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Impregnation of polyurethane foam with activated carbon for enhancing oil removal from water

A. Keshavarz[1] · H. Zilouei[1] · A. Abdolmaleki[2] · A. Asadinezhad[1] · A. A. Nikkhah[1]

Abstract To enhance the oil sorption capacity of polyurethane foam, different amounts of activated carbon (0.5, 1, 2 and 3 wt%) were grafted onto the surface of polyurethane foam. The modified polyurethane foam was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis and tensile elongation test. Grafting of activated carbon improved the polyurethane foam toughness and thermal resistance as revealed by tensile elongation and thermogravimetric tests, respectively. Experimental results showed the enhancement of oil sorption capacity and reduction in the water sorption in all cases. The optimal amount of activated carbon on the surface was 1 wt% which enhanced the oil sorption capacity up to 33.2 %. Reusability feature of the optimum sorbent was examined through four cycles of chemical regeneration, and about 85 % of the initial sorption capacity of the modified polyurethane foam was remained at the end. Equilibrium isotherms were analyzed using Langmuir, Freundlich and Redlich–Peterson isotherms using linear and nonlinear regression methods. The Marquardt's percent standard deviation and hybrid fractional error functions were minimized and normalized to investigate the effect of error criteria to determine the parameters of isotherms. The nonlinear method was found to be more accurate to determine the isotherm parameters, and the Langmuir isotherm was the best-fitting model.

✉ H. Zilouei
hzilouei@cc.iut.ac.ir

[1] Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

[2] Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

Introduction

Water pollution by oil as a result of oil release during transportation and storage has raised grave worldwide concerns (Adebajo et al. 2003). About 5 million tons of oil is transported yearly overseas by tankers posing risk of oil spillage or leakage to the marine ecosystem. Oil spill adversely affects the diverse marine species, the seaside plants and animal such as fish, birds and mollusks (Al-Majed et al. 2012; Aguilera et al. 2010). Moreover, human is exposed to potential health problem as the sea foods can carry oil pollutants and cause genotoxic damage in consumers (Aguilera et al. 2010). As the spilled oil undergoes several processes such as spreading, evaporation, dissolution, biodegradation and emulsification, developing effective methods for the quick removal of oil from the polluted environment is essential (Banerjee et al. 2006; Annunciado et al. 2005). Methods of oil spill removal can be classified into three main groups: oil separation and collection from water surface, mixing oil and water by dispersants and in situ burning (Avila et al. 2014).

Among the oil removal methods, using sorbents is of great interest from the economical and ecological point of view (Sidik et al. 2012). Adding the sorbent material to an oil spill area forms a semisolid phase which eases the oil removal through sorption (Teas et al. 2001). Selectivity, high adsorption capacity, fast adsorption kinetics, easy regeneration and reusability, good mechanical strength, low cost and biodegradability are ideal requirements of a commercial sorbent (Teas et al. 2001). Inorganic mineral sorbents such as graphite have showed good oil sorption;

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however, their shortcomings such as oil release, sinking to the water and high cost have made them inappropriate choice for oil removal in large scale (Tryba et al. 2003). Organic vegetable products such as cotton are cheap, biodegradable and easily available, but their low sorption capacity besides high total cost of removal process has made them unfavorable choice for oil sorption (Said et al. 2009). Synthetic organic products such as polyurethane and polypropylene foam have good oleophilic properties. However, the main disadvantage of this group is non-biodegradability (Al-Majed et al. 2012).

Polyurethane foam (PUF) and activated carbon (AC) are among the widely used sorbent for oily water treatment. PUF is commercially produced, has shown good oil sorption capacity and is reusable (Wu et al. 2014; Li et al. 2012). Surface modification of PUF can be an effective method to improve the hydrophobic and oleophilic properties of this sorbent without changing the bulk properties. Wu et al. (2014) for developing polyurethane sponges with hydrophobic surface treated the PUF samples with SiO₂ sol and improved the sorption of motor oil from water. Li et al. (2012) improved the oleophilic properties of PUF by grafting lauryl methacrylate to the surface of PUF which increased the sorption of kerosene.

Activated carbon is widely used as sorbent for wastewater treatment due to its high surface area ranging from 500 to 1500 $m^2\ g^{-1}$, the presence of different functional groups on its surface, well-developed internal microporous structure and hydrophobic internal surface (Yin et al. 2007; Marsh and Reinoso 2006). It is a common effective sorbent for the removal of organic and inorganic contaminants from water (Rivera-Utrilla et al. 2011; Okiel et al. 2011). The unique adsorption properties of AC are mainly attributed to lactones and quinones functional groups (Bhatnagar et al. 2013). However, AC application is limited because of its poor mechanical strength and sorption selectivity and incomplete regeneration (Zhou et al. 2008). In recent years, intense researches have been performed to improve the AC selectivity for adsorbing specific contaminates by improving the carbon surface through different chemical, physical and biological methods (Bhatnagar et al. 2013). The number of acidic functional groups on the AC surface is related to uptake of organic contaminants (Emam 2013). The acidic character of AC is attributed to oxygen containing surface groups (i.e., carboxyl, carbonyl and phenols) on the outer surface or edge of the basal AC plane (Shafeeyan et al. 2010). Emam (2013) investigated the effect of AC acidic treatment on oil sorption from water at pH 7, which oil sorption was increased up to 12 mg in comparison with untreated AC.

