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Removal of oil from seawater using charcoal and rice hull

Aslam Abdullah M and Ayush Choudhary
Department of Chemical Engineering, School of Civil and Chemical Engineering,VIT University, Vellore, Tamil Nadu 632014, India

Email: aslamabdullah.m@vit.ac.in

Abstract. Adsorption has been implemented to remove oil from sea water, because it is very efficient and can ensure purification to any required level in the case of multi-step arrangement of the process. Oil was expelled from seawater in a clump procedure using 2 different natural adsorbents which are charcoal and rice hull. Samples collected after adsorption were characterized using UV Spectroscopy and subsequently, the adsorption capacity of crude oil was studied. The outcome of contact time and adsorbent dosage were studies concerning their impact on removal of oil. It was seen that as the adsorbent amount and contact time are increased, oil removal is enhanced. Charcoal was proven to be the most efficient adsorbent with removal efficiency of 99.67% followed by rice hull.After performing batch experiments, continuous adsorption in an adsorption column was also accomplished for the two of most efficient adsorbents after including beef tallow as our third adsorbent in discussion. Effect of bed height with respect to removal efficiency was studied here. The result showed that with increase in bed height, removal efficiency increases too.Adsorption isotherms of oil on adsorbents were determined and correlated with the usual isotherm equations such as Langmuir and Freundlich. The Freundlich adsorption isotherm model was found to correlate the adsorption equilibrium data better than the Langmuir model.

1. Introduction
1.1 Background
Hydrocarbon-based oil is one of the most important energy resources in the modern era. If oil is explored, transported, stored and used, there is a risk of spillage in the space. Oil spills creates a major problem and concern on the environment. When oil is spilled into a marine environment, it is subject to several processes including spreading, drifting, evaporation, dissolution, photolysis, biodegradation and formation of water–oil emulsions.
Low cost of adsorbent could be generated from agricultural waste because of their low-cost and widespread availability. The use of adsorbents to clean-up oil spill presents nearly many advantages due to simplicity of approach and the inexpensive nature of the materials. In addition, plant derived organic adsorbents are biodegradable thus leaves no permanent residue [1].
 This work measures equilibrium and kinetics of the effectiveness of crude oil spill cleanup using cheap and readily available natural adsorbents like rice hull and charcoal.

1.2 Adsorption
In 1881, "adsorption" was presented by German physicist Heinrich Kayser (1853-1940). It is a surface-based restricting procedure including the grip of any substance (gas/fluid/broke up solids),

particles, atoms or particles on the surface of the other substance.Figure 1 explains the steps involved in adsorption mechanism.
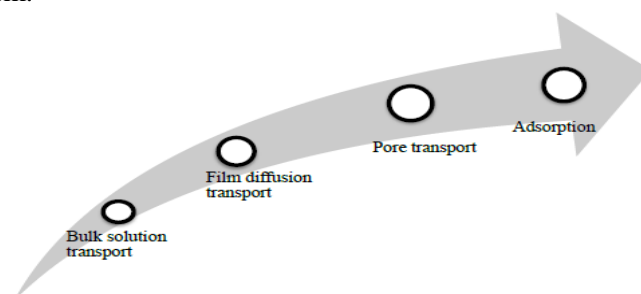

Fig. 1:Steps associated with the progression of adsorption

1.3 Adsorption Isotherm

An adsorption isotherm gives a connection between add up to mass of adsorbed adsorbate per unit mass of sorbent and focus at steady encompassing conditions. With a specific end goal to create adsorption isotherms, adsorption tests are performed.

The equilibrium of adsorption is regularly clarified by the Isotherm Equations. The parameters of isotherms depict the surface properties and fondness at a steady temperature and pH. In this examination, distinctive adsorption isotherm models were connected to control the sorption limit. The adsorption limits were figured utilizing the connection beneath:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

where, C_i is the underlying oil focus C_e is equilibrium oil fixation[2], V is the volume of the created water produced and m is the mass of adsorbent[3].

2   Methodology

2.1 Materials

Seawater was collected from Mahabalipuram beach, Chennai. Crude oil was obtained from Indian Oil Company located in Haryana. Charcoal was purchased from an iron shop owned by blacksmith. Rice hull was obtained from rice mill located in Kumbakonam, Tamilnadu.

These adsorbents were dried in oven maintained at 250 ˚C to reduce the moisture content. Salt content in sea water was determined using UV spectrophotometer. Blank test of sea water sample was taken to note down the absorbance. Absorbance recorded was 1.734 and its corresponding concentration was found to be 29.12 mg/L using calibration curve given in Figure 2.

