Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1010235

57 (2016) 6693–6701
March

Taylor & Francis
Taylor & Francis Group

Produced water treatment using naturally abundant pomegranate peel

Taleb H. Ibrahim[a,*], Abdul S. Gulistan[a], Mustafa I. Khamis[b], Hussain Ahmed[a], Ahmed Aidan[a]

[a]*Department of Chemical Engineering, American University of Sharjah, P.O. Box 26666, Sharjah, UAE, Tel. +971 6 515 2460; email: italeb@aus.edu (T.H. Ibrahim), Tel. +92 333 817 9715; email: Sami_Gulistan@ffc.com.pk (A.S. Gulistan), Tel. +971 6 515 2982; email: huahmed@aus.edu (H. Ahmed), Tel. +971 6 515 2563; email: Aidan@aus.edu (A. Aidan)*
[b]*Department of Biology, Chemistry and Environmental Sciences, American University of Sharjah, P.O. Box 26666, Sharjah, UAE, Tel. +971 6 515 4751; email: mkhamis@aus.edu*

Received 9 September 2014; Accepted 14 January 2015

ABSTRACT

Pomegranate peel powder (PPP) was employed as a low cost adsorbent for the removal of crude oil from simulated produced water (SPW). The effect of contact time, adsorbent dosage, pH, as well as temperature on the efficiency of oil removal was investigated. The optimum parameters for oil removal were: pH 9.5, adsorbent dose = 2.33 g/L, contact time = 50.0 min, and adsorption temperature = 55.0˚C. The results showed that as the adsorbent dosage, pH, and salinity of SPW were increased, the removal efficiency increased. The adsorption of crude oil by PPP was found to follow the Langmuir adsorption isotherm, with adsorption capacity of 555 mg/g. The adsorption kinetics of crude oil are best described by a pseudo-second-order kinetic model, with a rate constant of 3.75×10^{-4} g/mg h. These results render PPP as an excellent adsorbent for the removal of oil from produced water with an efficiency exceeding 92% in 50 min.

Keywords: Produced water; Pomegranate peel; Biosorbent; Equillibrium isotherms; Kinetic model; Organic and inorganic pollutants

1. Introduction

The Arabian Gulf countries are major producers of oil and gas. Oil extraction and recovery require the injection of surfactant solutions into oil wells, thus generating wastewater as byproducts. The characteristics of the generated wastewater are drastically different from those of domestic or industrial wastewater and, hence, are referred to as produced water (PW) [1]. Oil and gas industries have to deal with a massive amount of produced, which appeared as a byproduct during exploration of oil and gas. The amount of PW increases with the well operation time, and may increase up to 80% of the total oil field [2]. Oil-field PW contains organic and inorganic compounds [1]. Discharge of PW can lead to serious pollution on surface, underground water, and soil. Alkali, surfactants, and polymers (residual chemicals) are accountable for the stability of the oil droplets, resulting in a decrease in interfacial tension of the oil–water and zeta potential on the surface of oil droplets. The environmental standards for discharge of PW as set by EPA are very strict and difficult to achieve [3]. Usually, to remove the stable oil droplets from the produced water,

---

*Corresponding author.

adsorption, filtration, flocculation, coagulation, and de-emulsification are carried out [4].

Several technologies are employed for PW treatment. Conventional methods for treating PW can be divided into biological, chemical, or physical methods [1,2]. The current practice of disposal of PW in this era of high technology is very uneconomical, and invokes a major environmental pollution concern [5]. Only a fraction of offshore platforms in the Gulf can obtain such quality, especially when it comes to the removal of dissolved oil components, which may exceed the concentration of the dispersed phase. Thus, it is necessary to improve upon existing technologies to meet the required environmental regulations at lower cost [6].

Adsorption has been found to be the most effective technique to remove matters from water [7]. Activated carbon is the mostly widely used adsorbent. However, it has a major drawback in terms of its high initial and regeneration costs [8,9]. Recently, many natural adsorbents have been developed for the removal of oil from PW [10–22]. These include eggshells [13], modified barley straw [22], banana peels [11], and surface-modified ball media filtration fibers [23].

Pomegranate peels can be used as adsorbent. Promising results for the application of pomegranate peels as biosorbents for removal of heavy metals and dyes from aqueous solution were obtained [24–26]. In these studies, activated carbon from pomegranate peels was prepared using different techniques.

The main worldwide producing countries of pomegranate are India, Turkey, Iran, Spain, Tunisia, Afghanistan, Greece, Japan, United States of America, China, France, Armenia, Cyprus, Egypt, Italy, and Palestine. The largest producing country among these is India with annual production reaching 33,415 tons in 2009–2010 [27]. It is estimated that 70% of fruit yields waste peal [28]. Hence, this waste can be treated and reused for PW treatment.

In this paper, pomegranate peel powder (PPP) is investigated as a natural adsorbent for the removal of crude oil from PW. The optimum adsorption parameters such as pH, sorption dosage, sorption time, and temperature are determined. Furthermore, adsorption isotherms as well as kinetic parameters are determined.