The main purpose of this study is to modify the surface of PUF with impregnation of AC in order to increase the oil sorption capacity of the PUF. Then, the performance of surface-modified PUF is determined in terms of oil sorption capacity, sorption efficiency and reusability. This study was performed in a 12-month period between December 2013 and December 2014 at Isfahan University of Technology, Iran.

Materials and methods

Materials

Activated carbon (AC) with acidic pH and particle size under 100 μm was obtained from Merck Company (Germany). 1,1-Dichloro-1-fluoroethane (HCFC 141b) was purchased from Lin'an E-COOL Refrigeration Equipment CO (China). NIXOL AM-313 polyether polyol was obtained from KPX Chemical CO (South Korea), and methylene diphenyl diisocyanate (MDI) was obtained from Daeyang International CO (South Korea). Light crude oil was obtained from Isfahan refinery feed stream (Iran). Industrial grade xylene was purchased from Isfahan petrochemical complex (Iran). Petroleum ether (boiling range of 30–60 °C) was purchased from Pars Chemie Co (Iran).

Synthesis of polyurethane foam

To synthesize the open-cell polyurethane foam (PUF), deionized water and HCFC 141b were used as the chemical and physical blowing agents, respectively. At first, at ambient temperature (23 ± 2 °C), 10 g of polyol was completely mixed with 0.1 g of deionized water and 1.5 g of HCFC 141b. Once the mixing was complete, 4 g of MDI was added to the prepared mixture and again was mixed by use of a mixer at 1000 rpm. Finally, the mixture was left for 1 h to provide enough time for the foaming reaction.

Impregnation of polyurethane foam with activated carbon

Impregnation of PUF was done by utilizing the reaction between carboxylic and phenolic OH agents on the surface of AC and OH agents in the foam structure. The reaction schematically presented in Fig. 1 was done by MDI in which one MDI tail reacted with OH groups on the surface of AC and the other reacted with the OH agents existing in the polyether polyol chains. Samples with 0.5, 1, 2 and 3 wt% of AC on the PUF surface were prepared. At first, 300 mL petroleum ether was poured in a glass beaker, and then, 10 times more than the final weight of AC on the surface was added to the beaker and was stirred for 5 min at 1000 rpm. Then, 1 g of PUF cubes was added and was stirred for 15 min to let the AC particles penetrate into the foam pores. After that, while still mixing, as much as two
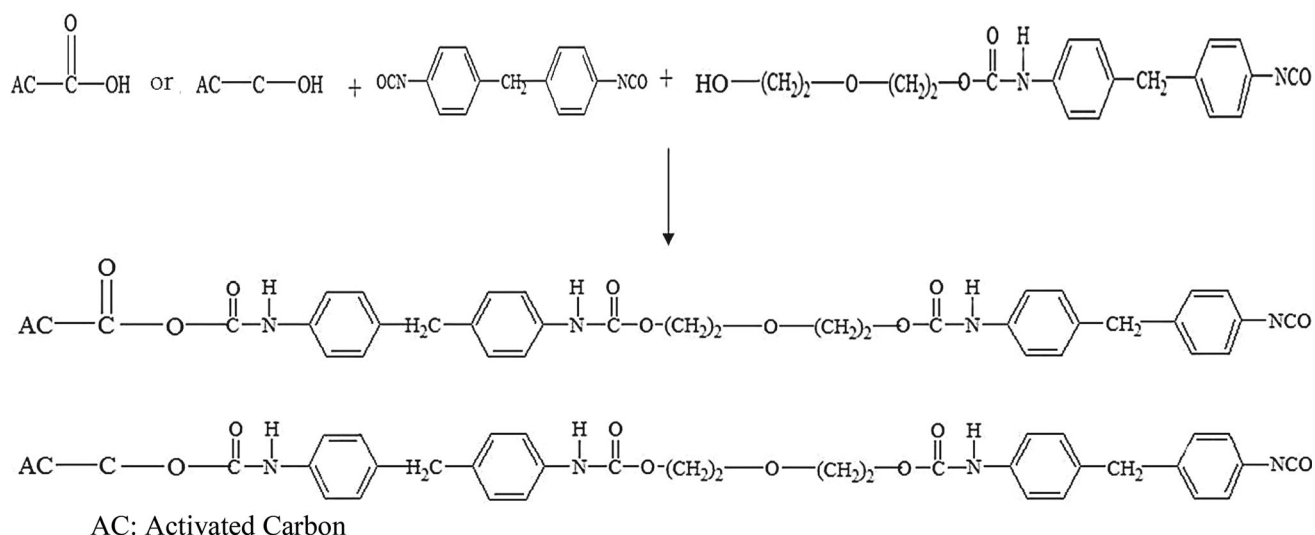
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AC: Activated Carbon

Fig. 1 Schematic of the reaction between MDI and OH groups

times the weight of the added AC, MDI was added to the reaction environment drop by drop and was stirred for 40 min. The cubes were taken out and dried in an oven at 100 °C for 10 min. Then, again, the cubes were washed by petroleum ether, to remove the particles that have just been trapped in the pores without reaction with the surface, and were dried in oven at 100 °C for 30 min. Finally, the dried cubes were scaled, and their weight in comparison with the blank cubes weight showed the weight of the added AC to the surface. The samples with over ±10 wt% deviation from the mean were excluded.

