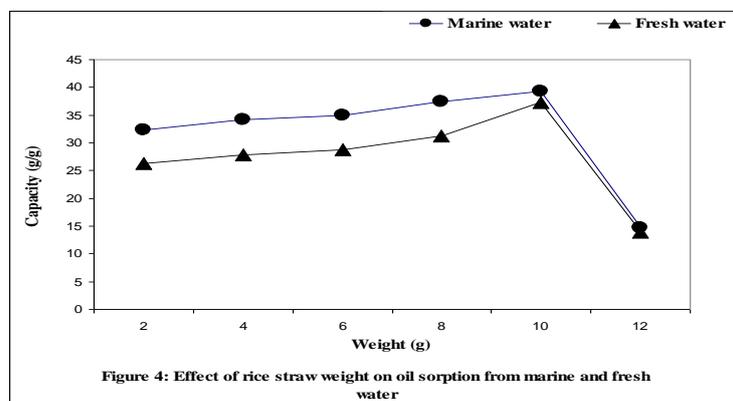
**In medium size (4.0 mm)**

Sorption of oil from marine using rice straw with different weights (2, 4, 6, 8, 10, and 12 g) is given in table 2. This showed that the efficacies of all weights were different. Percentage of residual oil at different weights (2, 4, 6, 8, 10, and 12 g) reached 84.7, 67.9, 50.6, 29.4, 7.43 and 58.4%, respectively. At the same treatment, the percentage of oil removed at different weights reached 17.9, 32.1, 49.4, 70.6, 92.6, and 41.6 %, respectively. The highest removal for oil was observed at 10 g weight. Also the results indicated that the sorption capacity (figure 4) is enhanced by increase the weight of sorbent till it reaches the maximum value at 10 g of rice straw. On the other hand, minimum decline of removal oil from marine water using rice straw at weight 12 g. Sorption capacity at different weight (2, 4, 6, 8, 10, and 12 g) reached 32.3, 34.1, 35.0, 37.5, 39.3, and 14.7, respectively.

**Effect of different weights of rice straw on sorption of crude oil from fresh water**

**In medium size**

Removal of oil from fresh using rice straw (4 mm) with different weights (2, 4, 6, 8, 10, and 12 g) is presented in table 2. Percentage of residual oil at different weights (2, 4, 6, 8, 10, and 12 g) reached 87.6, 73.8, 59.4, 41.2, 12.4 and 60.7%, respectively. The percentage of oil removed at different sizes reached 12.4, 26.2, 40.6, 58.8, 87.5 and 39.3 %, respectively. Maximum removal for oil was observed by using rice straw with 10 g weight. The results indicated that the sorption capacity (figure 4) is enhanced by increase the weight of sorbent till it reaches the maximum value at 10 g of rice straw. On the other hand, minimum decline of removal oil from fresh water using rice straw at weight 12 g. The sorption capacity increases with the sorbent thickness until it reaches a maximum of 10 g of rice straw. Sorption capacity at different weight (2, 4, 6, 8, 10, and 12 g) reached 26.3, 27.8, 28.8, 31.3, 37.2, and 13.9, respectively.