2. Experimental

2.1. Materials and instrumentations

The pomegranate peels were bought from local market in Dubai, UAE. Crude oil was obtained from Abu Dhabi National Oil Company (ADNOC), UAE. All chemicals used were of analytical grade. n-Hexane (95% pure, J.T. baker) was used as supplied. Double distilled water was used in all experiments (Water Still Aquatron A4000D, UK). A fluidized bed dryer (Sherwood Scientific, UK) was used for drying pomegranate peels. Precise vacuum oven (Model WOV-30, DAIHAN Scientific Co. Ltd, Korea) fitted with a vacuum pump (Model G-50DA, Ulvac Kiko, Japan) was used to dry the powdered sorbent. A fuzzy control system was used as a digital reciprocating shaker (Model SHR-2D, DAIHAN Scientific, Korea). For temperature control, a hotplate stirrer (Model MSH-20D, DIHAN Scientific Company, Korea) was used. A mechanical shaker was used for thorough mixing. Oil was analyzed spectrophotometrically (HACH DR-5000) at wavelength 450 nm [11]. pH measurements were performed by a pH meter (3320, JENNWAY Ltd, UK). The pH of all solutions was adjusted using either 0.1 M HCl or 0.1 M NaOH. Sieves (Stainless steel; Aperture 150–500 micro meter; Pascal Engineering Company, UK) were used for particle separation and classification. The topography images and chemical composition were obtained using scanning electron microscope with energy dispersive spectroscopy (SEM: TESCAN VEGA.3-LMU, USA). Fourier transform infrared spectroscopy (Bomem MB-3000 FT-IR equipped with ZnSe optics and a DTGS detector) was used to obtain spectra for PPP before and after treatment.

2.2. Biosorbent preparation

Pomegranate peel was thoroughly washed with doubled distilled water and then air-dried for 24 h. It was then ground to particle sizes between 2 and 3 mm, and further dried using the fluidized bed drier at 60˚C. The shredded peel was then refluxed for 2 h in n-hexane in order to remove hydrophobic soluble organic matter and colored pigments. The treated pomegranate peel was then washed thoroughly with doubled distilled water and dried in the fluidized bed dryer. A grinder was used to obtain fine PPP and it was sieved through 500–150 microns sieve. Finally, the fine PPP was washed with double distilled water and dried in a vacuum oven at 80˚C for 24 h. The product was stored in glass containers and stored in a desiccator at room temperature.

2.3. Adsorption experiments

To find the equilibrium time, eight samples of 150 mL simulated produced water (SPW) with oil concentrations of 200 ppm and 1.5 g of PPP were placed in 250 mL conical flasks. The solutions were agitated at 140 rpm for different time intervals using mechanical shaker at ambient conditions and initial pH of 9.5. Then the biosorbent and sorbate were separated by filtration. Oil remaining in the treated water was extracted using 150 mL of n-hexane solvent. The absorbance of the n-hexane extract at wavelength = 450 nm was then recorded using the Hack spectrophotometer. The amount of oil removed by the PPP was determined from a calibration curve [11]. The same experimental procedure as above was performed using SPW of 400, 600, 800, 1,000, 1,200, 1,400, and 1,600 ppm.

2.4. Effect of pH, salinity, and temperature and PPP dosage

The effect of pH, salinity, temperature, and PPP dosage on oil removal efficiency was investigated. The initial pH was varied between 0.1 and 13.7. In this experiment, PPP loading was kept at 10 g/L, oil content at 300 mg/L, and contact time for 50 min. Similarly, the salinity was varied between 100 and 2000 mg/L using NaCl and adjusting the initial pH to 9.5. Furthermore, the effect of temperature was determined by varying the solution temperature in the range of 25–70˚C at constant initial pH of 9.5. Finally the biosorbent dosage was varied between 0.33 and 2.64 g/L.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. Fourier transform infrared spectroscopy

Fig. 1 shows the FT-IR spectra of PPP before and after n-hexane extraction. Both spectra show a strong absorption band at 3,436 cm^{-1} for OH stretching mode. The absorption band at 2,918 cm^{-1} is attributed to the –CH$_2$– bond stretching and the weak absorption band at 2,845 cm^{-1}is assigned to the –CH– bond of methylene group. The peak at 1,734 cm^{-1}can be assigned to C=O stretching vibration of carboxylic acid. A strong absorption band appears at 1,628 cm^{-1} corresponding to the stretching vibration frequency of carboxylic acid with intermolecular hydrogen bond [29,30]. The C=C deformation mode which appears at 1,530 and 1,440 cm^{-1} can be attributed to aromatic hydrocarbons rings. These two bands appear only in the natural PPP. However, the n-hexane extracted PPP lacks both bands, presumably due to the extraction of this aromatic hydrocarbon by the solvent. Furthermore, several absorptions bands appear between 1,384 and 872 cm^{-1}, which represent C–O stretching modes presumably of phenols [30]. However, those absorptions bands are much less pronounced in n-hexane extracted PPP. These results strongly suggest that the majority of phenolic components are extracted efficiently by n-hexane.

