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OILY EFFLUENTS CLEANUP USING AN OIL FILTER

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ABSTRACT

Egypt is rich with a wide marine life which is ranked as one of the most sensitive environmental habitats in the world as well as a worldwide tourist attraction. However, there are major oil exploratory zones. The global oil spills can cause a lot of distress to affected communities. Accidental spills of oil can deposit very large volumes into a sea over a short period. The high concentrations of toxic components released from the oil, will affect the marine resources causing an ecological damage. So, quick removal of that pollution source and prevention of its distribution plays an important role in water purification and wastewater treatment engineering. Removal of oil by sorption has been observed to be one of the most effective techniques for complete removal of spilled oil under ambient conditions. In the present study, a crude oil was collected from Assuit oil refinery plant, Assuit, Egypt for the purpose of studying the treatment of effluent streams polluted with that oil. Rice straw, as an example for a natural agricultural residue, was used as an adsorbent. In addition, different methods were examined to explore the process of lignin removal from rice straw in order to maximize its efficiency in removing the oil. Besides, a synthetic sorbent material, namely, RP 18, produced by OPEC (Oil Pollution Environmental Control Ltd), was used for the object of comparison. Moreover, the combination between the synthetic and agricultural sorbents was studied. The process parameters such as the initial oil concentration in the effluent and the sorbent material surface area were optimized for the maximal removal rate. The results demonstrated that one gram of rice straw could absorb approximately 6.7 grams of oil to reach saturation. This corresponds to 12.16 grams for the synthetic sorbent. The rice straw removal efficiency reached 100% at low concentrations, however, the efficiency decreased after saturation. Finally, a new design criterion for an oil filter for marine pollution fighting was outlined.

Keywords

Oily wastewater; low-cost sorbent; Organic and synthetic sorbents; Rice straw; Chemical oxygen demand (COD); Oil filter design.

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1. INTRODUCTION

Crud petroleum oil and its products may travel thousands of miles and through dozens of hands before it reaches us. According to industry estimates, almost 80% of this world trade is moved by ships, making commercial marine shipping one of the cornerstones of the modern world economy. Oil spill is one of the major sources that contribute to environmental pollution. Oil spills have been a major cause of concern as they pose a danger to public health, devastate natural resources and disrupt the economy. Oil tankers are related to oil spilling as their cargo were spilled into the seas and oceans. However, the spills may be also due to any operations and accidents occurring in the oil industry. Spills can be caused by natural disasters like hurricanes and some oil that lies below the ocean floor and can seep into the ocean. Nevertheless, some spills are caused by man-made reasons such as the marine engines hydrocarbon emissions into the marine environment (Thomas et al., 1995; Lessard and Demarco, 2000) Each oil spill accident participates greatly in polluting the environment. Compared to other sources of pollution, oil has the added characteristic of quick spreading on the surface of water and covering large areas. Thus, this is necessitates a rapid technique for oily-water clean-up. Mechanical means of oil clean-up are common and have been used extensively; however, these methods are also less effective in removing the smaller oil droplets and emulsions (Portela et al., 2003; Li et al., 2006). Therefore, removing of oil by sorption has been observed to be one of the most effective techniques for complete removal of spilled oil under ambient condition. Adsorption, using a sorbent material, is often used as a secondary method for oil removal following gross oil removal, such as skimming.

Sorbents are materials that have the capability of absorbing both aqueous and oily fluids (Hyotylainen and Riekkola, 2008). The best sorbents are those composed of fine fibers with large surface areas. Optimum absorbency occurs when the fibers are fine and evenly spaced. Sorbents may be used for all types of oil. A survey on the literature shows that there is ample waste and low cost materials such as fly ash, peat, soil organic matter which can be exploited for simple, effective and inexpensive treatments of oil spillage (Wardley-Smith, 1983). A study performed by Choi and Cloud (1992) demonstrated that the oil values of kenaf core and fiber were similar to polypropylene web for heavy bunker oil. Bayat et al, 2005, studied the efficiency of three sorbents, polypropylene nonwoven web, rice hull, and bagase - with two different particle sizes- in terms of its oil sorption capacities and oil recovery. It was found that oil viscosity plays an important role in oil sorption by sorbents. All adsorbents used in their work could remove the oil from the surface of the water preferentially. Moriwaki et al., 2007 investigated the utilization of silkworm cocoon waste. The results show the high sorption capacity of the silkworm cocoon waste sorbent (42-52 goil/gsorbent for motor oil and 37- 60 goil/gsorbent for vegetable oil). The oil sorbet onto the material could be recovered by squeezing the sorbent, and the squeezed material showed an oil sorption capacity over15 goil/gsorbent. Barlianti and Wiloso (2007) applied the coir dust for remediating the contaminated oily wastewater. A natural sorbent, namely peats, was used by Bahadir and Duca (2009). Rice straw is a lingo-cellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) (Hills and Roberts, 1981). In Egypt, bulky amounts of rice straw are produced annually as a by-product of rice production. The smoke caused by open-field burning rice straw commonly results in serious air pollution and traffic troubles, hence new economical technologies for rice straw disposal and utilization must be developed.

Thus, the present investigation deals with oily water treatment through physical means; i.e., absorption; where both synthetic fiber (polymer) and agricultural wastes were used individually. Next a combined sorbent of both materials is used. This gave a comparative study for each system and led to a reliable determination for the efficiency of oil removal. The results illustrated a reasonable treatment technique using both sorbents and the process parameters were optimized. Subsequently, the experimental results led to a proposal for a filter design for the treatment of the oily wastewater.

