

Adsorption of crude and engine oils from water using raw rice husk

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ABSTRACT

The raw rice husk (RRH) was used as a low cost adsorbent to remove three oil compounds with different viscosities (crude oil, engine oil and spent engine oil) from an aqueous environment. Some of the sorbent specifications were characterized using a CHNSO analyzer, Fourier transform infrared, scanning electron microscope and inductively coupled plasma spectroscopy. With decreasing RRH particles size, the oil adsorption percentage was reduced for crude, spent and engine oils from 50 to 30%, 65 to 20% and 70 to 0.01%, respectively. This was probably due to damage of the microcavities. The removal percentage by sorbent at optimized conditions was 88, 80 and 55% for engine, spent and crude oils, respectively, corresponding to their descending viscosity. The adsorption of crude and spent oils on rice husk followed the Freundlich isotherm model, while the adsorption of engine oil was fitted by the Langmuir model. The maximum adsorption capacity (q_{\max}), calculated from the Langmuir model for the adsorption of engine oil on RRH, was 1,250 mg/g.

Key words | adsorption, isotherm models, oil pollution, rice husk

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INTRODUCTION

Oil pollution is one of the most serious environmental problems, particularly in aquatic ecosystems, where it can cause irreversible economic and ecological impacts. Various techniques that have been employed for oil spill cleanup can be classified into three main categories: physical methods like booms, skimmers and sorbents; chemical methods like dispersants, burning and solidifiers; and gelling agent and biological methods (Clark 1997).

The adsorption process is an economic and eco-friendly approach used to remove oil pollutants in aqueous environments. The sorbent characteristics related to oil adsorption include hydrophobicity, retention over time, high oil recovery rate, high oil sorption capacity, and the reusability and biodegradability of sorbent (Lee *et al.* 1999; Teas *et al.* 2001; Adebajo *et al.* 2003; Lim & Huang 2007). The use of agricultural wastes as sorbents for environmental remediation has attracted considerable interest due to various advantages such as environmentally friendly features, simple techniques, low cost and biodegradability (Adebajo *et al.* 2003; Annunziado *et al.* 2005).

Asia has the biggest rice production with about 90% of the world's production and consumption. In Iran, rice production is increasing and becoming the most important crop, so rice husk is produced in significant quantities

(Ramzanipour *et al.* 2009). Unfortunately, it is burnt in some cases, causing air pollution. The use of rice husk as sorbent not only removes environmental pollutants, but also reduces the problems of burning and the disposal of agricultural by-products (Noor Syuhadah & Rohasliney 2012).

The use of rice husk and its derivatives as an effective sorbent to remove different types of environmental pollutants such as dyes, phenols, organic compounds, and heavy metals has been intensively studied. Most researchers used modified rice husk as the sorbent and reported its efficiency for removing a variety of compounds. It should be noted that the pre-treatment steps are always expensive and time consuming (Ahmaruzzaman & Gupta 2011; Noor Syuhadah & Rohasliney 2012). Therefore, in some emergency oil-spill situations, the use of raw sorbents for rapid and economic treatment of contaminated water seems preferable.

The objective of the present study is to investigate the use of raw rice husk (RRH) as an efficient and low cost adsorbent for the removal of three oil compounds with different viscosities including crude, spent and engine oils from water. The effects of different parameters such as pH of solution, contact time, sorbent particle size, initial oil concentration and sorbent dosage during adsorption process were also investigated.

METHODS

Materials preparation

Three oil compounds with different viscosities, including Iranian light crude oil (ILCO) (0.0617 Cm²/sec), Behran engine oil (BGTX[®]) (1.774 Cm²/sec) and spent engine oil (1.278 Cm²/sec) were used in the experiments. The rice husk sample was collected from a local rice miller in Isfahan, Iran. RRH was ground and sieved into different particle sizes for the adsorption experiments.

Analytical methods

The elemental composition of RRH was determined by C-H-N-S analyzer (Vario EL III Elemental instrument, GmbH, Germany). The silica content was measured by inductively coupled plasma (Optima[™] 7300 DV ICP-OES instrument, PerkinElmer, USA). Autoclave-induced digestion was used prior to ICP analyses (Elliott & Snyder 1991). The surface morphology and chemical compositions of the sorbent were studied by scanning electron microscope (SEM) (XL30 SERIES, Philips, The Netherlands). The structure of RRH was investigated by Fourier transform infrared (FT-IR) spectroscopy (Bruker Equinox 55, Wissemburg, France) at ambient temperature in the wave number range of 4,000–400 cm⁻¹.