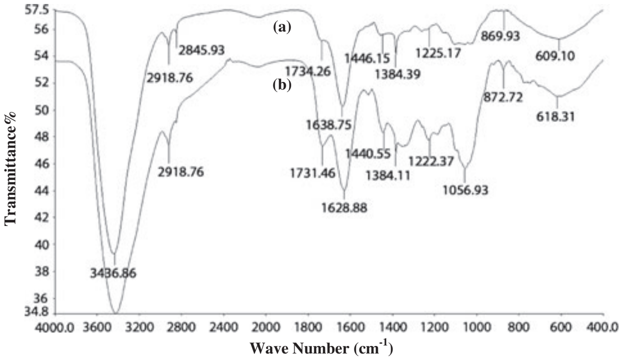

Fig. 1. FT-IR Spectra of PPP (a) treated with n-hexane (after reflux for 2 h) and (b) without treatment. Spectrum was obtained at 4 cm^{-1} resolution and 200 scans.

3.1.2. Scanning electron microscope

The physical morphology of the n-hexane extracted PPP surfaces before and after crude oil adsorption was determined using SEM (Fig. 2). Fig. 2(a) shows that the oil free PPP has clear cavities and pores, whereas the PPP loaded with oil lacks these pores and cavities (Fig. 2(b)). This finding was further supported by the energy dispersive X-ray spectrometry analysis which clearly shows that the carbon peak in the PPP-oil-loaded samples is larger than that in PPP-oil-free samples.

3.2. Adsorption isotherms

Effect of contact time on the oil removal efficiency at different initial oil concentrations.

The effect of contact time on the removal efficiency of crude oil by n-hexane extracted PPP was investigated at 25.0˚C. Inspection of Fig. 3 reveals that the optimum contact time for the adsorption of oil by PPP is 50 min. Furthermore, Fig. 3 reveals that at a given contact time, the oil removal efficiency decreases with increasing initial oil concentration. Specifically, at 60 min contact time, the oil removal efficiency decreased from 95 to 76% as the initial oil concentration increased from 200 to 1,400 ppm. This finding can be explained on the basis that at high initial oil concentration, the extent of surface coverage increases, leading to the observed saturation of surface which gives rise to the observed decrease in removal efficiency.

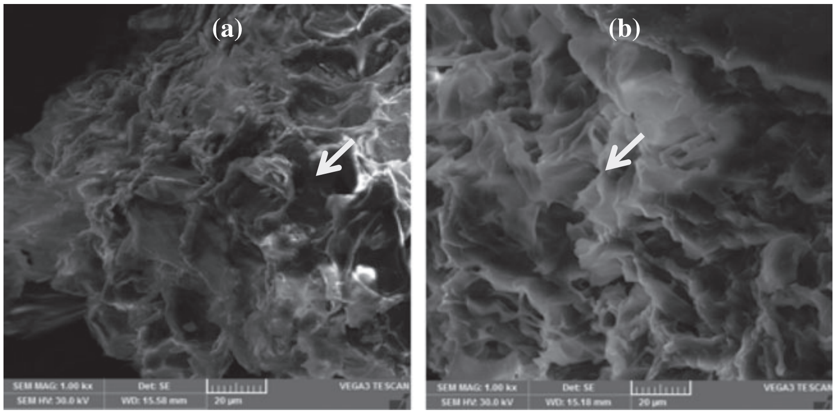

Fig. 2. SEM of PPP (a) before and (b) after adsorption.

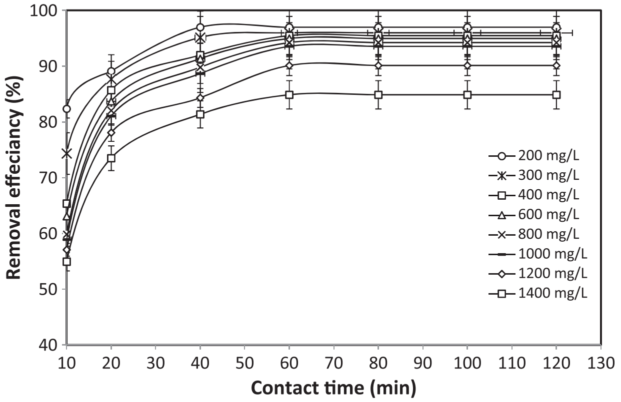

Fig. 3. Effect of contact time and initial oil concentration on the removal oil efficiency by PPP (initial pH: 9.5 ± 0.2; temperature: 25 ± 2˚C, adsorbent dosage 10 g/L).