2. Materials and Methods

Sorbent and tested oil

A crude oil from Assuit Oil Refinery Plant, Assuit, Egypt is used for the purpose of the study. The analysis of this crude oil is listed in Table 1. Two types of sorbent materials were used. A synthetic sorbent hydrophobic material, namely, RP 18, produced by OPEC (Oil Pollution Environmental Control Ltd), which mainly consists of polypropylene fiber and polyester yarn fibers coated with cationic emulsifiers. In addition, a natural hydrophobic rice straw was also applied. Turkey-Red oil is used to raise the efficiency of removing lignin from rice straw. It is prepared by treating Caster oil with sulphuric acid followed by washing and neutralization.

Treatments for improving the hydrophobicity of rice straw

Rice straw was collected from a local farm. The collected biomaterial was cut into segments of 10 cm length and washed with tap water to remove soil and dust, and then dried. There were two treatment methods for improving the hydrophobicity of rice straw by removing lignin, i.e. sodium hydroxide method and N-Bromo Succinimide (NBS) method. Sodium hydroxide method was applied by placing the rice straw in a 14 gm of NaOH (concentration, 20%) which is added to 420 ml water. This is enough to remove lignin from 70 gm rice straw. Heating was done by heating the mixture for one hour at 170ºC under pressure to remove lignin. Subsequently, the solid material is separated and washed by acetic acid to remove the un-reacted sodium hydroxide. Next, the solid material is dried at 60ºC in a furnace then weighed. The drying process is repeated until a constant weight is reached. NBS treatment was done based on (Raton, 1997) method, where 15 gm of dried rice straw is added to a 300 ml of concentrated acetic acid. Consequently, 1% of NBS is added and the solution is left for 3hours in a water bath (at 80ºC). The solid material is separated and washed by ethanol, after that it is dried for use.

Experimental Methodology

The experiments were performed in a batch mode at laboratory scale using a rectangular glass basin (26cm length; 13cm width and 6 cm depth). First, the polluted water was fed to the basin and the initial COD was recorded (see Figure 1). The agricultural sorbent material is prepared by sodium hydroxide treatment method since the preliminary study showed better results rather than the NBS method. Then the sorbent material, whatever agricultural or synthetic, is added to the oily water surface after its initial weight is recorded. The sorbent material is left for 5 minutes, according to preliminary tests, and then the sorbent material is raised from the effluent. Samples were taken to determine the degree of COD reduction from the wastewater. Finally, the relation between the initial and final values for COD is plotted.

Analytical Methods

The samples were analysed using a HACH machine (model HACH DR/2000) in order to measure the efficiency of the treatment process. HACH machine is simultaneously used for COD measuring. Three samples were taken and the average value is considered for plotting. In addition, a relation between the COD value and oil volume was plotted (Figure 2), to facilitate the oil volume estimation remaining in the aqueous solution after treatment using the COD readings.

3. Results and discussion

3.1. Oil sorption using a synthetic sorbent

3.1.1. Effect of initial oil concentration

The effect of the initial oil concentration in the oily wastewater was estimated by using different concentrations of (10, 20, 30, …… 140 ml/l). Pieces of synthetic sorbent (10cm × 12cm, weighing 6.841 gm) were used to affect the removal process. It is clear from Figure 3 that the mass transfer of oil to the sorbent decreases with the increase of initial oil concentration. This is illustrated by the fact that the oil removal in the initial period is due to adsorption only. An initial oil concentration of 10 ml/l water led to a final oil concentration of 0.802 ml/l, which means a percentage removal of 91.2%. However, this percentage decreased to 85% for 40 ml/l initial concentration. However, the percentage removal increased again for initial concentrations ranging from 50 to 80 ml/l. This could be because both adsorption and absorption take place and the removal efficiency reached 97.33% (for 50 ml/l initial concentration). Thereafter, the increasing in the final oil concentration is attributed to decreasing the removal efficiency which is due to the full saturation of the sorbent with oil.

3.1.2. Effect of sorbent area

Samples with two different surface areas of the synthetic sorbent materials were used (10cm × 12cm, weighing 6.841 gm) and (12cm × 20 cm, weighing 13.306 gm). Figure 4 is a graphical plot for the results obtained from applying sorbents with different areaa. When sorbent area increases the adsorption per unit area increases and saturation occurs at higher concentrations. Although, the saturation absorbency per unit area should be constant for a specified material, it is noticed that in the case of synthetic sorbent it increases with increasing the sorbent area. This is because increasing the area of the adsorbent material is accompanied by an increase in its peripheral area (edges).

3.2. Oil sorption capacity using agricultural sorbent (rice straw)

3.2.1. Effect of initial oil concentration

The plot in Figure 5 shows the effect of the initial oil concentration on the removal efficiency by using 5 gm rice straw as a sorbent material. The concentration of oil remaining in the

effluent is neglected in the initial stages and then it begins to increase linearly with time at initial oil concentration 40 ml/l water. This means that the rice straw is saturated with the oil at concentration 40 ml/l water. The removal efficiency reaches almost 100% at low initial oil concentrations and it keeps constant at this value till an initial concentration of 40 ml/l water, after which the efficiency begins to decrease. However, a removal efficiency of 43.08% was recorded for an initial concentration 90 ml/l. In addition, in order to determine the absorbency of rice straw, the mass of oil absorbed per unit mass of straw is determined (see Figure 5). The results clarify that saturation is reached at initial oil concentration 50 ml/l water (50 ml of oil weighs 43.25 gm). This is in accordance with the previous findings of Abdel-Aal et al. (2006) and Gong et al. (2006) in the treatment of dye-polluted water with rice straw.
Compared to the synthetic sorbent rice straw demonstrated higher efficiency of oil removal even with low initial oil concentrations. This may be due to the nature of the structure of rice straw as a fibrous material with capillary tubes that participate in oil removal.