Sorption capacity experiment

Light crude oil was used to study the sorption capacity of the prepared sorbents. The sorption experiments were conducted based on the Standard Test Method for Sorbent Performance of Adsorbents (ASTMF726-99).

All the experiments were conducted in water–oil system. To do this, 250 mL of water was poured into a 600 mL beaker and then crude oil was added to the water so that at least a layer with thickness 2–4 mm was formed on the water surface. Then, 1.0 g surface-modified sorbent was added to the beaker which was placed on a shaker table with frequency 150 rpm for 15 min. The content of the beaker was allowed to settle for 2 min after shaking. Then, the sorbent cubes were removed from the system by a forceps and allowed to drain for 30 ± 3 s and were weighed. After that, the oily cubes were fully washed with industrial grade xylene to extract the adsorbed oil and water. The final extracted solution was used to determine the weight of the water trapped in the oil based on the Standard Test Method for Water in Crude Oil by Distillation (ASTMD4006-81). The extracted solution was poured into a 1000-mL round-bottom, glass distillation flask which was connected to a 400-mm Liebig condenser and a 10-mL water trap. The extracted solution in the flask was heated. After initial heating, boiling rate was adjusted so that the condensate passed not longer than three quarters of the condenser inner tube length and distillate was discharged into the trap at the approximately 2–5 drops per second rate. Distillation was continued until the volume of the water in the trap remained constant and no water was visible in the other part of the apparatus. When the distillation operation was complete, the trap content was allowed to cool down to 20 °C. Finally, the collected water in the trap was weighed. The experiments were conducted in triplicate. If the value of any obtained result (g/g) deviated beyond 15 % of the mean, then the samples would be excluded.

The oil sorption capacity of the sorbents was calculated by following relation:

$$M = \frac{m_s - m_w - m_0}{m_0} \quad (1)$$

where M is the oil sorption capacity (g/g), m_s is the weight of saturated sorbent (weight of the water plus oil and sorbent), m_w is the weight of adsorbed water (g) and m_0 is the initial dry weight of sorbent (g). Oil removal percentage was determined by:

$$P_r = \frac{m_o}{m_i} \times 100 \quad (2)$$

where P_r is the oil removal percentage, m_o is the weight of removed oil (g) and m_i is the initial weight of oil (g). Oil sorption efficiency of the sorbent is defined as the ratio of adsorbed oil weight to the total weight of adsorbed oil and water and is calculated by:

$$E = \frac{m_o}{m_o + m_w} \times 100 \tag{3}$$

where E is oil sorption efficiency, m_o is the weight of adsorbed oil (g) and m_w is the weight of adsorbed water.

Sorbent regeneration

To identify the reusability feature of the developed sorbent, the sorbent cubes after the sorption experiments were chemically regenerated. The chemical method was done through washing the sorbent cubes with 150 mL fresh petroleum ether in a 250-mL beaker for three times so that no color change was observed in the fresh washing petroleum ether at the third final stage. Then, the sorbent cubes were dried in an oven for 30 min at 100 °C.

Sorbent Characterization

The presence of the AC particles on the surface of PUF was explored by scanning electron microscopy (SEM) (TES-CAN—VEGA3, SBU—Easy Probe, Czech). FTIR spectra of blank PU and AC surface-modified PUF cubes were obtained by FTIR spectrometer (JASCO, Model 6300, Japan). In this study, FTIR technique was used to ensure the presence of the carboxylic acids and phenol on the AC surface, the PU synthesis confirmation and also to validate the surface modification procedure through identifying created bond between AC and PUF. To study the effect of surface modification on thermal properties of the PUF, thermogravimetric analysis (TGA) was performed by a thermogravimetric analyzer (STA6000, PerkinElmer, USA). Tensile elongation test was performed to study the change in mechanical property of the developed sorbents by Zwick Universal Testing Machine 1446-60, Germany.

Adsorption isotherms

Equations of equilibrium isotherms were used to describe the experimental sorption data. The thermodynamic assumptions and parameters of the equations provide useful information about the sorption mechanism, the surface properties and affinities of the sorbent (Ho et al. 2005). In this study, the applicability of Langmuir, Freundlich and Redlich–Peterson isotherm models onto blank PUF and AC surface-modified PUF for oil removal from water was studied.

The linearization of nonlinear experimental data may distort the error distribution (Kumar et al. 2008). In addition, the linear analysis method is based on the assumption that the scatter of points around the line follows a Gaussian distribution and the error distribution is the same at every value of the equilibrium concentration (Ncibi 2008). Therefore, in selecting the optimum isotherm a comparison

between the linear and nonlinear regression method was made to the experimental equilibrium data.

The linear regression analysis was done through the least square method, and the nonlinear regression was performed by use of the *solver* add-in function, Microsoft Excel, Microsoft Corporation, to directly estimate the model parameters from the nonlinear equations.

Langmuir isotherm

Langmuir model is based on the assumptions of a homogeneous surface with constant adsorption energy over the all sites, localized adsorption on the surface and monolayer a desorption (Limousin et al. 2007). The nonlinear and linear forms are represented as (Langmuir 1918):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{5}$$

where q_m (g g^{-1}) is the monolayer capacity of the adsorbent, K_L (L g^{-1}) is a constant related to the free energy of the adsorption and C_e and q_e are equilibrium concentration and the equilibrium oil concentration on the adsorbent, respectively. For the linear method, the isotherm constants q_m and K_L can be determined from the slope and intercept of the plot between C_e/q_e and C_e.