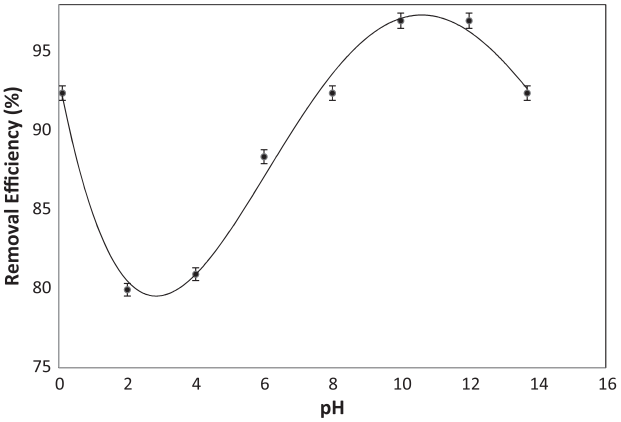

Fig. 4. Effect of pH on adsorption of crude oil. Initial oil concentration is 300 mg/L; temperature is 25 ± 2˚C, adsorbent dose is 10 g/L, contact time is 50 min, and shaking/stirring speed is 140 rpm.

3.3. Effect of pH

One of the most important parameters that controls the adsorption process is pH. The concentration of protons or hydroxide ions in solution affects both the surface properties of bio-sorbent as well as its binding sites [31]. Thus, it is expected that pH plays a vital role in the removal of crude oil by PPP. In this study, the effect of pH on the removal of crude oil by PPP was investigated at 50 min contact time, 300 ppm initial concentration of oil, and PPP dose of 10 g/L. The data are presented in Fig. 4. Inspection of this figure reveals that a decrease in the removal efficiency occurred as the pH increased from 0.1 to 3.5. However, further increase in pH from 4 to 10 was accompanied by a sharp increase in the removal efficiency of crude oil by PPP. These observations could be attributed to the fact that at very low values of pH (pH < 1), the electrostatic attractions between the protonated binding sites on the surface of PPP and oil molecules are very high, thus leading to the observed high efficiency at this pH [29]. On the other hand, at pH between 1 and 3.5, the availability of proton ions in solution competes with oil molecules, leading to the observed decrease in the efficiency of oil removal. The sharp increase in the removal efficiency of oil by PPP above pH 4 could be attributed to two factors: the first factor is presumably due to the destabilization of the oil–water emulsion at high pH, which produces unstable flocs of oil leading to coalescence of oil, and larger oil droplet size that enables larger efficiency [16]. The second factor could be attributed to the increase in the hydrophobicity of the biosorbent surface as the pH increases [32]. At pH 12 ± 0.2, the oil adsorption efficiency decreased slightly which could be attributed to an increase in oil emulsion stability leading to decreasing the contact area between PPP and oil droplets [33]. Thus, the optimum pH for the removal of oil is 9.5 ± 0.2.

3.4. Effect of salinity

Adsorption experiments of crude oil removal from SPW at NaCl concentrations from 0 to 2,000 mg/L were performed. The salinity study was conducted at the following conditions: initial oil concentration of 300 mg/L, initial pH 9.5 ± 0.2, 50 min of contact time, 140 rpm of shaker stirring, and biosorbent dose of 10 g/L. Fig. 5 shows that the oil removal efficiency increases as the salinity increases. A percent recovery of 96% at highest salinity was achieved. As the concentration of NaCl in the SPW increases, the solubility of oil in SPW decreases, resulting in an increase in the oil uptake [34]. However, for practical purposes, no measurable changes could be observed between the natural salinity of PW and the optimum salinity found in this study within the uncertainty of the experiments. Hence, salinity is not a determining factor for oil removal from SPW.

3.5. Effect of temperature

The effect of temperature could be the one of the most important factors which has a great influence on the oil removal from the produced water. In this study, the effect of temperature on the oil sorption was investigated. Experiments were conducted at different temperatures between 25 and 70°C. The temperature study was conducted at the following conditions: initial oil concentration of 300 mg/L, initial pH 9.5 ± 0.2, 50 min of contact time, 140 rpm of shaker stirring, and biosorbent dose of 10 g/L. Fig. 6 shows that the oil removal efficiency increased from 92 to 96% when the temperature was increased from 25 to 55°C, but it started decreasing when temperature was increased further to more than 60°C. The increase in the efficiency of the oil removal is due to the decrease in the oil viscosity. As the viscosity of the oil is decreased, the oil uptake of the biosorbent will be increased [15]. The rate at which the oil penetrates into the interior surfaces of the biosorbent is inversely proportional to the viscosity of oil [35]. In the liquid, the adsorbate molecules are in random Brownian motion and get adsorbed (by effective collisions) when they are close to the sorbent. Increasing the temperature actually raises the velocities or the movement of the molecules. This results in instability of the oil molecules and an increase in the interaction between the oil and the sorbent particles. Therefore, the oil removal efficiency increases with temperature. The increase in the adsorption also indicates that the rate is being controlled by the kinetics of the process. The decrease in the oil removal efficiency after 60°C indicates that the rate of adsorption is being controlled by the exothermic process. In this study, room temperature was selected for the removal of oil from SPW since no noticeable gain will be obtained at higher temperature within the uncertainty of the experiment which will in turn makes this process more economic and feasible.