Experimental procedure

The adsorption experiments were conducted by adding a specific amount of oil compounds into an Erlenmeyer flask 250 ml containing tap water. The pH of the solutions was adjusted with 0.01M HNO₃ or NaOH using pH meter (3310 model, Jenway, UK). Then, the sorbent was added, shaken at 150 rpm for a fixed time and separated by vacuum pump filtering with filter paper (No. 41 Whatman). The sorbent was dried in the oven for 24 hours at a temperature of 50 °C. The oil adsorption percentage was determined by the weighting method (Equation (1)):

$$\% \text{Adsorption} = \left(\frac{S_t - S_0}{\text{Initial oil}} \right) \times 100 \quad (1)$$

where S_t was the weight of sorbent containing adsorbed oil (g), S_0 was the initial weight of the sorbent (g) and C_0 was the initial oil (g) (Lee et al. 1999). The effect of various parameters, including the pH of oil solution (in the range of 1–10), contact time (1–60 min), initial oil concentration (10–50 g/L), sorbent dose (10–40 g/L) and particle size

(in the range from >2 to <0.035 mm) on oil adsorption were investigated by varying one parameter and keeping the other parameters constant at the same time (Hamby 1994). All tests were repeated three times at a room temperature of 23 °C.

Statistical analysis

The Microsoft Office 2003 Excel program was used to draw the graphs. SPSS statistical software (version 19.1) was used for ANOVA (analysis of variance) analysis and Tukey's test to compare the adsorption difference between the oil compounds.

RESULTS AND DISCUSSION

Characterizations of sorbent

The elemental composition of RRH consisted of C (35.57%), H (5.29%), N (1.71%) and SiO₂ (19.86%). Typically, RRH has a round structure with its outer epidermis structure being extremely ridged (Foo & Hameed 2009), but this structure is damaged after grinding as observed by SEM image (Figure 1(a)).

The FT-IR absorption bands of RRH (Figure 1(b)) were attributed to the functional groups of carbonaceous material, inorganic Si component and the adsorbed water. The wide and strong absorption band with a maximum of about 3,420 cm⁻¹ can be related to the vibration of the O–H bond in water molecules. The absorption band observed at 2,922 cm⁻¹ was from aliphatic C–H groups, and the very small peak at 1,638 cm⁻¹ was attributed to both C–OH groups of the water molecules and the presence of C=C bonds in the organic component. The bands at 1,050 and 469 cm⁻¹ resulted from the presence of Si–O in inorganic components (Foo & Hameed 2009; Chen et al. 2011).

Oil adsorption

The pH had no significant effect on oil adsorption by RRH, to the extent that when increasing the pH of the oil solution from 1 to 10 (10 g l⁻¹ oil and sorbent), the adsorption percentage remained constant at about 50, 57 and 63% for crude, engine and spent oils, respectively. During oil adsorption, the final pH did not vary notably. Moreover, due to the contamination of electrode surface for pH determination, all future experiments were done in the initial pH value of oil solutions (between 8 to 10). Brandão et al. (2010) reported

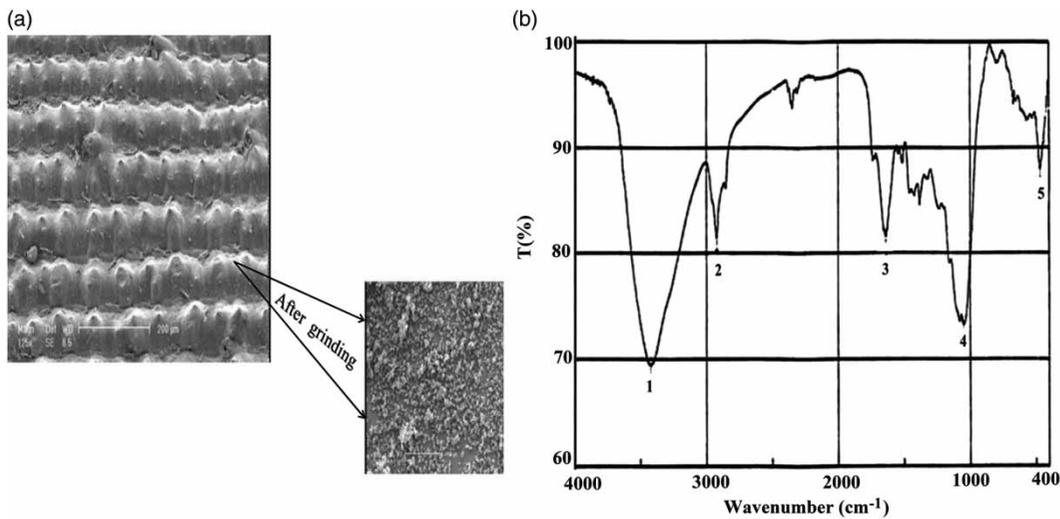


Figure 1 | Characterization of RRH by (a) SEM and (b) FT-IR spectra.