Freundlich isotherm

The Freundlich isotherm is an empirical equation that can be used for the systems on the assumption of heterogeneous sorption energy and interaction between the adsorbate molecules (Radhika and Palanivelu 2006). Freundlich isotherm model is not restricted to the monolayer adsorption and describes the non-ideal and reversible adsorption (Vasanth Kumar and Sivanesan 2006). The nonlinear and linear form of this model can be written as:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F (g g^{-1})(L/g)^n and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The n parameter, known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($n = 1$), whether it is a chemical process ($n < 1$) or whether it is a physical process ($n > 1$) (Vargas et al. 2011). To determine the constants K_F and n, the linear form of the equation shown below may be used to plot the $\log(q_e)$ against $\log(C_e)$.

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{7}$$

Redlich–Peterson isotherm

Redlich–Peterson isotherm is a three-parameter isotherm model which includes the features of the Langmuir and Freundlich isotherm models (Hamdaoui and Naffrechoux 2007). Redlich–Peterson isotherm is written as:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \tag{8}$$

where K_R (L g^{-1}) and $a_R \left(L\, g_R^{1-1/K}\right)$ are Redlich–Peterson equation constants and g is the exponent. When $g = 1$, this isotherm is the same as Langmuir isotherm, and when $g = 0$, the model is the same as Henry's equation. The linear form of Redlich–Peterson may be written as (Wu et al. 2010):

$$\frac{C_e}{q_e} = \frac{1}{K_R} + \frac{a_R}{K_R} C_e^g \tag{9}$$

Fitting the linear equation of Redlich–Peterson model was done through a trial and error procedure. The value of g was assumed and substituted in the linear equation. Then, the regular least square regression was performed and the value of coefficient of determination (R^2) was determined so that the value of R^2 became closer to one. The procedure continued until the difference between the values of the R^2 obtained from two respective iteration was less than 10^{-4}.

Estimation of the best-fitting isotherm model

The coefficient of determination represents the variance and shows the goodness of the fit between the experimental data and isotherm model (Foo and Hameed 2010). However, the value of R^2 has no consideration for the degrees of freedom (number of the data minus the number of parameters) in ranking adsorption isotherm models. Other obvious issues with R^2 are sensitivity to extreme data points and the potential of being large in the case of models with more parameters (El-Khaiary and Malash 2011). Therefore, to avoid the pitfall of comparing the models with different number of parameters (Langmuir and Freundlich: two parameters and Redlich–Peterson: three parameters), using

an index that considers the number of parameters is necessary. In the present study, to compare the models, the hybrid fractional error function (HYBRID) and Marquardt's percent standard deviation (MPSD) were used as error functions which are presented in Table 1.

In the case of nonlinear method, previous research studies showed that the predicted isotherms would vary with the error function used for the minimization of the error distribution between the experimental and predicted isotherms (Kumar et al. 2008). Therefore, to determine the parameters of the models and analyze the effect of the error function on the obtained results, HYBRID and MPSD were used in nonlinear regression to minimize the error distribution between the experimental data and the calculated data from the isotherm models.

As each of the error function is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to be identified directly. Hence, to determine the parameter set that best fit experimental results, the following procedure (so-called sum of the normalized errors, SNE) was performed for each set of parameters (Ho et al. 2002):

- Select one isotherm and one error function and compute the parameters of that isotherm by minimizing the selected error function.
- By using the determined parameters from the previous stage, compute the value of other error functions.
- Repeat last two stages for the rest of isotherm models and error functions.
- For each set of determined error values, normalize the numbers through dividing them by the maximum value of error in that set. Sum the normalized values.
- The parameter sets with the lowest value of SNE are accepted as the best.

Results and discussion

FTIR

The FTIR spectra of blank PU, AC and surface-modified PUF are presented in Fig. 2. As for the blank PUF, the peak

Table 1 List of the error functions

Error function	Definition/expression	References
Coefficient of determination (R^2)	$\dfrac{\sum_{i=1}^{N}(q_{e,meas} - \overline{q_{e,calc}})_i^2}{\sum_{i=1}^{N}(q_{e,meas} - \overline{q_{e,calc}})_i^2 + \sum_{i=1}^{N}(q_{e,meas} - q_{e,calc})_i^2}$	Ho (2006)
Hybrid fractional error function (HYBRID)	$\dfrac{100}{N-P}\sum_{i=1}^{N}\left[\dfrac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}\right]_i$	Ng et al. (2002)
Marquardt's percent standard deviation (MPSD)	$100\sqrt{\dfrac{1}{N-P}\sum_{i=1}^{N}\left[\dfrac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}}\right]_i^2}$	Najafi et al. (2011)