3.2.2. Effect of sorbent weight

To investigate the effect of sorbent weight on the absorbency of the rice straw, the concentration of the former was varied and all the other parameters were kept constant. The results, illustrated in Figure 6, show that 5 gm of rice straw removes the oil completely from effluents of oil concentration ranging from 5 to 40 ppm. However, on increasing the concentration of oil after that, the amount of oil left in the effluent begins to increase slightly. In addition, two other concentrations of the sorbent materials were used, 10 and 15 gm. It is noticed from Figure 6, that the removal efficiency nearly reaches 100% when using 15 gm rice straw for the oil concentration ranging from 10 to 120 ml/l. However, the efficiency decreased drastically afterwards. This could be illustrated by the fact that the saturation of the sorbent with oil begins at a critical concentration. After that concentration the removal efficiency decreases. Moreover, this ability is almost the same when using different weights of rice straw. Furthermore, the enhancement of the adsorption process with higher amount of sorbent can be attributed to the increased surface area of sorbent and accessibility of more sorption sites (Karimia et al., In press).

3.3. Combination treatment

For increasing the oil sorption capacity of the sorbent, a combination treatment has been performed. Use of rice straw sorbent is combined with synthetic sorbent so as to investigate the effect of using combined sorbents on the removal efficiency of oil. Synthetic sorbent materials were used (surface area: 10cm $\times$ 12cm, weight 6.841 gm) as a bag and 5gm of rice straw is enclosed in it. The results in Figure 6 showed that the characteristics of absorbency of both sorbent are clear. When the initial oil concentration is low, the oil is not enough to reach the enclosed rice straw. Thus, only the synthetic fiber works. The concentration of oil left in the effluent decreases preliminary with increasing initial oil concentration and next it decreases to approach zero value. At this point, the synthetic sorbent is almost saturated with oil. Increasing the initial oil concentration above 40 ml oil/l water, results in increasing the amount of oil left in the effluent. A point is reached (at initial oil concentration 70 ml oil/l water), at which a drastic increase in the concentration of oil left is noticed. Although it is expected that the combined use of both sorbents may achieve an improved performance, however, this is not noticed practically. The outer encloser of synthetic fiber, when it reaches saturation with oil (at initial concentration of 40 ml/l), prevents reaching the oil to the interior containing rice straw. Thus, the concentration of oil remaining in the effluent keeps increasing.

4. Design development

The experimental results were used as a guide for designing oil pressurized vertical filter to be used for oily water clean-up (as shown in Figure 8). The cartridge media was categorized to be a synthetic or a rice straw sorbent. The maximum initial oil concentration from the conducted experiments was suggested to be 240 mg/l. While, the final oil concentration was assured in proportion to the Egyptian Environmental Law 93/1962 and its Decree No. 44/2000 (for oil and grease the concentration should not be higher than 0.1 ppm; COD is not exceeding 10 ppm (Badawy et al., 2009). Consequently, the preferable flow rate according to the preliminary experimental work is 5-12 l/s. However, the selected flow rate for the design criteria was 8 l/s. A time of five minutes was chosen as a retention time according to the experiments performed. Thus, the amount of water fed to the filter in 5 minutes is 2.64 m^3, whereas the safety factor is assumed to be 10%. Accordingly, the amount of accompanying oil might be calculated as the initial oil concentration multiplied by the amount of oil input in a minute, which is found to be 115.2 gm/min.

4.1 Synthetic sorbent cartridge

As previously illustrated by experiments, the synthetic sorbent may remove 200 mg oil from 240 mg/l and one gram of the synthetic sorbent adsorbed 12.16 gm oil. Thus, the mount of oil removed per minute will be 96 gm/min. Assume the sorbent cartridge will be changed after one day and the safety factor is 10%, hence (Assuming 3 shifts, each 8 hours):

$$Amount\ \ of\ \ oil\ \ removed\ \ in\ \ one\ \ day = 96 \times 60 \times 24 \times 1 \sim 138.24\ \ kg\ \ oil \tag{1}$$

Therefore, weight of synthetic sorbent needed to remove this oil is determined as:

$$Synthetic\ sorbent\ \ weight = (138.24/12.16) \times 1.1 \sim 12.5\ \ kg \tag{2}$$

As mentioned before the synthetic sorbent used is 10×12 cm with a weight 6.813 gm, consequently, the weight of unit area of the sorbent (cm^2) equals to 0.0568 gm. Thus, the area of sorbent needed is the total weight of sorbent needed per unit weight which equals to 220070.4 cm^2. In order to reach the best performance, this volume will be distributed as 30 layers of the sorbents with a layer thickness of 0.5 cm. Therefore, the area of one layer is 7335.68 cm^2. Since the sorbent will be in a cylindrical shape, the area might be:

$$Layer\ \ area = 2\pi rh = 7335.68 cm^2 \tag{3}$$

Where:

r: synthetic sorbent radius in the filter

h: synthetic sorbent height in the filter

Solving equation (3) with trial and error yields the following termination: the synthetic cartridge consists of a stainless steel bar screen with a diameter of 30 cm by comprising 30 layers of the sorbent with outer diameter 60 cm and a height of 78 cm.

