Pomegranate Peels Powder for the Remediation of Oil Polluted Water from Waste Lubricating Oil

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Abstract - Remediation of oil-polluted water from waste lubricating oil by adsorption was investigated using pomegranate peels powder. Many parameters such as the oil sorption capacity, oil retention, water and oil uptake, kinetic behavior of remediation process, adsorption isotherm model, and reusability were studied. The oil sorption capacity of adsorbent was equal to 2.316 g oil /g sorbent. The sorbent has a very good retention time; it can keep 48% of the adsorbed oil after three minutes of drainage. This property makes the material a unique behavior to keep the oil for this long time. The reusability of sorbents showed a 76.2 % of the sorption capacity after 6 reusability cycles. The total amount of adsorbed oil is 11.659 g oil/ g pomegranate peels powder. The kinetic study showed that the rate of adsorption followed the first order kinetics. Langmuir, Freundlich adsorption isotherm models were applied to check if any of these models is fitting the adsorption remediation process.

Keywords: Pomegranate Peels, Waste Lube Oil, Oil Spill, Water Remediation.

1. Introduction

Natural sorbent are widely used to remediate water from waste lube oil spill. Many works has been published related to the adsorption of oil from the surface of water. Vegetable fibers were used for oil remediation from the surface of water which have densities close or even lower than the synthetic polymers and they are environmentally friendly materials. These fibers showed a high oil sorption capacity with low cost [1]. Hydrolysis lignin showed a low ability for releasing water and low rate at the equilibrium state [2-3]. Cotton grass fiber and cotton grass mats were compared with commercially available synthetic sorbents [4]. Cotton grass fiber has better sorption capacity than other material. Cotton grass fiber is sorption because it is not adsorbing any significant amount of water. Mixed leaves residues, mixed sawdust, sponge-gourd, coir fiber, sisal, and silk-floss were used as sorbent materials of crude oil from the surface of water [5]. Pinecone powder was used to adsorb crude oil from the surface of water [6]. Adsorption capability of pinecone for different oil-containing produced water mixtures (250 mg/l to 750 mg/l, sorbent concentrations (0.1g to 0.3g / 200 ml of adsorbate). Potato peels was used for remediation of water from waste oil spill [7]. The oil sorption capacity was 2.15 g of oil/g sorbent and the reusability was not good comparing with other natural sorbents. The adsorption process followed the second order kinetics adsorption process. Date palm kernel powders of different forms were used for remediation of oil polluted water [8]. The type of activation of adsorbent had a significant rule on oil sorption capacity. The form of $ZnCl_2$ CDPKP had the highest sorption capacity.

2. Experimental Work

2.1. Materials

For pomegranate the colour part of the peel and the inner layer of spongy white tissue were carefully taken. Rinse with water many times and then dried at 60° C for more than 24 hrs using lab oven and then the dried parts were ground to obtain a fine powder. The peels represents about 14% of pomegranate mass. Other work showed the percentage of peels is 5 to 15% of its total weight [9]. The properties of pomegranate peels are shown in the Table 1 [10].

Table 1: properties of pomegranate peels.

For pomegranate, Yield (g/100 g of fresh weight of fruit) = 11.69 ± 0.03
Crude protein (g/100g dry peel) = 3.46 ± 0.02
Lipids (g/100g dry peel) = 3.36 ± 0.37
Ash (g/100g dry peel) = 6.07 ± 0.07
Crude fibres (g/100g dry peel) = 17.63 ± 0.05
Carbohydrates (g/100g dry peel) = 59.98 ± 1.52

Waste lubricating oil was collected from oil change carriage in Regina. The waste lubricating oil was mixed thoroughly for more than 5 minutes before any test. The mixed waste oil has been tested using ASTM methods for measuring the following physical properties.

Table 2: Physical properties of waste lubricating oil.

Property	ASTM Method	Value
Specific gravity @15.6/15.6 °C	ASTM D 1298	0.863
Kinematic viscosity, cSt at 40 °C	ASTM D 445	71.995
Carbon residue, mass%	ASTM D 189	0.6019
Ash content, mass%	ASTM D 582	0.63
Sulphated ash, mass %	ASTM D 874	0.69
Asphaltene content as heptane insoluble, mass%	ASTM D 3279	0.802
Water content, vol%	ASTMD 96	Nil
Water and sediment, vol%	ASTMD 4007	Nil

2.2. Experimental Methods

Oil sorption capacity of pomegranate peels powder in water was determined by adding 40 g of oil to 400 ml of artificial seawater (3.5% NaCl) as described in [11]. 1-6 grams of dry pomegranate peels powder was added, the mixture was mixed for 30 sec. Medium term sorption tests were achieved using contact time of 15 minutes. The work was performed in a batch process at ambient temperature. The wet oil sorbent was removed, let to drain for 30 seconds and weighed. The amount of adsorbed oil (oil sorption capacity C , in g oil g^{-1} of sorbent) was calculated according to the following general equation:

$$C = \frac{mf - (mo + mw)}{mo} \quad (1)$$

mf is the mass of the wet oil after draining (g), mo is the initial mass of dry sorbent (g), and mw is the water content in the sorbent (g). Water content was determined by after adding heptane as solvent for several times with squeezing the sorbent to remove all the entire oil and water.