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Fig. 2 FTIR spectra of blank PUF and surface-modified PUF
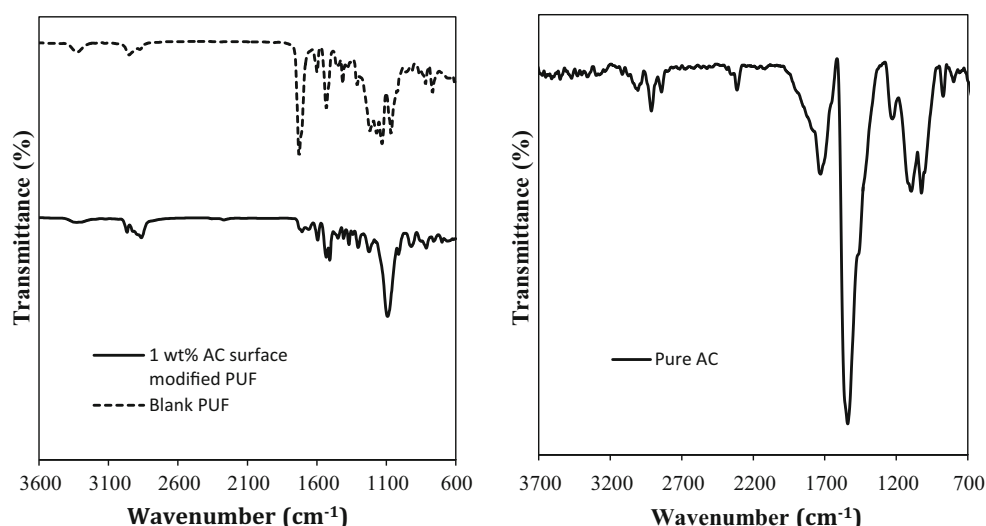
at 1070, 3375 cm^{-1} and the strong peak at 1730 cm^{-1} are assigned to the etheric C–O, N–H and C=O stretching bands, respectively.

In the case of AC, the presence of carboxylic acids and phenol on the AC surface is confirmed through the following observed peaks; the strong peak at 1745 cm^{-1} is assigned to C=O, the O–H stretching vibration appears in the spectrum as a very broad signal within 3400–2400 cm^{-1} range and overlaps with the C–H stretching band at 2925 cm^{-1}, and the peak at 1240 cm^{-1} is assigned to the C–O vibration. The broad peak at 3394 cm^{-1} and the weak peak at 1126 cm^{-1} are assigned to the phenolic OH and C–OH, respectively.

In the case of surface-modified PUF, except for the C=O and N–H groups, the observed peaks are almost the same as blank PUF. As it is observed, the C–O peak at 1126 cm^{-1} and N–H peak at 3357 cm^{-1} become weak and broad compared with those of blank PU. The weakness of the peaks reveals the occurrence of various interactions (like H-bonding) and validates the presence of the AC on the surface of the polymer. The broadness is due to the heterogeneity of the carbonyl environments and validates the connection between the AC and the polymer. The strong peak at 1132 cm^{-1} is from the etheric C–O stretching band. The peak at 1537 cm^{-1} is assigned to the aromatic rings.

Tensile elongation

The elongation test has been performed for the blank PUF and 0.5, 1 and 2 wt% AC surface-modified PUFs. The obtained results of $F_{\max}$(N) and *Elongation* (mm) are, respectively, reported as follows: (4.99 N, 16.08 mm), (5.71 N, 14.15 mm), (6.18 N, 13.49 mm), (9.97 N, 13.27 mm). Based on the results, it is clear that PUF toughness is improved by the presence of AC on the PUF surface, as in all samples, the elongation to break quantity decreases and the strength increases. Toughness improvement of the surface-modified PUF can be attributed to the strong interaction between AC particles and PUF which reduces the polymers chain mobility during mechanical deformation. It also confirms the good distribution of the AC particles on the foam surface.

TGA

The thermogravimetric curves of blank PUF and 1 wt% AC surface-modified PUF are shown in Fig. 3. The curves show higher char yield (at 780 °C) and lower mass loss (29.47 % lower than blank PUF) for the surface-modified sample which shows the improvement of thermal resistance. The observed improvement can be explained based on the significant decrease in polymeric chains mobility as a result of the interaction between AC particles and PUF surface molecules. Such a reduction in molecular mobility along with the inherent tendency of AC particles to eliminate free radicals prevents polymer chains from thermal decomposition as revealed by TGA curves. The higher the chain mobility, the higher the probability of thermal degradation reactions will be. This fact has also been fully explained in the literature (Pal and Gautam 2013). Similar degradation pattern of the blank and surface-modified PUF indicates that the bulk structure of foam is not affected by the surface treatment (Alves et al. 2009).

Oil adsorption capacity

The experimental results of the sorption tests are presented in Table 2. As is seen, at each initial weight of oil, the oil removal percentage is increased in comparison with the blank PUF, and the amount of AC on the surface of PUF influences the sorbent oil removal performance. It is apparent that the PUF with 1 wt% of AC on the surface has the best performance and the maximum sorption is reached at 30 g