The filter diameter is calculated to be:

$$\frac{\pi(60+y)^2 h_f}{4} = 2640000 \tag{4}$$

Where:

y: the inner filter diameter

h_f: filter height, where:

$$h_f = \text{carttridge height} + 10\ \text{cm (cartridge inserted at the top)} + 10\ \text{cm (cartridge inserted in the filter bath)} \quad (5)$$

Mathematical manipulation gives, filter diameter = 185 cm. Thus, filter design is:

Diameter= 185 cm,
Height = 98 cm,
Filter volume = 2.64 cm^3.

Calculation of the discharge pipe diameter is based on the input flow rate and is equal to 5 times of the output flow rate. In addition, the velocity is a linear velocity, which is constant. Thus, the radius of the discharge pipe will be ~ 6.7 cm.

4.1. Agricultural sorbent cartridge

Agricultural sorbent decreased the oil concentration in the effluent, as shown by experiments, from 40 mg/l to 0 mg/l. Furthermore, one gram of the agricultural sorbent adsorbed 6.7 kg. Thus, the amount of oil removed by the sorbent will be 27.648 gm/day and the amount of sorbent required per day is 4.126 kg. The same synthetic filter dimensions may be applied in this case since the water flow rate is constant. Thus, we can suggest that the agricultural sorbent cartridge consists of two stainless steel pipes with a 30 cm inner diameter and 60 cm outer one. However, the agricultural sorbent (hydrophobic rice straw) is located between those two pipes. The cartridge height is 78 cm.

4.2 Treatment of the waste disposal sorbent

Firstly, the inner pipe is moved out and the saturated sorbent is removed. Afterwards, the saturated sorbent is passed through three squeezing units in order to remove oil from it (as illustrated in Figure 9). Then, the squeezed sorbent is transferred to a tank containing a solvent. After that, it is passed between three squeezing units with the aim of removing solvent and oil, which is fed to an evaporator to separate oil and solvent for re-use. In addition, the treated synthetic sorbent is re-used again in filtration; however, the rice straw sorbent is used as a burning fuel.

5. Conclusions

Two types of sorbents, natural (rice straw) and synthetic (RP-18), were applied for oil removal from aqueous solution. This study confirmed that rice straw was an excellent sorbent for the oil removal at low initial oil concentrations. One gram of rice straw could absorb approximately 6.703 gm-oil to reach saturation. Practically, the combination between the two sorbent showed reversible results than expected as the outer enclosure of the synthetic fiber, after reaching saturation with oil, prevented the oil to reach the interior rice straw fibers. Finally, the design of oil filter cleanup unit for both sorbents cartridge was suggested.

References

[1] Abdel-Aal, S.E., Gad, Y.H., Dessouki, A. M., “Use of rice straw and radiation-modified maize starch/acrylonitrile in the treatment of wastewater”, J. Hazard. Mater., 2006, B129, 204–215.

[2] Badawy, M. I.; Rifaat Wahaab, A.; El-Kalliny, A. S.; “Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater”, J. Hazard. Mater., 2009, 167, 567–574.

[3] Bahadir, A. M.; Duca G., “Application of Low-Cost Sorbent for Oil Spill Sorption Using Response Surface Methodological Approach”, The Role of Ecological Chemistry in

Pollution Research and Sustainable Development, Springer Netherlands publisher, 2009, 109-118.
[4] Barlianti, V.; Wiloso, E.I.; “Physicochemical Treatment On Coir Dust To Improve Hydrophobicity And Oil Sorption Capacity”, Akta Kimindo, 3 (1) 2007, 21 – 26.
[5] Bayat, A.; Aghamiri, S. F.; Moheb, A.; Vakili-Nezhaad, G. R., “Oil Spill Cleanup from Sea Water by Sorbent Materials”, Chem. Eng. Technol., 2005, 28 (12), 1525 – 1528.
[6] Choi, H.; Cloud, R. M., “Natural Sorbents in Oil Spill Cleanup”, Environ. Sci. Technol., 1992, 26, 772-776.
[7] Hills D. I.; Roberts D. W., “Anaerobic digestion of dairy manure and field crop residues”, Agric. Waste, 1981, 3, 179-189.
[8] Hyotylainen, T.; Riekkola, M., “Sorbent- and liquid-phase microextraction techniques and membrane-assisted extraction in combination with gas chromatographic analysis”, A review, Analytica Chimica Acta, 2008, 614, 27-37.
[9] Karimia, M.; Entezari, M. H.; Chamsaza, M., “Sorption studies of nitrate ion by a modified beet residue in the presence and absence of ultrasound, Ultrasonics Sonochemistry”, In press, doi:10.1016/j.ultsonch.2009.12.002.
[10] Lessard R. R.; Demarco, G., “The Signifcance of Oil Spill Dispersants”, Spill Science & Technology Bulletin, 6 (1), 59-68, 2000.
[11] Li, Y. S.; Yan, L.; Xiang, C. B.; Hong, L. J., “Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes”, Desalination. 2006, 196, 76–83.
[12] Moriwaki, H.; Kitajima, S.; Kurashima, M.; Hagiwara, A.; Haraguchi, K.; Shirai, K.; Kanekatsu, R.; Kiguchi, K., “Utilization of silkworm cocoon waste as a sorbent for the removal of oil from water”, J. Hazard. Mater., 2009, 165(1-3), 266-270.
[13] Portela, J. R.; Sanchez-Oneto, J.; Lopez, J.; Nebot, E.; Ossa, E. M., “Hydrothermal oxidation of oily wastes: An alternative to conventional treatment methods”. Eng. Life Sci. 2003, 3(2), 85– 89.
[14] Raton, B., “Paper and composites from agro-based resources”, Lewis publisher, 403-425, 1997.
[15] Thomas, K.V.; Donkin P.; Rowland, S. J., “Toxicity enhancement of an aliphatic petrogenic unresolved complex mixture (UCM) by chemical oxidation”, Wat. Res., 1995, 29(I), 379-382.
[16] Wardley-Smith, J., “The control of oil pollution”, Graham and Trotman, Inc., Gaithersburg, MD pulisher, 1993, 39-145.
[17] Gong, R.; Jin, Y.; Chen, F.; Chen, J.; Liu, Z., “Enhanced malachite green removal from aqueous solution by citric acid modified rice straw”, J. Hazard. Mater., 2006, B137, 865–870.