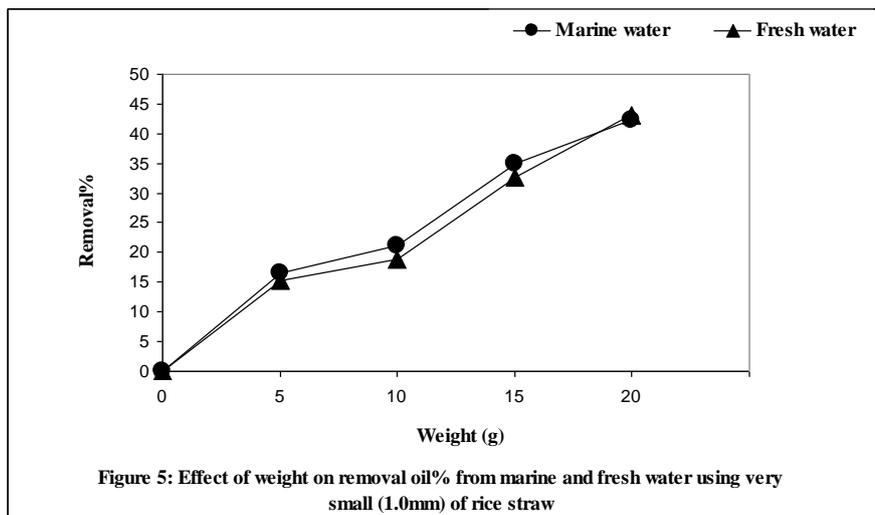


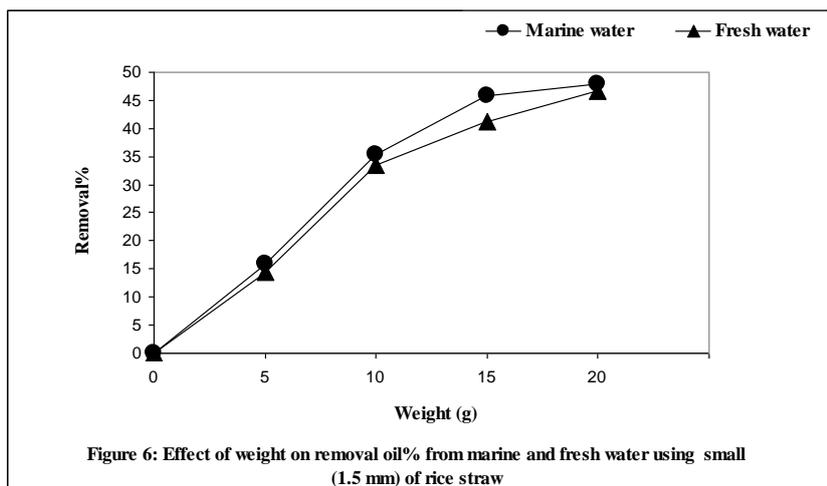
**Table 2: Effect of rice straw weight on oil sorption from marine and fresh water**

Sorbent weight before (g)	Weight of oil (g)	Sorbent weight after (g)	Amount of removal (g)	Residual (g)	Removal %
Marine water					
2.0	425	66.6	64.6	360.4	17.9
4.0		140.5	136.5	288.5	32.1
6.0		216.0	210.0	215.0	49.4
8.0		308.0	300.0	125.0	70.6
10.0		403.4	393.4	31.6	92.6
12.0		188.6	176.6	248.4	41.6
Fresh water					
2.0	425	54.6	52.6	372.4	12.4
4.0		115.2	111.2	313.8	26.2
6.0		178.6	172.6	252.4	40.6
8.0		258.0	250.0	175.0	58.8
10.0		382.0	372.0	53.0	87.5
12.0		179.2	167.2	257.8	39.3

**In small and very small sizes**

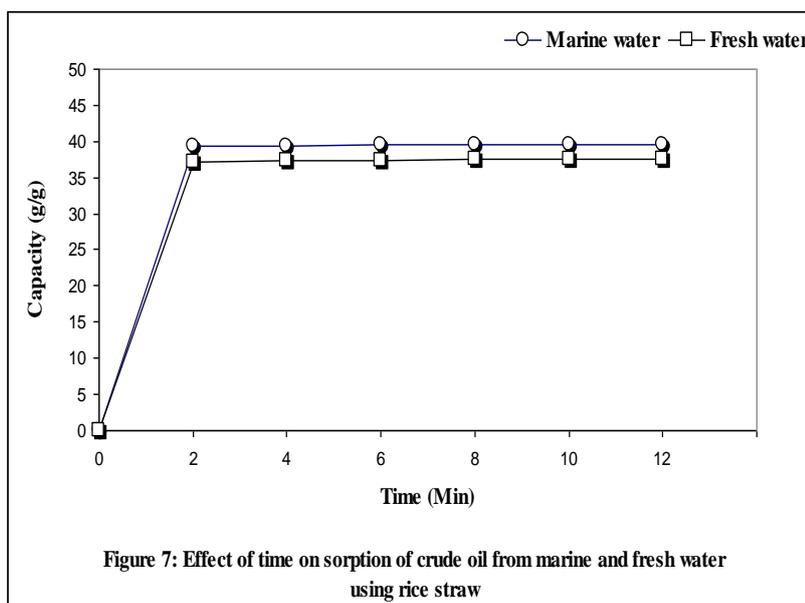
Concerning the removal of oil from marine and fresh water using small and very small sizes of rice straw with different weights (5, 10, 15, and 20 g) is shown in figure 5 and 6. Figures show that as the weight of the rice straw increases the removal oil % increases till it reaches at a maximum value.