that the pH of the solution was not important in the adsorption of contaminants such as petroleum hydrocarbons on raw sugarcane bagasse. This indicates that the adsorption process can be used for water and wastewater treatment with different pH values without any adjustments.

The oil adsorption by RRH was very fast, mostly done in the first 5 min (Figure 2(a)). Therefore, a time of 5 min was selected for the following experiments. The adsorption of crude oil on RRH (50%) was less than engine (57%) and spent oils (63%). The fast adsorption of the three oil samples by RRH may be due to a large number of vacant surface sites that are firstly accessible for the solute adsorption. The

remaining vacant surface sites are not able to hold the oil compounds because of repulsive forces between the solute molecules in the liquid phase and the sorbent (Saadi Ibrahim & Nor Ismail 2012).

Oil adsorption was closely related to the particle size of the sorbent, to the extent that decreasing particle size reduced the adsorption percentage for crude, spent and engine oils from 50 to 30%, 65 to 20% and 70 to 0.01%, respectively (Figure 2(b)). The sorbent grinding resulted in the reduction of the surface trapping because of a decrease in void volume accessible to the oil. In addition, the oil adsorption was reduced due to pore damage and the

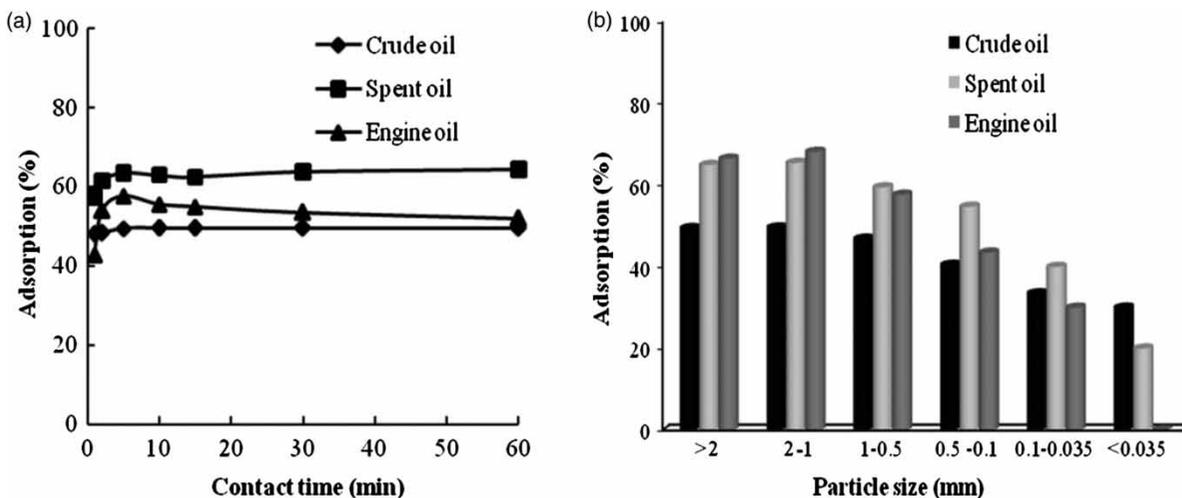


Figure 2 | The effect of (a) contact time and (b) particles size on the oil adsorption by RRH (oil concentration 10 g/L, sorbent dose 10 g/L).

accumulation of fine particles into pore cavities by grinding (Lee et al. 1999). Generally, the oleophilic compounds tend to be adsorbed into the available large pores (Kim et al. 2008).

The oil adsorption percentage was increased with an increase in the initial oil concentration until 10 g/L; then it remained constant for crude oil (50%) and spent oil (65%), whereas it decreased from 81 to 20% for engine oil at an initial oil concentration of 7 and 50 g/L, respectively (Figure 3). Generally, the number of sorption sites for a sorbent is limited and after its saturation, there are not sufficient sites for further adsorption (Haussard et al. 2003; Ibrahim et al. 2010).