3.6. Effect of biosorbent concentration

Fig. 7 shows the relationship between the crude oil removal efficiency and biosorbent dosage. It can be observed that oil removal efficiency increased from 70.8 to 95.5% when the biosorbent dose was increased

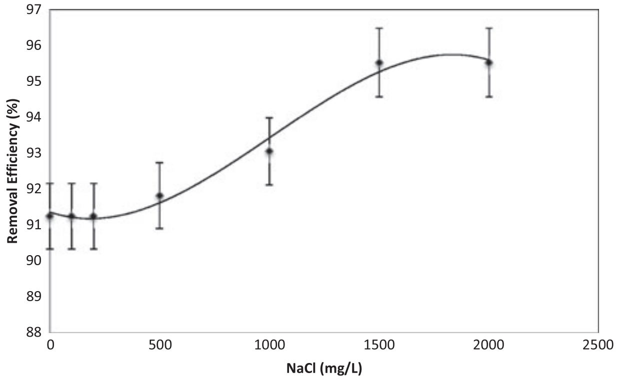

Fig. 5. Effect of salinity on the crude oil removal efficiency. Initial oil concentration is 300 mg/L; initial pH is 9.5 ± 2, temperature is 25 ± 2°C, adsorbent dose is 10 g/L, contact time is 50 min, and shaking/stirring speed is 140 rpm.

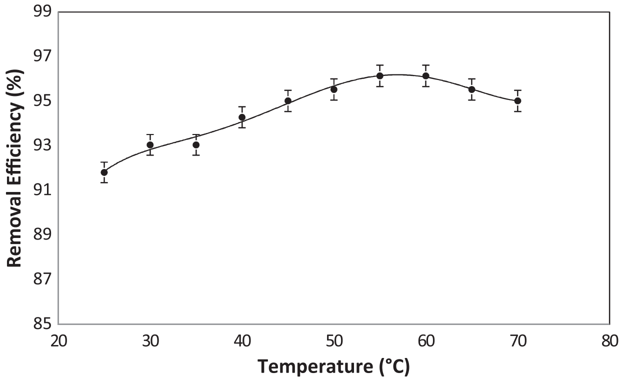

Fig. 6. Effect of temperature on the crude oil removal efficiency. Initial oil concentration is 300 mg/L, initial pH is 9.5 ± 2, temperature is 25 ± 2°C, adsorbent dose is 10 g/L, contact time is 50 min, and shaking/stirring speed is 140 rpm.

from 0.05 to 2.325 g/L of the solution. The optimum biosorbent dose was identified as 0.35 g per 150 mL (2.325 g/L) of produced water. Removal efficiency was enhanced due to the increase of available sites for adsorption.

3.7. Adsorption isotherms models

The adsorption isotherm provides a relation between total mass of adsorbed adsorbate per unit mass of sorbent at constant ambient conditions. In order to develop adsorption isotherms, adsorption experiments were performed. In these experiments, the amount of adsorbent was kept constant while the initial concentration of the adsorbate was varied. Langmuir adsorption isotherm and Freundlich adsorption isotherm are the most common isotherms which are used for adsorption studies [36].

The equilibrium data were correlated using Langmuir (Eq. (1)), Freundlich (Eq. (2)), and Temkin (Eq. (3)) isotherms.

$$\frac{C_e}{q_e} = \frac{1}{k_a q_m} + \frac{C_e}{q_m} \tag{1}$$

$$\log\ q_e = \log\ k_f + \frac{1}{n}\log\ C_e \tag{2}$$

$$q_e = B\log\ k_t + B\log\ C_e \tag{3}$$

where q_e is the amount of the substance adsorbed at equilibrium per amount of adsorbent; q_m is the saturation monolayer adsorption capacity, C_e is the equilibrium concentration, k_a is the Langmuir adsorption equilibrium constant, k_f and n are the Freundlich constants, and B is the Temkin equilibrium adsorption constant.

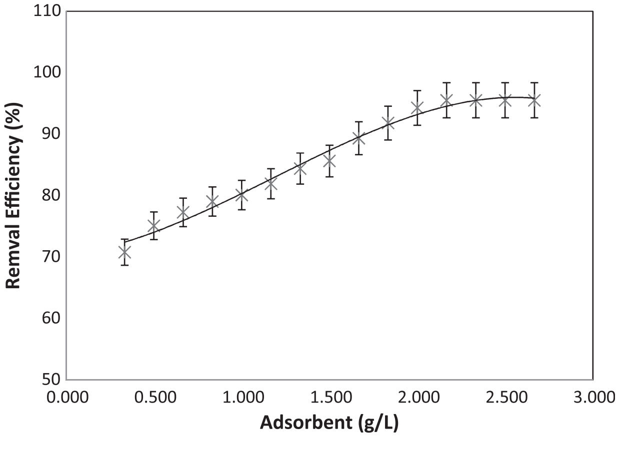

Fig. 7. Effect of adsorbent dosage on the removal efficiency of oil. Initial oil concentration is 300 mg/L, initial pH is 9.5 ± 2, temperature is 25 ± 2°C, contact time is 50 min, and shaking/stirring speed is 140 rpm.