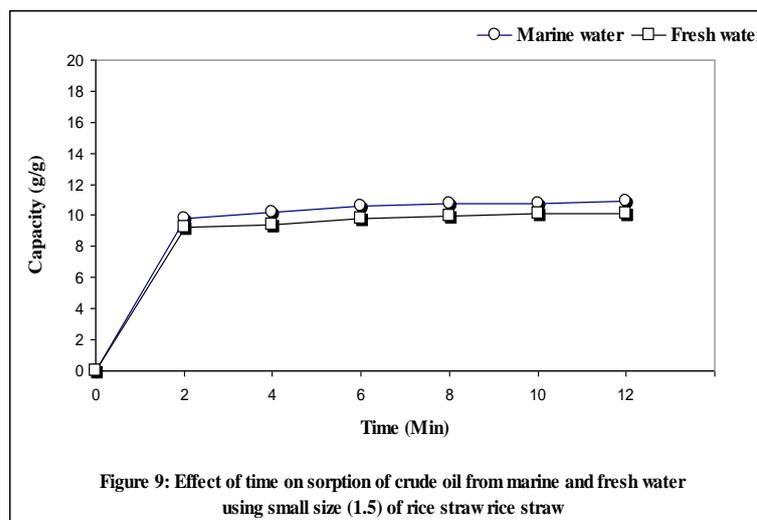
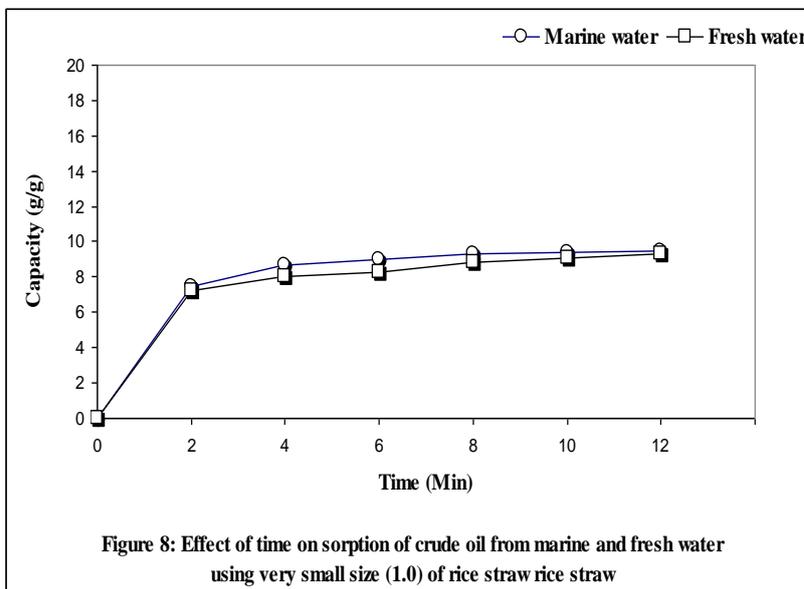
**Effect of time on sorption of crude oil from marine and fresh water using rice straw**  
**In medium size**

The effect of time on sorption of crude oil from marine and fresh water using 10 g of rice straw (medium size) in rice straw bag are presented in Figure 7. Data show that the maximum sorption capacity was observed at 2 min and very slightly increases with increasing the sorption time until it reach nearly constant value of sorption capacity irrespective to the soaking time.



**In small and very small sizes**

Regarding the effect of time on sorption of crude oil from marine and fresh water using 20 g of rice straw at two different small sizes (1.0 and 1.5 mm) in rice straw bag are presented in Figures 8 and 9. Figures shown that the sorption capacity increases with increasing the sorption time until it reaches a maximum.



Finally, from the previously obtained results, the efficiencies of different sizes and weights of rice straw in removing oil spill are very different.

Removal of oil spill from polluted water (marine or fresh) using different sizes of rice straw was observed in the following order: medium > small > very small > long. It worth mentioning, the medium size had a more efficiencies for removal spill oil from polluted water compared to other sizes. This result may be due to 1) the presence of surface activity 2) Function groups 3) heterogeneous particles that causes increases in spacing pores. On the other hand, the small and very small sizes had less efficiency for removal spill oil from polluted water. This result may be due to 1) homogenous particles that causes decreasing in spacing pores and increasing in bulk density (Behnood *et al.*, 2013). It is noteworthy; the efficiency of removal oil from polluted water increases with increasing weight till it reaches a maximum value at 10 g of medium size from rice straw. But the efficiency of removal oil from polluted water decreased at using 12 g of medium size from rice straw. This result may be due to a big thickness sorbent be able to increase compress to its original size so there was a tendency toward increased the falling down of crude oil and decreased the sorbent efficiency. Removal of oil spill from polluted water (marine or fresh) using different weights of rice straw was observed in the following order: 10.0 g > 8.0 g > 6.0 g > 12.0 g > 4.0 g > 2.0 g. Rice straw at 10.0 g weight achieved a maximum removal of oil spill. Regarding the efficiency of long size of rice straw, removal of spill oil from polluted water was lower compared to other sizes; this result may be due to the absences of surface activity and function groups.