Fig. 3 Thermogravimetric curves of blank PUF and 1 wt% AC surface-modified PUF
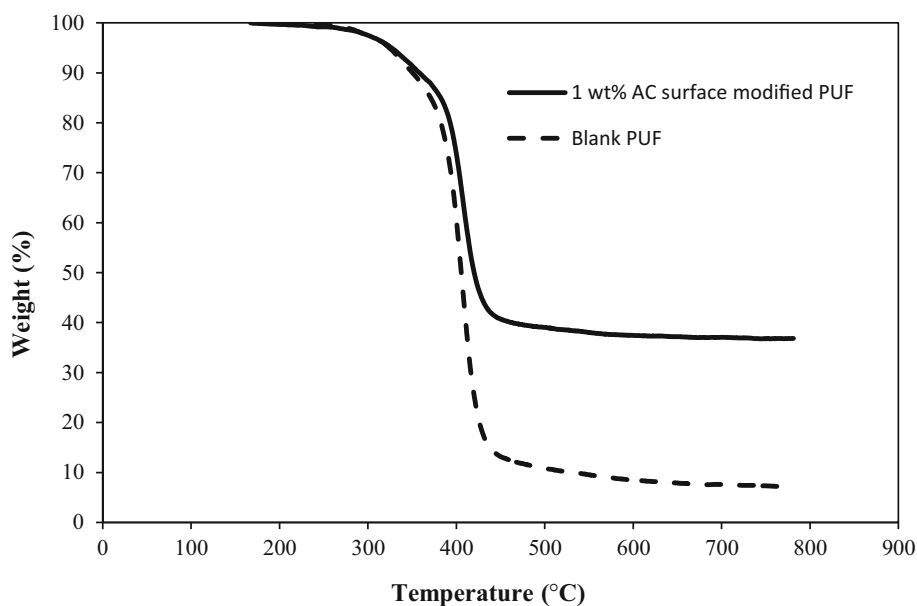
Table 2 Oil removal and efficiency percent of the prepared sorbent and their corresponding standard deviation (σ)

| Initial amount of oil (g)	Sorbent removal and efficiency percent	Blank PUF	AC surface-modified PUF			
			0.5 wt%	1 wt%	2 wt%	3 wt%
5	Removal %	91.20	95.80	97.00	96.40	96.00
	$\sigma_{removal}$ %	1.58	1.66	1.68	1.67	1.66
	Efficiency %	29.66	37.87	45.29	46.32	50.12
	$\sigma_{efficiency}$ %	1.09	1.12	0.50	1.16	0.92
10	Removal %	93.10	95.40	98.20	97.80	97.50
	$\sigma_{removal}$ %	1.23	1.26	1.00	1.29	1.29
	Efficiency %	40.29	52.15	52.61	57.59	60.39
	$\sigma_{efficiency}$ %	0.81	0.67	0.39	0.49	0.23
20	Removal %	86.00	90.85	96.40	96.15	92.15
	$\sigma_{removal}$ %	1.00	1.06	1.12	1.12	1.07
	Efficiency %	70.66	76.54	79.45	83.80	85.21
	$\sigma_{efficiency}$ %	2.35	1.91	1.60	1.19	1.10
30	Removal %	67.93	78.33	90.50	84.33	83.70
	$\sigma_{removal}$ %	1.79	2.06	2.38	2.22	2.20
	Efficiency %	75.85	92.10	93.93	94.85	95.91
	$\sigma_{efficiency}$ %	0.89	0.40	0.49	0.41	0.21
50	Removal %	40.54	46.80	50.36	46.28	45.60
	$\sigma_{removal}$ %	1.05	1.22	1.31	1.20	1.19
	Efficiency %	90.61	96.24	97.79	98.41	99.09
	$\sigma_{efficiency}$ %	1.31	0.53	0.24	0.20	0.13
80	Removal %	25.14	27.29	29.55	28.90	27.74
	$\sigma_{removal}$ %	1.20	1.19	1.56	2.56	3.05
	Efficiency %	99.02	97.99	99.38	100.00	100.00
	$\sigma_{efficiency}$ %	0.24	0.48	0.13	0.00	0.00

initial weight of oil by adsorbing up to 27.15 g/g (i.e., 33.2 % increase in oil sorption capacity (g/g) in comparison with the blank PUF sorption capacity of 20.38 g/g).

The maximum sorption capacity of the surface-modified PUF cubes and some other studied sorbents are reported in Table 3. The reported data reveal that the

Table 3 Maximum oil sorption capacities of some sorbents reported in literature

Sorbent	Type of oil	Maximum sorption capacity (g/g)	References
Carbonized pith bagasse	Gas oil	25.5	Hussein et al. (2008)
Natural wool fibers	Motor oil	5.56	Rajakovic et al. (2007)
Exfoliated graphite	Wasted engine oil	13.2	Tryba et al. (2003)
Nonwoven polypropylene	Light crude oil	9	Wei et al. (2003)
Macroporous organogel	Crude oil	18.2	Tuncaboylu and Okay (2009)
Blank PUF	Light crude oil	20.38	This study
1 wt% MWCNT surface-modified PUF	Light crude oil	27.15	This study
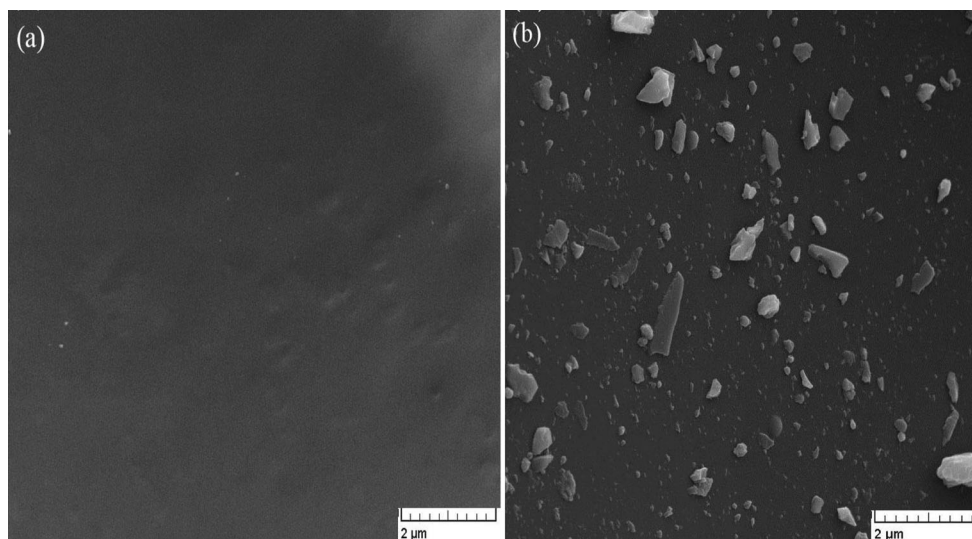
Fig. 4 SEM images of blank PUF **a** and AC surface-modified PUF **b**