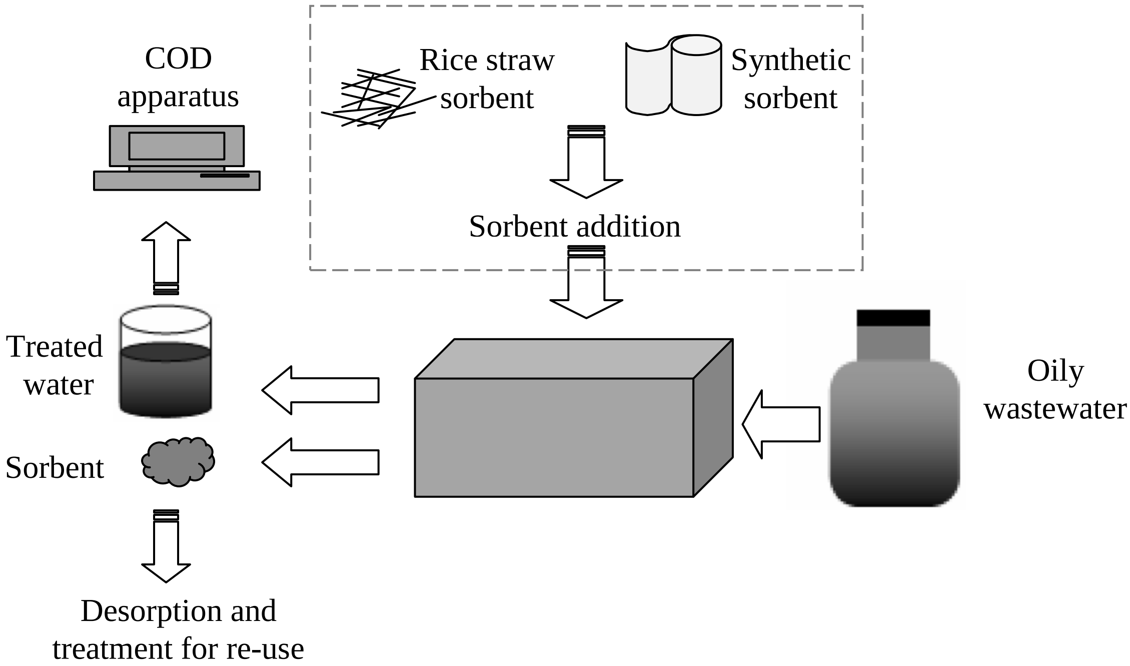


Figure 1: Scheme methodology of oil sorption treatment test

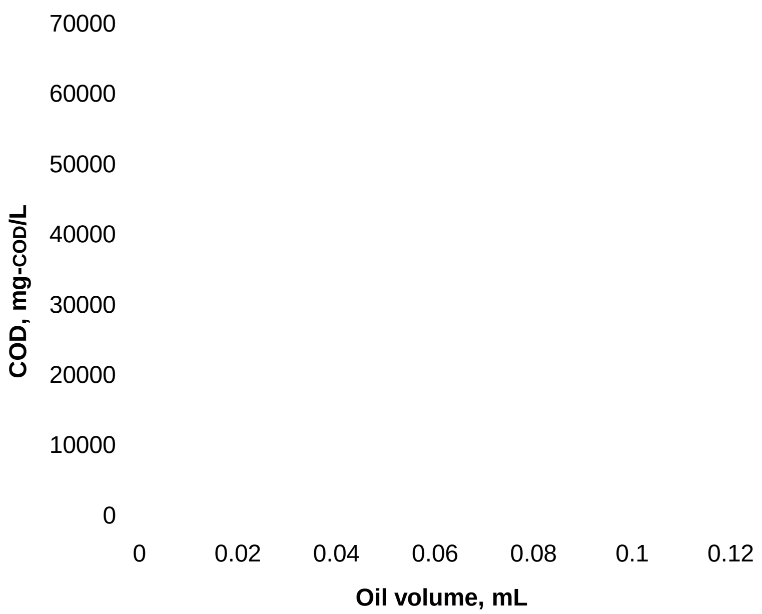


Figure 2: Plot of the measured COD values and initial oil volume

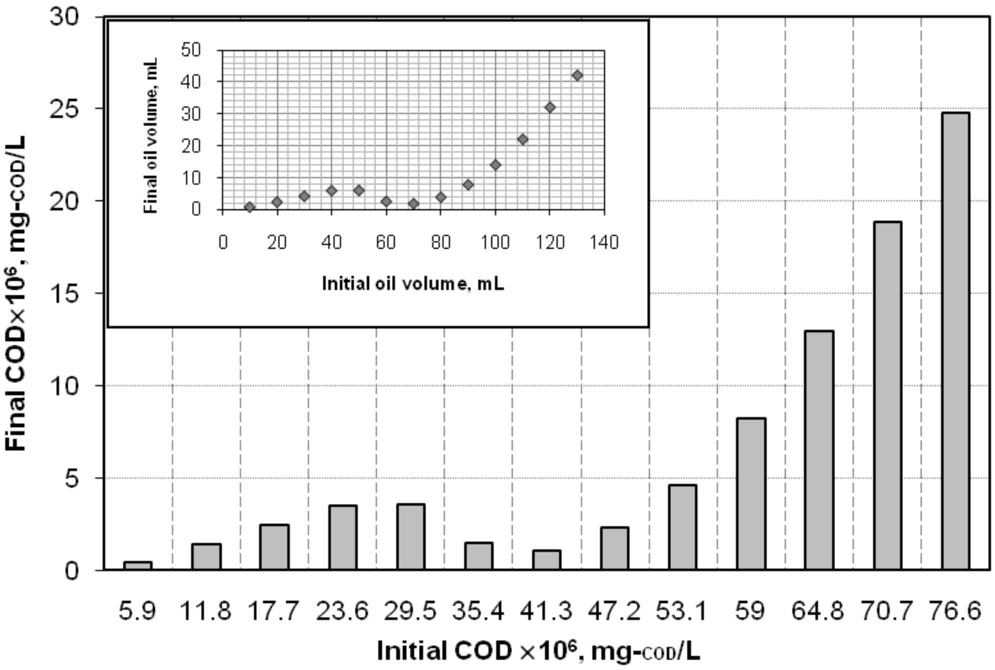