Table 1. Adsorbents Characterization

Adsorbent	Before Adsorption	After Adsorption
Charcoal		
Rice hull		

2.2 Method

2.2.1 Gravity Settling: Prior preparation involved gravity settling of mixture of crude oil and sea water. The main objective of gravity settling in this project is to separate out any dirt or impurities present in the crude oil and sea water.

For carrying out this sediment procedure the mixture was first poured in a separating funnel and agitated vigorously so that proper mixing takes place. After mixing, the separating funnel was left for settling purpose for 24 hours. Next day it was observed that the mixture was separated into 3 different layers on the basis of density difference. Top most layer is found to be of crude oil followed by sea water and the bottom layer of impurities and dirt. Now, the crude oil from top was withdrawn into flask.

Figure 2. Gravity settling

2.2.2 Batch Adsorption Experiments: Mixtures of sea water and crude oil were prepared of different concentrations and certain amount of adsorbent was added to the mixtures. Water and oil do not mix but form emulsion. Now, the mixtures were blended utilizing a mechanical shaker at 140 rpm for various time interims.

 After adsorption the samples were taken out from the shaker and filtered using filter paper to separate out sea water and adsorbent with oil adsorbed on it. This spent adsorbent was weighed first and then placed inside the oven for 2-3 hours for drying purpose. Sea water samples collected after filtration were taken to lab to determine oil concentration using UV spectrophotometry method at the wavelength of 310 nm. From the data obtained, the equilibrium concentration was calculated using Beer-Lambert law. The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiation which is written as:

$$A = \varepsilon \, L \, C_e \qquad\qquad (2)$$

A=Absorbance; ε=Wavelength based Molar Extinction coefficient (L mg^{-1} cm^{-1}); L=Path length (cm); Ce = Equilibrium concentration (mg/L)

The coefficients were obtained from fitting the measured absorbance with known oil concentrations to Eq. (2). A very high R^2 (0.9988) indicated that Eq. (2) fitted the calibration curve well[4].
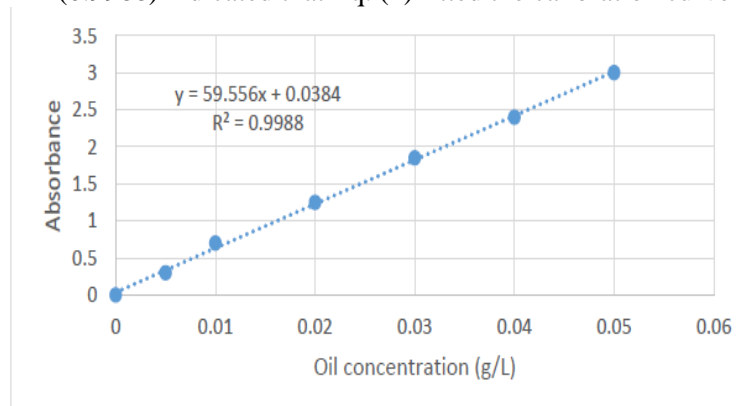

Figure 3.Calibration plot of absorbance at varying concentration

This experiment was performed for two different natural adsorbents (charcoal, rice husk).
The weight (M) of the adsorbent (CC), volume (V) of simulated oil spill and the corresponding equilibrium concentration (Ce) were recorded.

3   Experimentation
3.1 Continuous adsorption column set up

The glass column of 3 cm internal diameter 30 cm length was clamped vertically on the iron stand. A tube from the top was connected to the bottom of a tank by a pipe having valve in between. This valve is used to control the flow rate of mixture. The tank contains the mixture of crude oil and sea water was placed at a higher elevation. The setup was run using compressor in order to introduce mixture continuously to the column. A beaker was placed below the column to collect the treated water.

Figure 4. Column experimental set up

3.2 Experiment:
Mixture of crude oil and sea water was prepared by taking 100 mL of crude oil in 900 mL of sea water. The column was filled with the weighed amount of adsorbent to a defined height. The treated water was collected using a beaker below the column. The flow rate at each height was determined by the volume collected in the beaker and the time taken (started immediately the water began to drop in the beaker) to fill it. The experiment was repeated for bed height of 5, 10,15, 20 and 25 cm. Each of the samples was collected separately and labeled properly in a sample bottle. Oil Removal percentage is directly related to adsorption capacity.