Oil sorption capacity of sorbent in oil without water was measured; 1.00 g of sorbent was placed on top of 150 ml of oil, after 15 min of sorption under shaking, the oil was drained for 30 seconds and the sorbent was weighed. The amount of adsorbed oil can be determined according to Eq. 1, but in this case mw is equal to zero.

Reusability of pomegranate peels powder was studied in oil medium. 5 cycles of sorption processes were performed. After each cycle, the sorbent was squeezed and weighed again. The mass of the squeezed pomegranate peels powder was the initial mass of the material (m_o in Eq. 1) in each subsequent sorption cycle. To determine the oil retention, pomegranate peels powder was placed in 150 ml of oil for 15 minutes. The sorbent was removed and vertically hung, where upon the adsorbed oil began to drip from the sorbent, the weight of the material was measured after 45, 60, 75, 90, 105, and 120 seconds of draining. The quantity of the oil retained was calculated as the difference between the weight of the wet material following drainage and the initial weight of the material.

Pomegranate peels powder as sorbent material was subjected to evaluation using water uptake and buoyancy tests in static condition. The evaluation was conducted according to the test methods described in [12]. In static condition, the sorbent was placed in a glass vessel filled with approximately 7.5 cm deep layer of de-ionized water. After 15 minutes and 24 hrs, observations were done and the sorbent was removed from water. Any sorbent, which did not remain floating on the water will fail as sorbent material. The water uptake (c_{H_2O} , in gg^{-1}) after 30 seconds of drainage was determined according to:

$$c_{H_2O} = \frac{m_{wt} - m_o}{m_o} \quad (2)$$

Where

m_{wt} is the mass of the wet material after 30 seconds of drainage (g), and m_o is the initial mass of the material (g).

3. Results and Discussion

3.1. Bouncy Test and Water and Oil Uptake

The bouncy test for pomegranate peels powder was performed using water. The material was stayed on the top of water and not sinks in the water so the material passed the test as shown in Figure 1.

Fig. 1: (left) sorbent (pomegranate peel powder) in 3.5wt % seawater. (right): Buoyancy test, side view of sorbent in seawater solution.

The oil and water uptake was measured using 1 g of pomegranate peels powder in either water or waste oil. The water used is artificial sea water by adding 3.5% salt to the water. The oil and water uptake was measured. For pomegranate peels powder in oil only and oil/ seawater; the oil sorption capacity showed a higher value of 3.139 g oil/g sorbent for oil followed by 2.613 g oil/g sorbent for oil/seawater. The water uptake was almost zero which gives more space for oil sorption process as shown in Figure 2.

Fig. 2: Water and oil uptake.

3.2. Equilibrium Sorption Capacity

To measure the time required to reach adsorption equilibrium state, the sorption capacity of pomegranate peels powder was plotted versus time as shown in Figure 3.

Fig. 3: Oil sorption capacity as function of contact time.

The sorption capacity of pomegranate peels powder was increased sharply for the first 10 minutes and then reached equilibrium at about 25 minutes. The percent waste lube oil removal from water with time is measured and it showed that 68.25 % oil was adsorbed on the surface of the sorbent after 10 minutes of contact time and this value was increased to a total adsorption after 30 minutes to reach equilibrium. The amount of oil was increased with the amount of adsorbent as shown in Figure 4. This is true due to the high amount of sorbent. The oil sorption capacity of pomegranate peels powder is shown in Figure 5.

Fig. 4: Amount of adsorbed oil with the amount of pomegranate peels powder.

Fig. 5: Oil sorption capacity of pomegranate peels powder.

3.3. Oil Retention

Oil retention is defined as the amount of time that oil can stay inside the adsorbent material. No matter the sorption capacity is high but if the sorbent cannot hold the oil for long period, it is not easy to say that this is a good sorbent. So, it is regarded as one of the most important parameter to evaluate the performance of sorbent material toward oil spill to the water surface. The retention time was measured by calculating the amount of oil stays in the adsorbent material with different drainage time as shown in Figure 6. It is clear shown that after three minutes of drainage, the pomegranate peels powder can keep 48% of the adsorbed oil after three minutes of drainage. This can be regarded as a unique property of this adsorbent.