Figure 3: Effect of the initial oil concentration using synthetic sorbent

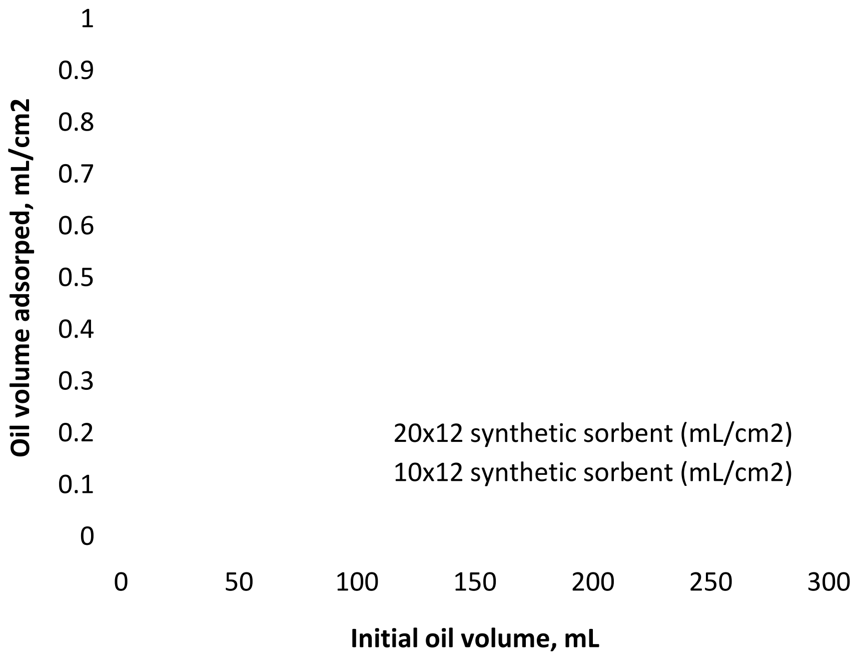


Figure 4: Effect of synthetic sorbent area

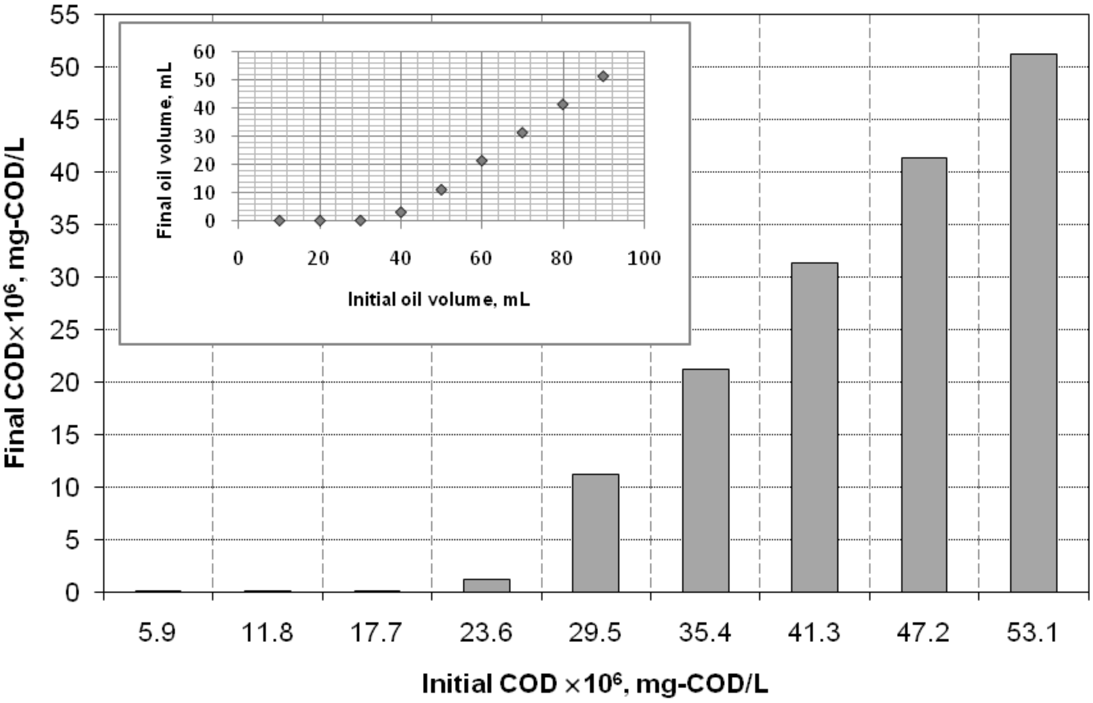