We included beef tallow in our experimentalong with charcoal and rice hull and found out that rice hull and charcoal are more efficient. Beef tallow was included just for the sake of comparing three adsorbents. Hence, continuous experiment was performed without beef tallow due to its poor efficiency[6].

4   Results and discussions
4.1 Batch experiment results

4.1.1 Effect of contact time: The adsorption curves of different adsorption time under the same adsorbent dosage of 50 g in 210 ml are presented in Table 2, which show us the oil concentration variation in oil polluted sea water and the removal efficiency (%) with respect to time. The oil concentrations decrease notably initially and then tends to balance after a certain time.
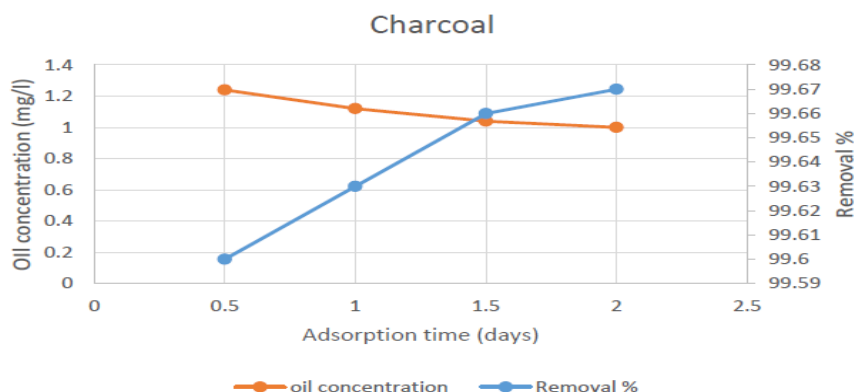
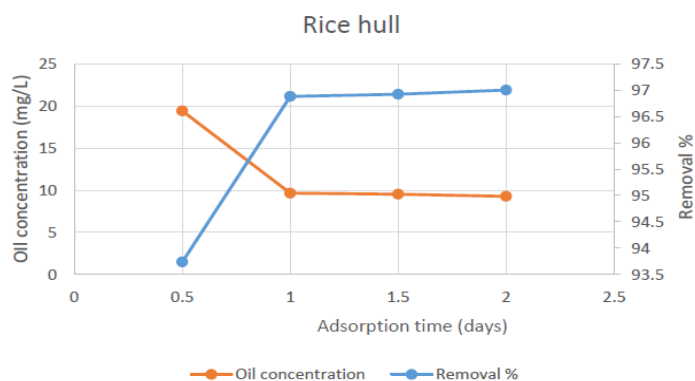Figure 5.Impact of contact time on adsorption of oil on charcoal**.**

Figure 6. Impact of contact time on adsorption of oil on rice hull

Table 2. Oil concentration and removal efficiency with optimum adsorption time

Sr. no.	Adsorbent	Maximum Removal Efficiency (%)	Minimum oil concentration (mg/L)	Optimum adsorption time (days)
1.	Charcoal	99.67	1	2
2.	Rice hull	97	9.27	1.5

4.1.2 Effect of the adsorbent dose: The percent adsorption increased as the adsorbent dose was increased at 310mg/L oil concentration. Increase in adsorption with the dose can be attributed to increased surface area and availability of more adsorption sites. A small quantity of adsorbent will be saturated more quickly than a larger one.
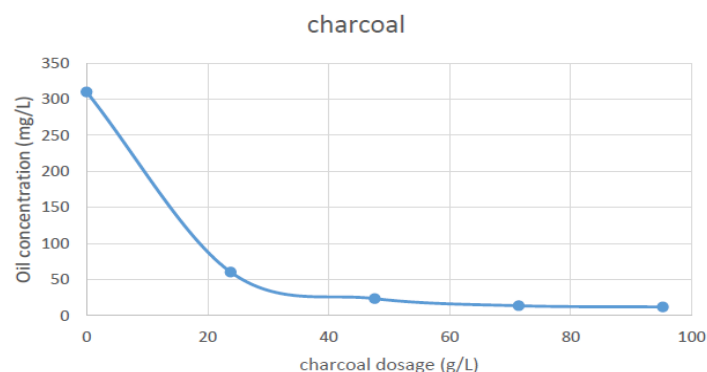
Figure 7. Effect of increase in adsorbent dose on adsorption of oil on charcoal
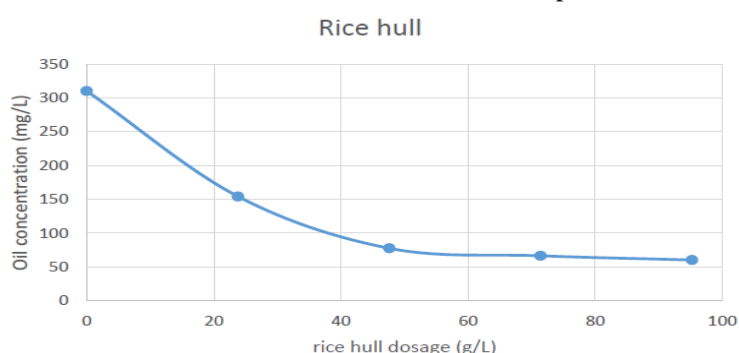