Brandão et al. (2010) explained that the decrease of petroleum hydrocarbons at the higher concentration is due to clustering the solute compounds into micelles, which made the adsorption process more difficult in some sorbent pores due to size exclusion. In addition, excess oil concentration (especially heavy oil) clogs the pores in the outer surface of the sorbent and consequently, the oil residue cannot penetrate the interior surface (Teas et al. 2001).

The percentage removal of oil compounds was initially increased with the increase of sorbent dose until 10 g/L and after that, it remained almost constant. The highest adsorption percentage of engine, spent and crude oils in the final step of optimizing was 88, 80 and 55%, respectively. The initial increase in the adsorption with sorbent dosage can be attributed to the availability of a larger number of adsorption sites (Nwokoma & Anene 2010).

Adsorption isotherm

Adsorption isotherms show the distribution of sorbate between the sorbent and solution (Foo & Hameed 2010).

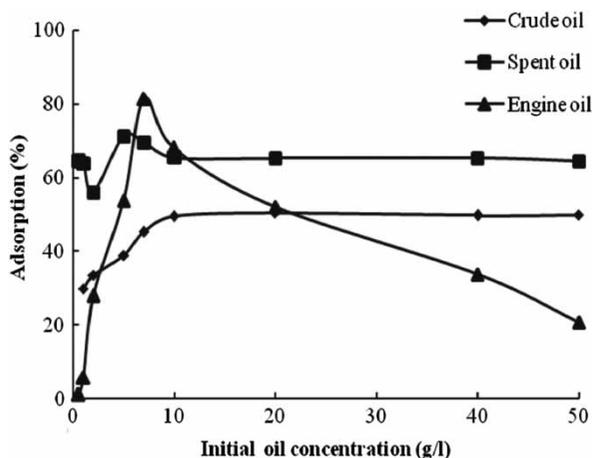


Figure 3 | The effect of oil concentration on the adsorption percentage by RRH.

The experimental data were validated using two well-known adsorption isotherm models: Langmuir and Freundlich.

The Langmuir isotherm model was derived on the assumptions that a monolayer adsorption on a homogenous surface occurs (Foo & Hameed 2010). The linear Langmuir model is defined by (Equation (2)):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \quad (2)$$

where q_e (mg/g) is the amount of adsorbed oil at equilibrium per unit weight of sorbent, C_e (mg/L) is the sorbate concentration at equilibrium, q_{\max} (mg/g) is the maximum adsorption capacity and K_L (L/mg) refers to the Langmuir constant that is related to adsorption energy. Separation factor (R_L , Equation (3)) shows the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The value C_0 (mg/L) is the sorbate initial concentration (Foo & Hameed 2010):

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

The Freundlich model describes non-ideal adsorption on heterogeneous surfaces, where there are interactions between adsorbed molecules involved in multilayer adsorption (Foo & Hameed 2010). The isotherm model can be defined as follows (Equation (4)):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

where k_f (L/mg) is the relative indication of adsorption capacity and n indicates the intensity of adsorption, which gives the favorability of the adsorption. It is generally stated that the values of n in the range 2–10, 1–2 and less than 1 represent good, moderately difficult and poor adsorption characteristics, respectively (Thompson et al. 2010). The Langmuir (plot of C_e/q_e versus C_e) and Freundlich (plot of $\ln q_e$ versus $\ln C_e$) isotherm models for adsorption of three oils by RRH are shown in Figures 4(a) and 4(b), and the constants derived from these isotherms are presented in Table 1.

The correlation coefficients obtained from the Langmuir isotherm for the adsorption of engine oil on RRH were high ($R^2 = 0.946$), while the adsorption of crude oil ($R^2 = 0.991$) and spent oil ($R^2 = 0.930$) obeyed the Freundlich model. The n value for adsorption of crude oil on RRH was less than 1, indicating relatively weak adsorption, while n constant more than 1 for spent oil indicated favorable