The linear plots of Langmuir, Freundlich, and Temkin isotherms gave the following regression coefficient (R^2): 0.989, 0.915, and 0.961, respectively, which strongly suggests that the data are best fitted by the Langmuir isotherm.

Table 1 summarizes the adsorption capacity of different bioadsorbents under several conditions. It is obvious that PPP displayed an adsorption capacity comparable with most adsorbents employed. Table 2 summarizes the adsorption parameters of the different isotherms employed to fit the adsorption isotherm.

3.8. Analysis of adsorption kinetics

The kinetics of adsorption of crude oil by PPP was studies at 25°C. The data were fitted to both pseudo–first-order and pseudo-second-order kinetics models [37]. The linear forms of the equations are given in Eqs. (4) and (5).

$$\ln\ (q_e - q_t) = -k_{\mathrm{I}} t + \ln\ q_e \tag{4}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_{\mathrm{II}}(q_e)^2} \tag{5}$$

where q_t (mg/g) is the amount of oil adsorbed at a given time and q_e (mg/g) is the amount of oil adsorbed at equilibrium, k_{I} is pseudo-first-order rate constant (1/h), and k_{II} is the pseudo-second-order rate constant (g/mg h).

The plots for the pseudo-first and pseudo-second-order kinetic models reveal that the latter model fits the data well as compared to the former model, based on the regression coefficients and the calculated q_e. Table 3 lists the different models parameters values such as k_{I}, k_{II} and $q_{e(\mathrm{cal})}$ together with q_e obtained from Langmuir isotherm, and R^2. Inspection of Table 2 reveals that $q_{e(\mathrm{cal})}$ given by the pseudo-second-order kinetic model (588.3 mg/g) was closer to the experimental value $q_{e(\mathrm{exp})}$ (555.6 mg/g, see Fig. 8) obtained from Langmuir isotherm than that obtained from pseudo first order kinetic model (65.4 mg/g). Also, the R^2 value for the pseudo-second-order kinetic model (0.9903) was higher than that of pseudo–first-order kinetic model (0.9366).

Table 1
Oil adsorption capacities of different adsorbents

Adsorbent	Emulsified oil studied	Sorption capacity (g/g)	References
Banana pseudo-stem fibers	Palm oil	0.169	[10]
Raw banana peel (RBP)	Crude oil	0.726	[11]
Bentonite	Crude oil	0.4933	[12]
Powdered activated carbon (PAC)	Mineral oil	0.322	
Deposited carbon (DC)	Mineral oil	0.374	
Surface-modified eggshell (SMES)	Crude oil	0.121	[13]
Raw eggshell	Crude oil	0.107	[14]
Treated vegetable fiber	Mineral oil	0.52	[15]
Natural feathers	Crude oil	0.65	
	Standard mineral oil	0.56	
Yellow horn shell residues	Cooking oil	0.42	[16]
Yellow horn shell residues (Treated)	Cooking oil	0.61	[16]
Chitosan powder	Palm oil mills effluent (POME)	3.42	[17]
Chitosan flake	Palm oil mills effluent (POME)	1.97	[17]
Bentonite organoclay	Valcool (cutting oil)	0.14	[18]
Acetylated rice straw	Machine oil	24.0	[19]
Acetylated sugarcane bagasse	Machine oil	18.8	[20]
Natural wool fibers (NWF)	Real oily wastewater (motor oils)	5.56	[21]
Recycled wool-based nonwoven material (RWNM)	Real oily wastewater (motor oils)	5.48	
Sepiolite	Real oily wastewater (motor oils)	0.19	
Expanded vermiculite	Standard mineral oil (SMO)	0.0150	[22]
	Canola oil (CO)	0.0463	
	Kutwell 45	0.0110	
	Refinery effluent (RE)	0.00809	
Hydrophobized vermiculite	Standard mineral oil	0.0230	[22]
	Canola oil (CO)	0.00612	
	Kutwell 45	0.00670	
	Refinery effluent (RE)	0.00270	
Modified barley straw (BMBS)	Canola oil (CO)	0.613	[23]
	Standard mineral oil (SMO)	0.584	
Pomegranate peel powder	Crude oil	0.555	This study

Table 2
Equilibrium adsorption parameters of three isotherms for the removal of oil from PW using PPP. Temperature = 25°C; adsorbent dosage = 2.35 g/L; pH 9.5; contact time = 50 min

Isotherm model	q_m (mg/g)	k_L (L/mg)	k_f (mg/g)	k_t	n	q_D (mg/g)	B (L/g)	R^2
Langmuir	555.56	0.0284	–	–	–	–	–	0.989
Freundlich	–	–	5.1454	–	2.1299	–	–	0.915
Temkin	–	–	–	0.282866	–	–	279.64	0.961

3.9. Desorption studies

Desorption experiment was performed on adsorbed crude oil on the PPP surface using n-hexane. Adsorption–desorption experiment was repeated three times. The crude oil was desorbed from the adsorbent PPP with 150 ml of n-hexane. The solutions were agitated at 140 rpm for 50 min. More than 90% of the oil was desorbed from the PPP surface. The adsorption capacity of PPP after initial use showed a slight change (89% of the crude oil was adsorbed compared to 94% for first use). These results indicate that the PPP adsorbent can be reused without pronounced change in its adsorption capacity.