The effect of water type on removal was observed. Oil is less dense than water and hence it floats on water. Besides, rice straw is hydrophobic. Consequently, the sorption of oil by rice straw is not hindered by the presence of either fresh water or marine water. The removal of oil spill from the marine water was higher than fresh water. It worth mention that rice straw can be reused for 2 and 3 times after removing oil from rice straw with organic solvent. These results are in agreement to Choi and Kwon (1993) and Deschamps *et al.* (2003). The sorbent is considered reusable if a loaded sorbent can easily compress or squeezed to its original size and shape even if there was a tendency toward decrease in sorbent efficiency with repeated sorption and desorption (Elsunni and Collier, 1996). Although many efficient ways to recover oil from the sorbent are available, compression of the sorbent is an economical and practical method.

Sorbents are the materials that soak up liquid. They can be used to recover oil through mechanisms of absorption, adsorption or both. Absorbents allow oil to penetrate into pore spaces in the material which are made of, while adsorbents attract oil to their surface but do not allow it to penetrate into the material. To be useful in combating oil spills, sorbents need to be both oleophilic and hydrophobic (Praba-Karan *et al.*, 2011)

### **Conclusions**

This research examined the efficiency of using raw rice straw of different sizes to remove crud oil by measuring its adsorption capacity in crude oil layer system. The following conclusions were found from this work:

1. The rice straw can be applied to effectively remove oil spill from fresh and marine water.
2. Maximum oil adsorption capacity of raw rice straw was obtained about 10 g form raw rice straw that reached 39.3 and 37.2 for marine and fresh water, respectively.
3. Particle size effect was evaluated and it was shown that the adsorption capacity improved with medium particle size.

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الاستفادة من المخلفات الزراعية لنبات الارز  
الجزء الثاني: الامتصاص النسبي للزيت المتسرب فى المياه البحرية والعذبة  
باستخدام قش الأرز  
شرين سامى احمد و جيهان حلمى عبد العزيز  
معهد بحوث الاراضى والمياه والبيئه

تسرب النفط إلى البيئة البحرية و العذبة والتسريب من خلال أنابيب وناقلات والسفن والمنصات البحرية و باستمرار أستخراج النفط ونقله وتخزينه واستخدامه سوف يكون هناك خطر حدوث تسرب. وجود النفط الخام في الحياة المائية يسبب أضرارا خطيرة على البيئة والحياة البحرية. علاج تسرب النفط لا يزال يمثل تحديا للعلماء البيئه والتكنولوجيا. في الوقت الحاضر يتم استخدام المواد الماصة الطبيعية لحل مشكلة انسكابات النفط لأن هذا الأسلوب هو فعال وسريع ويوفر التكاليف لتنظيف هذه الملوثات والحد من المخاطر البيئية. وقد أجريت هذه الدراسة لتحقيق إمكانات قش الأرز الخام لإزالة بقع الزيت المنسكبة. في هذا الصدد كانت هناك محاولة لتوفير أسلوب ذو كفاءة وفاعلية وسهل الانتشار لتنظيف الانسكابات النفطية وإعادة استخدام الزيت مرة أخرى. فمن الهام أن توفر نظام أمن لإزالة النفط وإعادة استخدامه. والنتائج التي عرضت ونوقشت في هذا البحث أشارت الى كفاءة استخدام احجام و أوزان مختلفة من قش الأرز في إزالة التسرب النفطى. وقد لوحظ إزالة التسرب النفطى من المياه الملوثة ( مياه مالحة أو مياه عذبه ) باستخدام أحجام مختلفة من قش الأرز بالترتيب التالي: المتوسطة < الصغيرة < صغيرة جدا < طويلة. وقد لوحظ إزالة التسرب النفطى من المياه الملوثة (البحرية أو العذبه) باستخدام أوزان مختلفة من قش الأرز بالترتيب التالي: 10.0 جم < 8.0 جم < 6.0 جم < 12.0 جم < 4.0 جم < 2.0 جم. كان لقش الأرز قدرة فائقة لأزالة تسرب النفط. وسوف يوفر وسيلة رخيصة لتنظيف المياه الملوثة الزيتية والبيئة، وبالتالي الحفاظ على صحة الإنسان والحياة المائية.

قام بتحكيم البحث

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