Fig. 6: Oil retention of pomegranate peels powder.

3.4. Reusability

Although pomegranate peels powder is a natural bio-waste material, the reusability of this sorbent shows the oil capacity of 76.2 % of the original oil capacity after 6 times usage as shown in Figure 7. The total amount of adsorbed oil was 11.659 g. This may encourage us to continue using this sorbent for longer times.

Fig. 7: Pomegranate peels powder reusability.

3.5. Kinetics of Adsorption

The adsorption rate order kinetics and adsorption model was studied and the relevant parameters of batch kinetic data in conjunction with proper models was investigated for both first and second orders adsorption kinetic models [13]:

The first order medium term adsorption kinetics can be applied using the following equation:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (3)$$

Where q_e is the equilibrium amount of adsorbed contaminant (g) per unit mass (g) of sorbent material, q is adsorbed amount at any time t , and k_1 is the first order rate constant (1/min). Integrating equation 3 with the limit $q = 0$ at time $t = 0$ gives:

$$\ln \frac{q_e - q}{q_e} = -k_1 t \quad (4)$$

This equation can also be written as:

$$\ln(q_e - q) = -k_1 t + \ln(q_e) \quad (5)$$

The plot of $\ln(q_e - q)$ vs. time gives a straight line with slope equal to $-k_1$ and intercept of $\ln(q_e)$. The experimental data fit is shown in Figure (8-A).

The kinetic parameters such as the rate constant and q_e are computed from the slope and the intercepts of the fitted curves and reported in Table (2).

On the other hand, the second order medium term adsorption kinetics is described by the following equation.

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (6)$$

k_2 is the second order rate constant(g sorbent per g contaminant per minute). The integration of this equation with the limit $q=0$ at time $t=0$ gives:

$$\left\{ \frac{1}{q_e - q} \right\} - \left\{ \frac{1}{q_e} \right\} = -k_2 t \quad (7)$$

or

$$\left\{ \frac{t}{q} \right\} = \left\{ \frac{t}{q_e} \right\} + \left\{ \frac{1}{k_2 q_e^2} \right\} \quad (8)$$

The plot of $\left\{ \frac{t}{q} \right\}$ vs. time gives a straight line with the slope $\left\{ \frac{1}{q_e} \right\}$ and intercept of $\left\{ \frac{1}{k_2 q_e^2} \right\}$.

The experimental data fits the second order kinetics is shown in Figure (8-B). The kinetic parameters such as the rate constant and q_e are computed from the slope and the intercepts of the fitted curves are reported in Table (2).

Fig. 8: (A) First order kinetic, (B) Second order kinetics.

Table 2: Summary of kinetic parameters for WTCF sorption.

Sorbent	Kinetic	Slope	Intercept	R ²	qe	Rate constant
sorbent	First order	0.0349	0.2948	0.993	1.343	0.0349
	Second order	0.1935	2.8684	0.8888	28.653	4.25x10 ⁻⁴

From the values of the slope, qe and R², it is quite accepted to say that the first order kinetics is better fit for pomegranate peels powder for waste lubricating oil removal from oil spill to the water surface.

3.6. Adsorption Model

It is required to fit the experimental data with different adsorption isotherm models reported in the literature. The Freundlich isotherm is commonly represented by the following equation:

$$qe = K Ce^{1/n} \quad (9)$$

where K and n are isotherm parameter and it can be changed to the following shape:

$$\ln(qe) = \frac{1}{n} \ln(Ce) + \ln(K) \quad (10)$$

The plot of $\ln(qe)$ vs. $\ln(Ce)$ gives a straight line with slope $\frac{1}{n}$ and y-intercept of $\ln(K)$. The plot of the isotherm model fit is shown in Figure (9-A) for pomegranate peels powder sorbent. On the other hand, the Langmuir isotherm is generally given as:

$$qe = \frac{qm \cdot b \cdot Ce}{1 + b \cdot Ce} \quad (11)$$

qm and b are Langmuir isotherm parameters, which can be estimated from the plot of $\left\{\frac{1}{qe}\right\}$ vs. $\left\{\frac{1}{Ce}\right\}$, this will give a straight line of slope $\left\{\frac{1}{qm \cdot b}\right\}$ and y-intercept of $\left\{\frac{1}{qm}\right\}$. The plot is shown in Figure (9-B). From R² values, it is clear that the Langmuir isotherm fit for pomegranate peels powder sorbent.

Fig. 9: Freundlich and Langmuir Isotherm Adsorption models.