Table 3
Kinetic model parameters for sorption of oil onto the surface of PPP

Kinetic model	Parameters	Values
Pseudo-first-order	K_I (g/mg h)	0.0339
	$Q_{e(\mathrm{cal})}$ (mg/g)	65.4
	R^2	0.9366
Pseudo-second-order	K_II (g/mg h)	0.000275
	$Q_{e(\mathrm{cal})}$ (mg/g)	588.2
	R^2	0.9903

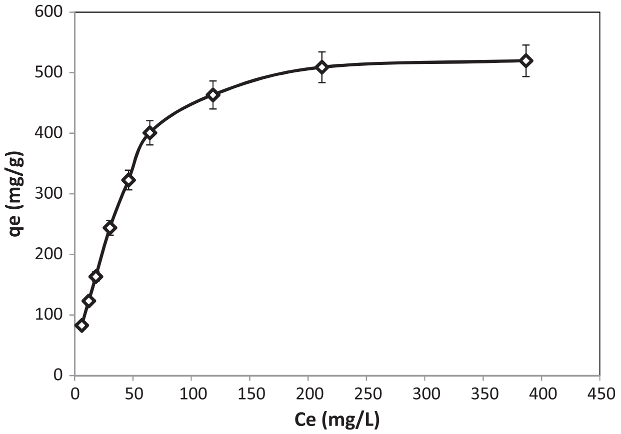

Fig. 8. The relationship between the amounts of crude oil adsorbed per amount of adsorbent and equilibrium concentration. Temperature = 25˚C; adsorbent dosage = 2.35 g/L; pH 9.5; contact time = 50 min.

3.10. Oil removal from real produced water

The sample of real PW was obtained from Sharjah National Oil Company (SNOC), Sharjah. The extraction of oil from this water using n-hexane revealed that its oil content is 230 mg/L. Upon treatment of 150 mL of PW with 0.350 g of PPP, the removal efficiency of oil was found to be 95.7 ± 1.0%. This result gives evidence that our proposed method is powerful in treating PW from oil and gas well.

4. Conclusion

In this study, a new promising and efficient natural adsorbent for the removal of oil from PW was developed. The adsorbent was prepared from PPP with an optimum adsorption efficiency greater than 92%. The adsorption process was optimized with respect to adsorbent dosage, temperature, pH, and contact time. The optimum parameters for oil removal were: pH 9.5, pomegranate dosage = 2.33 g/L, contact time = 50.0 min, and adsorption temperature = 55.0˚C. Furthermore, the efficiency was found to increase with increasing the salinity of produced water. The adsorption isotherm for crude oil removal was found to follow the Langmuir adsorption isotherm with adsorption capacity of 555 mg/g. The kinetics of adsorption were found to follow a pseudo-second-order kinetic model with a rate constant of 3.75×10^{-4} g/mg h. This newly developed adsorbent was found to be easily regenerated without noticeable change in adsorption capacity. These findings render PPP as an efficient, cost-effective, and environmentally friendly adsorbent.

References

[1] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, J. Hazard. Mater. 170(2–3) (2009) 530–551.

[2] P. McCormack, P. Jones, M.J. Hetheridge, S.J. Rowland, Analysis of oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry (ESI-MSn), Water Res. 35(15) (2001) 3567–3578.

[3] USEPA. Available from: http://www.epa.gov.

[4] S. Deng, G. Yu, Z. Jiang, R. Zhang, Y.P. Ting, Destabilization of oil droplets in produced water from ASP flooding, Colloids Surf., A 252(2–3) (2005) 113–119.

[5] F. Bayati, J. Shayegan, A. Noorjahan, Treatment of oil-field produced water by dissolved air precipitation/solvent sublation, J. Pet. Sci. Technol. 80(1) (2011) 26–31.

[6] A.L.N. Mota, L.F. Albuquerque, L. Beltrame, T.C. Chiavone-Filho, A. Machulek Jr, C.A.O. Nascimento, Advanced oxidation processes and their application in the petroleum industry: A review, Braz. J. Pet. Gas 2 (2008) 122–142.

[7] L.R. Radovic, C.D. Moreno-Castilla, Carbon materials as adsorbents in aqueous solutions, in: P. Thrower, Chemistry and Physics of Carbon, vol. 27, Marcel Dekker, New York, NY, 2000, pp. 227–405.

[8] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97(1–3) (2003) 219–243.

[9] S.E. Bailey, T.J. Olin, M. Bricka, D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33(11) (1999) 2469–2479.