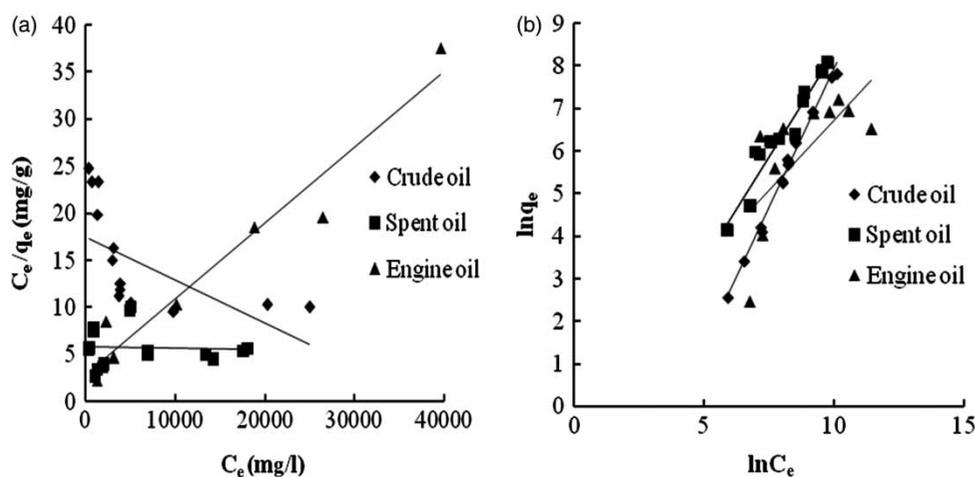


Figure 4 | Isotherm models of (a) Langmuir and (b) Freundlich for oil adsorption by RRH.

Table 1 | Isotherm parameters for oil adsorption by RRH

Oil samples	Langmuir model				Freundlich model		
	q_{\max} (mg/g)	K_L (L/mg)	R_L	R^2	K_f (L/mg)	n	R^2
Crude oil	–	–	–	0.352	5.75×10^{-3}	0.765	0.991
Spent oil	–	–	–	0.000	0.24	1.035	0.930
Engine oil	1,250	2.69×10^{-4}	0.063–0.77	0.946	0.178	1.53	0.485

– Not possible for computing parameters because of the inappropriateness of the model.

adsorption. The value of q_{\max} , calculated from the Langmuir model for adsorption of engine oil on RRH, was 1,250 mg/g. In addition, the R_L values of this model ($0 < R_L < 1$) confirmed favorable adsorption.

As expected, the difference in the behavior of engine oil adsorption was also confirmed by the Langmuir model. In fact, the adsorption decrease of engine oil at the higher concentration could be attributed to a monolayer sorption process (Brandão *et al.* 2010).

Comparison of oil adsorption

The results of ANOVA and Tukey's average comparison test for adsorption of oil compounds by RRH in identical experimental conditions (12 value for each compound) showed (Table 2) that the difference between the mean values of oil removal by RRH was significant ($p < 0.05$).

The oil removal efficiency was in the order of: engine oil > spent oil > crude oil. This was probably due to the higher viscosity of engine and spent oils compared to

Table 2 | Mean comparison of oil adsorption in the same experimental conditions on RRH

Oil compounds	Adsorption (%) \pm SD	p-value	R^2 (%)
Crude oil	^a 50.06 \pm 0.57	$p < 0.05$	0.987
Spent oil	^b 63.87 \pm 1.03		
Engine oil	^c 68.27 \pm 1.08		

Different letters (a, b, c) show significant differences according to Tukey's test.

crude oil. Even though viscous oil had lower velocity for penetration within the pores of the sorbent, its adherence on the surface of the solid phase was higher. In fact, low-viscosity oils could be weakly adsorbed and easily released from the sorbent when lifted out of the water (Teas *et al.* 2001; Hussein *et al.* 2009).

The adsorption capacity of RRH for crude oil in the present study (2,550 mg/g) was more than that of RRH (1,790 mg/g) reported by Thompson *et al.* (2010), and other sorbents such as meshed groundnut husk (1,110 mg/g) (Nwokoma & Anene 2010), ground kenaf bast (450 mg/g) and ground cotton (760 mg/g) (Lee *et al.* 1999).

CONCLUSIONS

In this study, the efficiency of RRH for the adsorption of three oil compounds from aqueous solutions was investigated. The oil adsorption by RRH was independent of pH. Decreasing particle size of the RRH reduced significantly the oil adsorption percentage due to damage of its micro-cavities. The highest adsorption percentage of engine, spent and crude oils at optimized conditions was 88, 80 and 55%, respectively, corresponding to their descending viscosity. The adsorption of crude and spent oils on RRH followed the Freundlich isotherm model, while engine oil adsorption was well fitted by the Langmuir model. Finally, it could be concluded that the use of RRH for the removal of oil pollutants, particularly heavy oil compounds from water, could be an economic and environmentally friendly method in emergency oil-spill cases.

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