Figure 5: Effect of initial oil concentration using rice straw sorbent

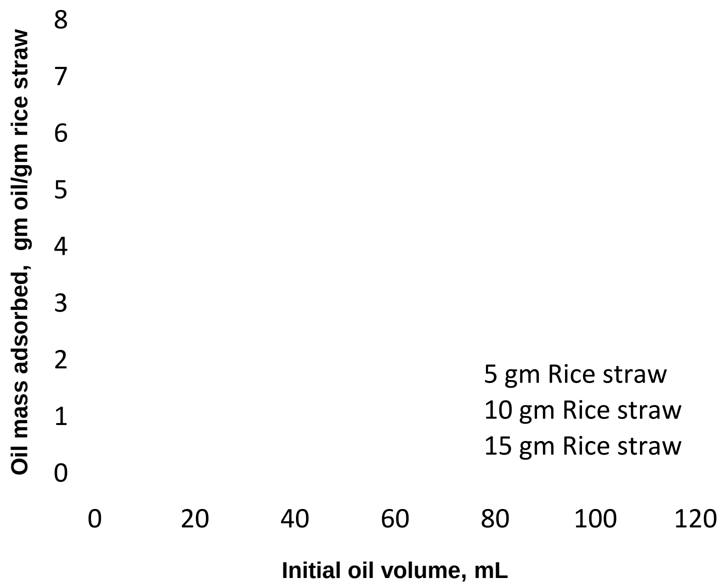


Figure 6: Effect of rice straw weight on the sorption of oil

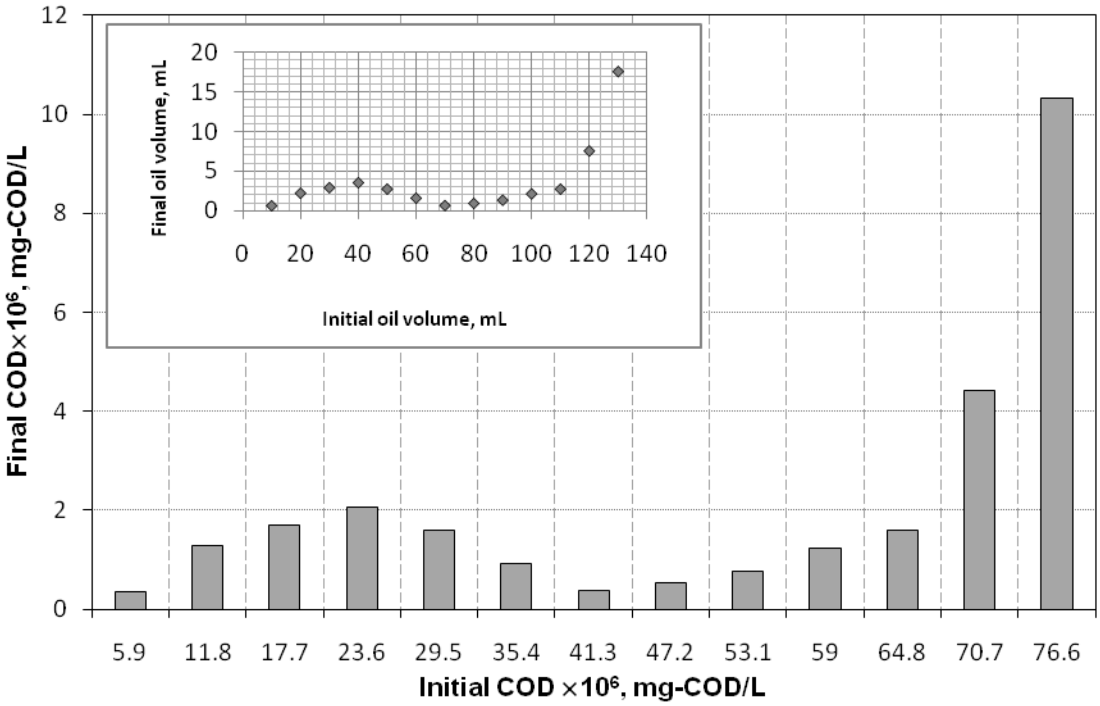
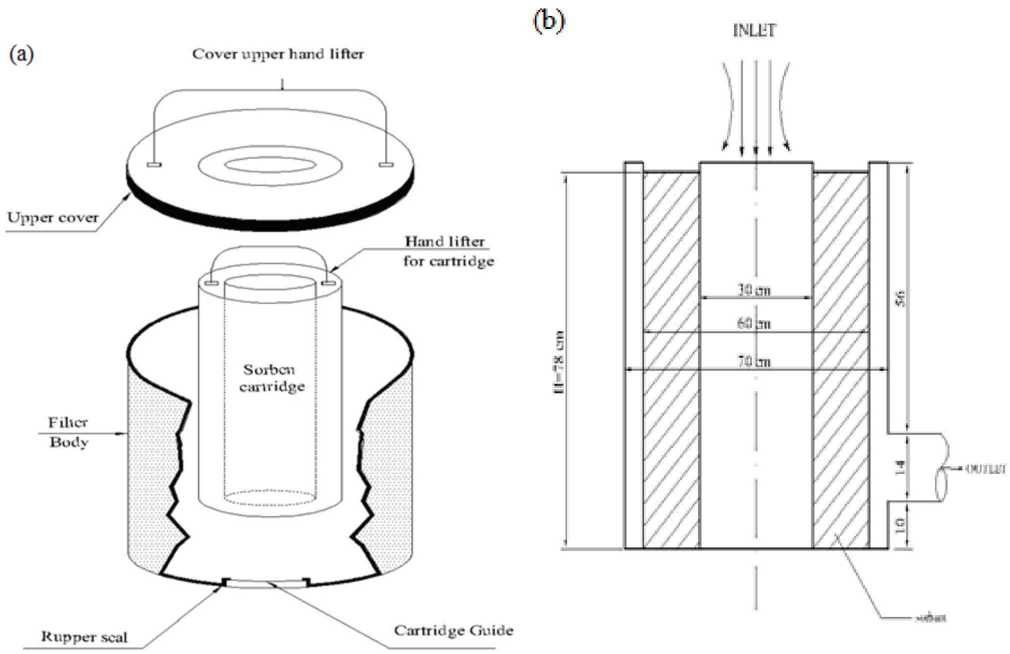