[10] N.I. Husin, N. Aimi, A. Wahab, N. Isa, R. Boudville, Sorption equilibrium and kinetics of oil from aqueous solution using banana pseudostem fibers, Int. Conf. Environ. Indus. Innov. 12 (2011) 177–182.

[11] U.A. El-Nafaty, I.M. Muhammad, S. Abdulsalam, Biosorption and kinetic studies on oil removal from produced water using banana peel, Civ. Environ. Res. 7 (2013) 125–136.

[12] K. Okiel, M. El-Sayed, M.Y. El-Kady, Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon, Egypt. J. Pet. 20 (2) (2011) 9–15.

[13] I.M. Muhammad, S. Abdulsalam, Y.I. Makarfi, Removal of oil from oil produced water using eggshell, Civ. Environ. Res. 2(8) (2012) 52–64.

[14] L.A. Robertson, Selection criteria and laboratory evaluation of oil spill sorbent, update II, Environment Canada-EPS report, EPS4-EP-83-4, 1985, Canada.

[15] J. Li, M. Luo, C.-J. Zhao, C.-Y. Li, W. Wang, Y.-G. Zu, Y.-J. Fu, Oil removal from water with yellow horn shell residues treated by ionic liquid, Bioresour. Technol. 128 (2013) 673–678.

[16] A.L. Ahmad, S. Sumathi, B.H. Hameed, Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetic studies, Water Res. 39(12) (2005) 2483–2494.

[17] H. Moazed, T. Viraraghavan, F. Asce, Removal of oil from water by bentonite organoclay, Pract. Per. Hazard. Toxic Rad. Waste Manage. 9(2) (2005) 130–134.

[18] X.-F. Sun, R.C. Sun, J.X. Sun, Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup, J. Agric. Food. Chem. 50(22) (2002) 6428–6433.

[19] X.-F. Sun, R.C. Sun, J.X. Sun, A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials, J. Mater. Sci. 38(19) (2003) 3915–3923.

[20] V. Rajakovic, G. Aleksic, M. Radetic, L. Rajakovic, Efficiency of oil removal from real wastewater with different sorbent materials, J. Hazard. Mater. 143(1–2) (2007) 494–499.

[21] D. Mysore, T. Viraraghavan, Y.-C. Jin, Treatment of oily waters using vermiculite, Water Res. 39(12) (2005) 2643–2653.

[22] S. Ibrahim, H.-M. Ang, S. Wang, Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw, Bioresour. Technol. 100 (23) (2009) 5744–5749.

[23] Y. Yang, X. Zhang, Z. Wang, Oilfield produced water treatment with surface-modified fiber ball media filtration, Water science and technolog, J. Int. Assoc. Water Pollut. Res. 46(11–12) (2002) 165–170.

[24] E.-S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination 223 (2008) 162–173.

[25] M.A. Ahmad, N.A.A. Puad, O.S. Bello, Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by micrwave-induced KOH activation, Water Resour. Ind. 6 (2014) 18–35.

[26] M.R. Moghadam, N. Nasirizadeh, Z. Dashti, E. Babanezhad, Removal of Fe(II) from aqueous solution using pomegranate peel carbon: Equilibrium and kinetic studies, Int. J. Ind. Chem. 4(19) (2013) 1–6.

[27] Available from: http://vc.vivekanandaedu.org/wp-content/uploads/pdf/Pomegranate_April%2011.pdf.

[28] D. MacLean, K. Martino, H. Scherm, D. Horton, Pomegranate Production. Available from: http://www.caes.uga.edu/applications/publications/files/pdf/C%20997_4.PDF, retrieved on June 4th, 2014.

[29] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy, fourth ed., Scitech B. News, New York, NY, 2008 (32(2)).

[30] F.A. Pavan, E.C. Lima, S.L.P. Dias, A.C. Mazzocato, Methylene blue biosorption from aqueous solutions by yellow passion fruit waste, J. Hazard. Mater. 150(3) (2008) 703–712.

[31] J.Y.A. Farah, Biosorption of Astrazone Blue basic dye from an aqueous solution using dried biomass of Baker's yeast, J. Hazard. Mater. 148(1–2) (2007) 402–408.

[32] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere 50(8) (2003) 1095–1105.

[33] S. Ibrahim, S. Wang, H.M. Ang, Removal of emulsified oil from oily wastewater using agricultural waste barley straw, Biochem. Eng. J. 49(1) (2010) 78–83.

[34] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon 42(1) (2004) 83–94.

[35] G. Ard, P. Schatzberg, Investigations of Sorbents for Removing Oil Spills from Water, Report No. 724110.1/2/1 , U.S. Coast Guard Headquarters, Washington, DC, 1971.

[36] T. George, F.L. Burton, H.D. Stensel, Wastewater Engineering-Treatment and Reuse, fourth ed., Metcalf and Eddi Inc, McGraw-Hill, New York, NY, 2003.

[37] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.-H. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162(2–3) (2009) 616–645.