surface-modified PUF cubes have noticeable oil sorption capacity compared with the other sorbents.

The oil removal increase in the case of surface-modified PUF may be explained by the fact that the AC presence on the PUF surface enhances the specific surface area of the PUF cubes which is directly related to the sorption capacity of the sorbent. According to the results of the tensile elongation test, one reason for the sorption increase may be the improvement of structural toughness which reduces the release of oil during the sorbent cubes removal from the polluted system. This is also inferred from the less shape reforming because of the gravitational force on the saturated cubes. According to the literature (Tanobe et al. 2009), another explanation for the adsorption capacity enhancement may be the increase in pores size which provides more space for the oil to be adsorbed. Similarly, Harikrishnan et al. (2006) and Wu et al. (2014) reported increase in the cells size after using nanoclays as the cell openers in the structure of the polyurethane foam and treating PUF sponges surface with SiO_2 sol and gasoline, respectively. Moreover, another possible reason is the presence of the AC on the foam surface which is obvious by comparing the

SEM images of the blank PUF (Fig. 4a) and AC surface-modified PUF (Fig. 4b). The presence of the AC particles increases the roughness of surface which in turn helps the foam to hold the adsorbed oil as the physical configuration of the sorbent is an important property for adsorption and capillary action. The same phenomenon about the surface roughness was reported by (Choi and Moreau 1993) and (Radetic et al. 2003) in the case of polymeric sorbents such as polyester and recycled wool-based nonwoven material, respectively, especially in oil-rich environment.

Oil removal efficiency

The oil removal efficiency of the sorbents in different initial weight of oil is reported in Table 2. The reported data reveal a clear trend of efficiency improvement by oil initial weight increase. For each initial weight of oil, the efficiency is improved upon the increase in AC amount existing on the PUF surface and the sorbent with 3 wt% of AC has the maximum efficiency. The observed increase in oil removal efficiency can be attributed to the fact that on oil initial weight increase, the thickness of oil layer on the water

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Table 4 Sorbent removal percent, removal efficiency percent and their corresponding standard deviation (σ) for the chemically regenerated 1 wt% MWCNT surface-modified PUF

Initial amount of oil (g)	Sorbent removal and efficiency percent	Regeneration cycle			
		1	2	3	4
5	Removal %	97.00	93.40	91.20	89.40
	$\sigma_{removal\ \%}$	1.14	1.10	1.08	1.05
	Efficiency %	36.76	40.94	42.51	44.88
	$\sigma_{efficiency\ \%}$	1.48	1.54	1.56	1.57
10	Removal %	98.70	97.20	90.80	88.60
	$\sigma_{removal\ \%}$	1.31	1.75	1.64	1.60
	Efficiency %	50.96	52.60	53.07	53.93
	$\sigma_{efficiency\ \%}$	0.57	0.21	0.21	0.21
20	Removal %	99.25	97.50	96.55	91.40
	$\sigma_{removal\ \%}$	2.29	2.25	2.23	2.11
	Efficiency %	72.19	72.47	72.30	75.92
	$\sigma_{efficiency\ \%}$	0.39	0.39	0.39	0.35
30	Removal %	83.67	80.77	79.60	76.67
	$\sigma_{removal\ \%}$	0.88	0.85	0.84	0.81
	Efficiency %	89.90	90.75	91.71	94.85
	$\sigma_{efficiency\ \%}$	0.41	0.38	0.35	0.22
50	Removal %	46.38	46.20	45.36	40.84
	$\sigma_{removal\ \%}$	0.81	0.81	0.79	0.71
	Efficiency %	95.67	97.51	98.68	99.28
	$\sigma_{efficiency\ \%}$	0.24	0.14	0.08	0.04
80	Removal %	28.79	28.13	26.73	25.05
	$\sigma_{removal\ \%}$	0.52	0.51	0.48	0.45
	Efficiency %	98.46	99.11	99.53	99.74
	$\sigma_{efficiency\ \%}$	2.67	1.54	0.82	0.44

surface increases and the sorbent cubes reach the water surface to less extent, and therefore, the lower amount of water sorption enhances the efficiency. Another possible factor affecting the oil removal efficiency goes back to the surface modification by petroleum ether that improves the affinity toward oil. This explanation may be validated by the results obtained by Wu et al. (2014). Based on the results of contact angle test, they reported an improvement of hydrophobicity after treating PUF cubes with gasoline.