Figure 8. Effect of increase in adsorbent dose on adsorption of oil on rice hull

Table 3. Effect of adsorbent dose on effluent oil concentration

Sr. no.	Adsorbent	Minimum oil concentration (mg/L)
1.	Charcoal	11.78
2.	Rice hull	60.2118

4.1.3 Adsorption isotherms study: The Langmuir and Freundlich equations were used to study the adsorption isotherms of oil. The linear form of the Langmuir equation is as follows:

$$\frac{1}{qe} = \frac{1}{Ce\,qm\,k} + \frac{1}{qm} \qquad (3)$$

where Ce (mg/L) defines the strength of dye solution upon reaching equilibrium, qe (mg/g) is total oil consumed via adsorption at equilibrium, qm defines the maximum adsorption capacity and represents a practical limiting adsorption capacity when the adsorbent surface is fully covered with monolayer adsorbent molecule and *k* is Langmuir constant.

The *qm* and *k* values are calculated from the slopes (*1/qmk*) and intercepts (*1/qm*) of the following linear plot of *1/qe* versus 1/*Ce*.
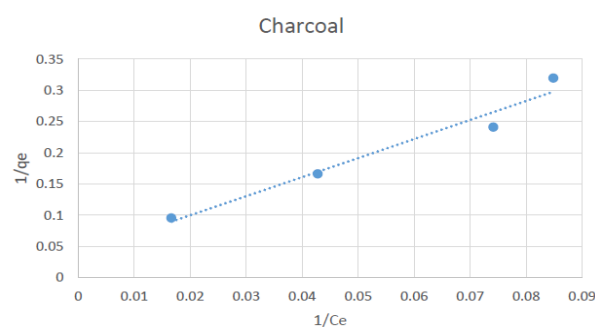

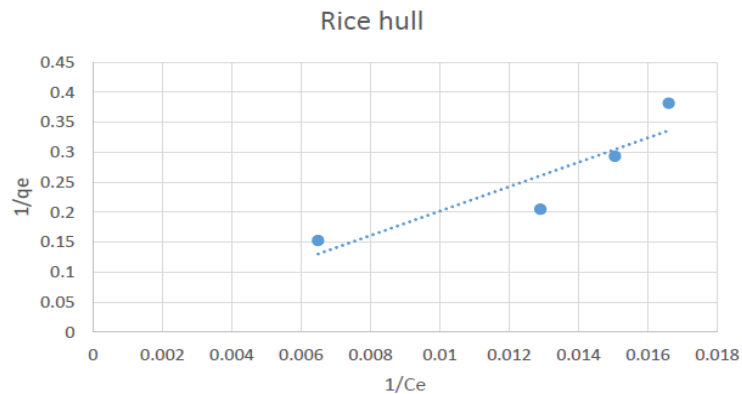Figure 9. Langmuir isotherm representation for adsorption of oil on charcoal

Rice hull

Figure 10. Langmuir isotherm representation for adsorption of oil on rice hull

The linear form of the Freundlich equation is as follows:

$$\ln qe = \ln Kf + \frac{1}{n} \ln Ce \qquad (4)$$

where qe is the measure of oil adsorbed at balance, Ce is the strength of phenol in arrangement at balance *Kf* and 1/n are empirical constant which indicate the adsorption capacity and intensity, respectively. Their values were obtained from the intercepts *(*ln *Kf)* and slope (1/n) of the following linear plots of ln qe versus ln Ce:

Charcoal
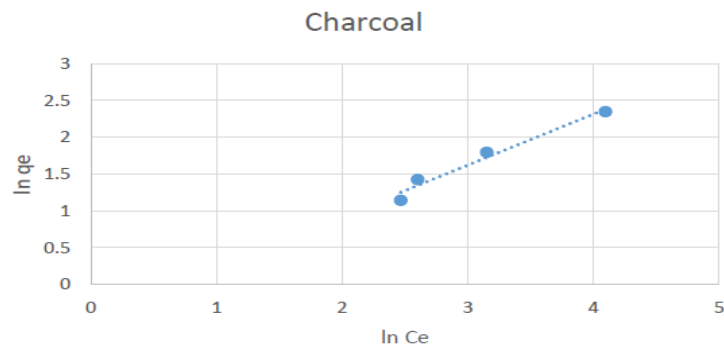

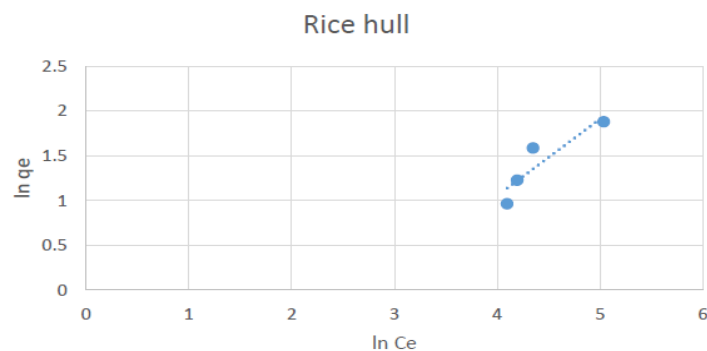Figure 11.Freundlich isotherm representation for adsorption of oil on charcoal

Rice hull

Figure 12.Freundlich isotherm representation for adsorption of oil on rice hull

Table 4. Langmuir and Freundlich constants for the adsorption of oil

Sr. no.	Adsorbent	Models	Constants	R^2
1.	Charcoal	Langmuir	k = 0.0126, qm = 25.84	0.9608
		Freundlich	1/n = 0.6931, Kf = 0.632	0.9702
2.	Rice hull	Langmuir	k = 9.33 x 10^{-5}, qm = 526.315	0.8086
		Freundlich	1/n = 0.857, Kf = 0.09305	0.8183

4.2 Continuous experiment result

4.2.1 Effect of bed height: The effect of bed height on the effluent oil content is presented below for flow rate of 0.019 ml/min and 86.11 mg/L of inlet oil concentration. The considered bed heights are 5, 10, 15 and 20 cm. It is observed that at smaller bed height the effluent oil content ratio is more than for a higher bed height. The reason can be that, smaller bed height corresponds to fewer amounts of adsorbent, and consequently, a smaller capacity for the bed to adsorb oil from aqueous phase; hence the bed is saturated in less time for smaller bed heights[8].
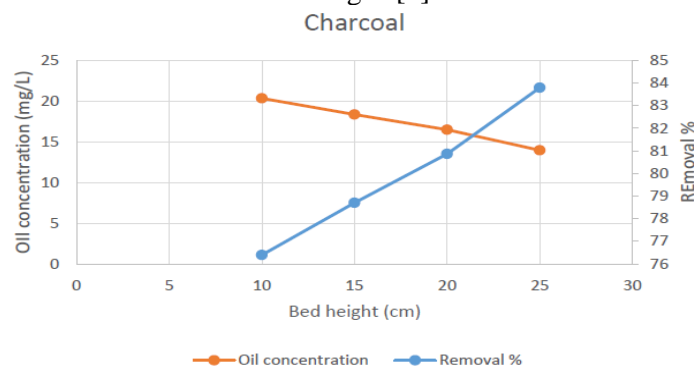

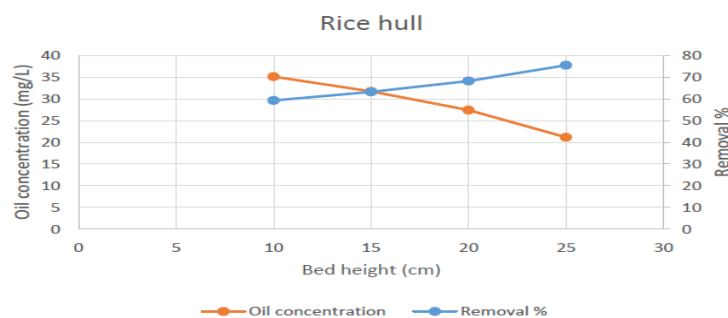Figure 13.Effect of bed height on adsorption of oil on Charcoal