The summary of the adsorption isotherm models for pomegranate peels powder is shown in Table 3.

Table 3: Summary of isotherm parameters for the adsorption of waste lubricating oil-using pomegranate peels powder as adsorbent material.

Adsorption isotherm	Slope	Intercept	R ²
Freundlich isotherm	3.8727	13.716	0.7441
Langmuir isotherm	21.368	2E-08	1

4. Conclusion

Pomegranate peels powder was used in this work as an oil sorbent material for water remediation from waste lubricating oil. To evaluate pomegranate peels powder, many parameters are required to investigate such as the rate of oil sorption, sorption capacity, oil retention, water and oil uptake, and reusability. Pomegranate peels powder needs 30 minutes to reach equilibrium. The oil sorption capacity was 2.316 g oil /g sorbent material using medium term sorption process. Pomegranate peels powder has a unique ability to keep the oil for long time. It can keep 76.2% of the total adsorbed oil after three minutes drainage. The reusability of sorbent showed of the reduction of oil sorption capacity from 2.316 to 1.764 g oil/ g of sorbent after six adsorption cycles. This means that 76.2% of its original activity can be achieved and it can be used for further oil sorption cycles. Within these six sorption cycles, 1g of pomegranate peels powder had the ability to absorb 11.659 g of oil from the surface of water. This sorbent followed a first order rate kinetic and Langmuir isotherm models.

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References

- [1] Q. F. Wei, R. R. Mather, A. F. Fotheringham, R. D. Yang, "Evaluation of nonwoven polypropylene oil sorbents in marine oil spill recovery," *Marine Pollution Bulletin*, vol. 46, no. 6, pp. 780-783, 2003.
- [2] O. A.I Wahab, "Assessment of raw luffa as a natural hallow oleophilic fibrous sorbent for oil spill cleanup," *Alexandria Engineering Journal*, vol. 53, pp. 213-218, 2014.
- [3] S. Nenkova, R. Garvanska, S. Jelev, "Fibrous wood sorbent for eliminating oil pollution," *AUTEX Research Journal*, vol. 4, no. 3, pp. 157-163, 2004.
- [4] S. Nenkova, M. Herzog, V. Gancheva, R. Garvanska, "Study of the sorption properties of technical hydrolysis lignin and wood shoddy towards oil pollution," *Journal of the university of Chemical Technology and Metallurgy*, vol. 43, no. 2, pp. 217-222, 2008.
- [5] A. L. D. J. Abejero, A. J. Alcontara, L. C. Trinidad, and M. E. Flavier, "Kapok (Ceiba pentandra (L) Gaertn fibers packed in nylon nets as sorbent for diesel oil spill and its ex-situ bioremediation," *Journal of Environmental Science and Management*, vol. 16, no. 1, pp. 72-83, 2013.
- [6] S. Ravikumar, H. Ibrahim, and I. Al Zubaidi, "Separation of oil from produced water by adsorption on pinecone powder," *Williston Basin Petroleum Conference*, Evraz Place, Regina, Saskatchewan, Canada, 2017.
- [7] P. Tontiwachwuthikul, I. Al Zubaidi, E. Rennie, S. Schubert, M. Seitz, C. Selinger-Silva, "Remediation of water from waste lubricating oil spill using potato peels," *3rd International Conference on Fluid Flow, Heat and Mass Transfer (FFHMT'16)*, Ottawa, Canada, 2016.
- [8] I. Al Zubaidi, "Remediation of oil polluted water using Date palm kernel powder," *2nd International Conference on Environmental Pollution and Remediation*, Montreal, Canada, Aug. 28-30, 2012.
- [9] M. H. Eikani, F. Golmohammad, and S. S. Homami, "Extraction of pomegranate (Punica granatum L.) seed oil using superheated hexane," *Food and Bioproducts Processing*, vol. 91, pp. 32-36, 2012.
- [10] F. Dibanda Romelle, A. Rani P, and R. Sai Manohar, "Chemical composition of some selected fruit peels," *European Journal of Food Science and Technology*, vol. 4, no. 4, pp. 12-21, 2016.
- [11] H. Choi and R. M. Cloud, "Natural sorbents in oil spill cleanup," *Environmental Science and Technology*, vol. 26, no. 4, pp. 772-776, 1992.

- [12] D. Cooper, and L. Keller, "Oil spill sorbents: 1992, Testing Protocol and certification listing Program," *River Road Environmental Technology center; ASTM F*, pp. 726-99.
- [13] S. Syed, M. I. Al hazzaa, M. Asif, "Treatment of oily water using hydrophobic Nano-silica," *Chemical Engineering Journal*, vol. 167, pp. 99-103, 2011.