Figure 7: Effect of combined rice straw and synthetic sorbent on the oil removal



Figuer 8: Vertical oil filter cleanup: (a) Filter assembly and (b) Filer cross-section

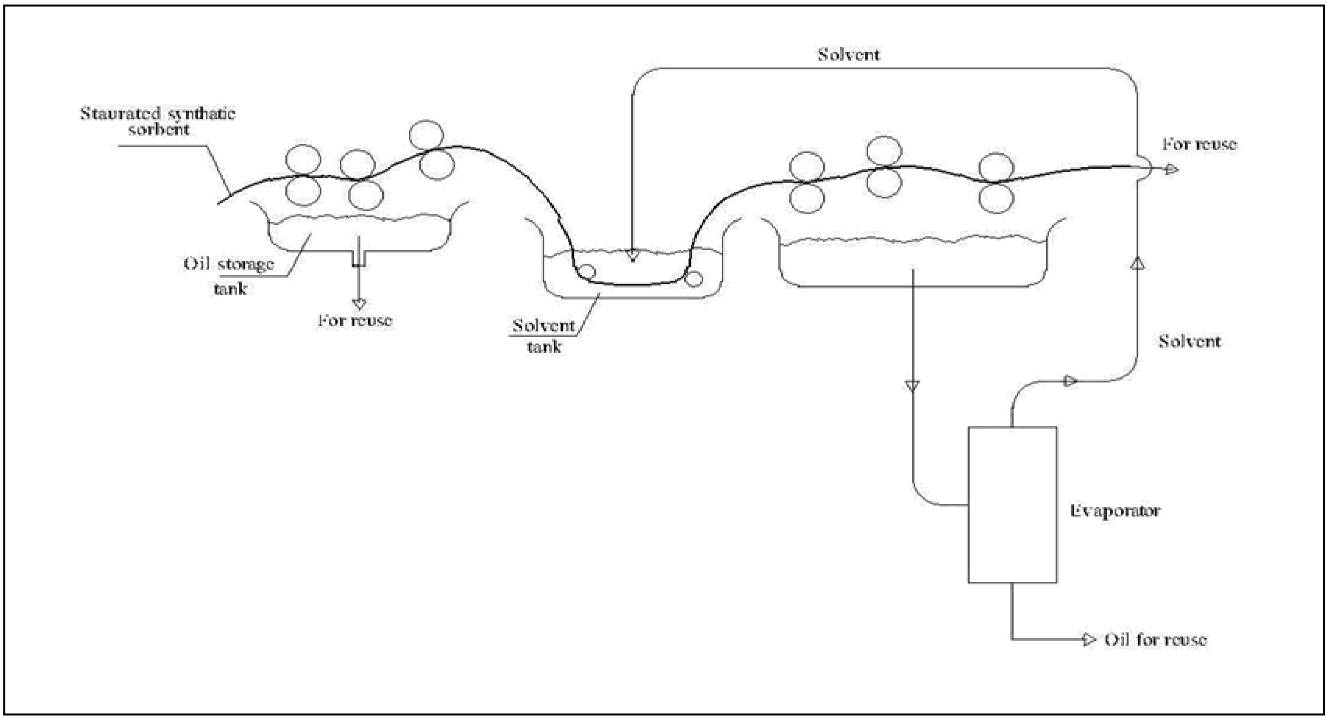


Figure 9: Treatment stages for waste sorbents

Table 1 Analysis of crude oil used in the study

Parameter	Value
Density @ 15°C	0.88
Sulphur content (wt. %)	1.88
Water content	0.3-1.5%
Saturated aliphatic hydrocarbons	31-35%
Unsaturated aliphatic hydrocarbons	25-28%
Aromatic hydrocarbons	33-37%
Resins	3-5%
Asphaltenes	0.5-1.9%

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