Figure 14.Effect of bed height on adsorption of oil on rice hull

4.3 Characterization of rice hull by SEM: A scanning electron microscope (SEM) is a type of electron microscope that provides surface images by scanning it with a high-energy beam of electrons.
Utilizing SEM, as Figure 15 and 16 shows, the physical morphology of rice hull surfaces was resolved previously and after the adsorption of crude oil. Figure 16 demonstrates that the rice body stacked with oil does not have these pores and cavities[7] while the oil free rice structure has clear holes and pores (Figure 15).
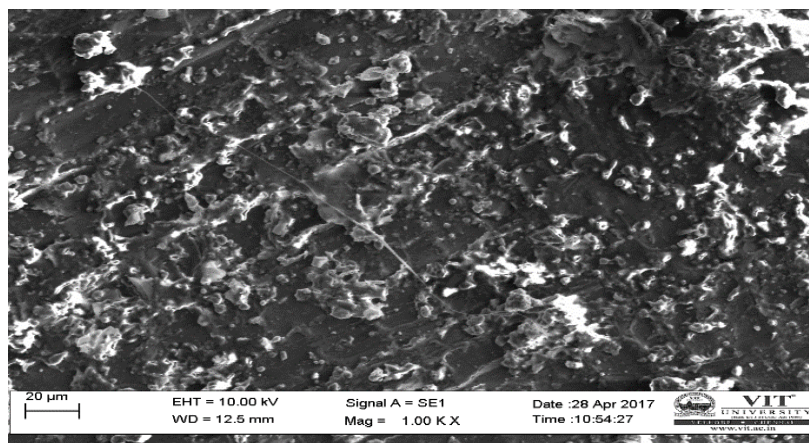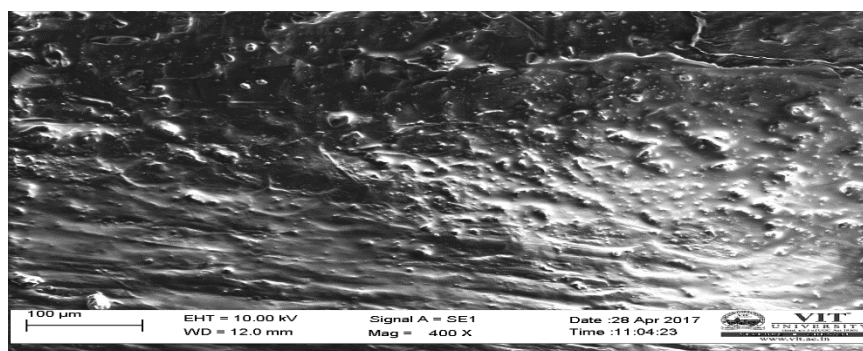
Figure 15. Rice hull SEM image before adsorption

Figure 16. Rice hull SEM image after adsorption

5   Conclusion

In this work, another promising and productive normal adsorbent for the expulsion of oil from seawater was created. Charcoal and rice hull were utilized for the evacuation of oil, and a relative report between the adsorbents was finished. Following conclusions can be drawn from this examination:

- The productive adsorbent was observed to be charcoal with most extreme evacuation effectiveness of 99.67 took after by rice hull. In any case, no adsorption took pace for beef tallow.
- Batch adsorption tests for the adsorption of oil from seawater have been completed by utilizing the two adsorbents. Impact of contact time and adsorbent dosage have been learned at temperature of 25±2 $°C$ and mechanical shaker at RPM of 140.
- The ideal parameters for oil expulsion were: pH = 9.5, pomegranate measurements = 2.33 g/L, contact time = 40.0 minutes and adsorption temperature = 55.0 °C.
- Scanning electron magnifying instrument (SEM) investigation demonstrates that rice body is exceptionally permeable and has depressions in charge of high expulsion proficiency of oil from seawater.
- Initially by expanding the adsorbent (charcoal) measurement, expulsion proficiency of the oil from seawater diminished quickly up to 60.14 and afterward turned out to be practically steady. At 60.14 mg/L, the ideal measurements is 23.81 mg/L. Rice hull showed similar trends.
- The adsorption isotherm for oil expulsion was found to adapt Freundlich adsorption isotherm when contrasted with Langmuir isotherm model[8]**.**

- These discovering render these two adsorbents as productive, practical and ecologically inviting adsorbent[5].

6   References

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