Sorbents reusability

Reusability feature of the 1 wt% AC surface-modified PUF has been investigated through four cycles of regeneration. The sorption and efficiency percentage of the regenerated sorbent are presented in Table 4. It is shown that for each initial weight of oil, the sorption percentage decreases which may be due to the incomplete regeneration of the sorbent. Incomplete regeneration stems from the permanent chemical sorption of some components on the surface which may not be released after chemical regeneration. Another reason for the decrease in sorption percentage may be loss of AC particle from the surface of foam, as the crude oil contains different types of organic and inorganic

materials that adversely affect the bond between the AC particles and foam. As the data reported in Table 4 show, at each initial weight of oil, the sorption efficiency is increased. The increase in sorption efficiency may be explained by considering the regeneration method in which the sorbents are regenerated by petroleum ether, meaning even after drying, some petroleum ether remained on the surface and this, besides the remained crude oil, increases the affinity for the oil; thus, less water is adsorbed which in turn enhances the sorption efficiency.

Adsorption isotherms

The parameters of the isotherm models obtained from the linear regression method and the values of R^2, HYBRID and MPSD are reported in Table 5. The values of R^2, reported in Table 5, for the Freundlich isotherm in comparison with the values for Langmuir and Redlich–Peterson suggest that it is not an appropriate model for the prediction of sorption of crude oil onto PUF. Moreover, ranking the Langmuir and Redlich–Peterson models on the basis of the R^2 values seems to be inaccurate as the obtained values of R^2 are too close to each other without considering degrees of freedom. Ranking the models based on the values of HYBRID and

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Table 5 Predicted parameters of Langmuir, Redlich–Peterson and Freundlich isotherm by linear regression method

Isotherm	Blank PUF	0.5 wt% AC surface-modified PUF	1 wt% AC surface-modified PUF	2 wt% AC surface-modified PUF	3 wt% AC surface-modified PUF
Langmuir					
$q_m (g\,g^{-1})$	20.4499	22.17295	23.8663	23.2558	22.3713
$K_L (L\,g^{-1})$	1.4215	6.5362	5.58	5.1807	6.9844
R^2	0.9995	0.9985	0.9993	0.9998	0.9995
HYBRID	65.1501	482.1056	209.8682	239.1541	422.2948
MPSD	36.7824	92.1263	62.7966	68.0075	89.2653
Redlich–Peterson					
g	1.035	0.99	1.195	1.09	1.05
$K_R (L\,g^{-1})$	20.2024	21.0084	24.2130	23.4192	23.3645
$a_R \left(L\,g_R^{1-1/K}\right)$	0.8545	1.0210	0.4866	0.7283	0.8171
R^2	0.9998	0.9968	0.9992	0.9993	0.9993
HYBRID	31.3523	134.5501	253.9653	214.9102	114.9809
MPSD	25.1785	31.2228	48.4838	41.0989	32.2954
Freundlich					
$K_F (g\,g^{-1})(L/g)^n$	13.6576	10.7263	11.2909	12.5221	11.6744
n	1.8661	3.9825	6.1012	4.655493	4.3706
R^2	0.8001	0.7525	0.7439	0.6349	0.6858
HYBRID	1.55E + 10	193.2091	378.8958	263.9201	235.2566
MPSD	277,584.5	37.8665	51.3192	49.4735	44.6967

MPSD suggests that Langmuir, Redlich–Peterson and Freundlich are the best fits to the experimental data.

In the case of nonlinear regression method, the calculated isotherm parameters, the corresponding error functions and SNEs for the minimum error distribution between the experimental equilibrium data and predicted isotherm are presented in Table 6. The bolded numbers in each column in Table 6 show the minimum of the SNEs, meaning the parameters obtained by minimization of that error are the most appropriate ones. For example, the best calculated parameters of the Langmuir isotherm in the case of blank PUF are the ones obtained by minimization of the SSE. It is obvious that the Langmuir model is the more appropriate model for explaining the saturation limitation of the sorption process. The reported data in Tables 5 and 6 reveal that the value of g for the Redlich–Peterson model is more than 1 in all cases. The exponent higher than one may be explained by the fact that the prominent mechanism of sorption of the foam-based sorbents is the capillary action.

As the fitted models have different numbers of parameters (Langmuir and Freundlich: 2; Redlich–Peterson: 3), ranking the isotherms is performed based on the values of MPSD and HYBRID error functions. Comparing the values of the MPSD and HYBRID error measurement reveals that the quality of the isotherm fit can be arranged in order of increasing weight of the errors as: Redlich–Peterson < Langmuir < Freundlich for the blank and 0.5 wt%

AC surface-modified PUF and Langmuir < Redlich–Peterson < Freundlich for the 1, 2 and 3 wt% AC surface-modified PUF. The reason to the change in ranking between Langmuir and Redlich–Peterson model may be explained by the little change in sorption mechanism after addition of AC particle to the surface of PUF. As previously stated, the prominent mechanism of sorption in the foams is capillary action; however, on the increase in AC particle concentration on the surface, the monolayer sorption (the main assumption of the Langmuir isotherm) on the surface of the AC particles and the PUF surface affect the sorption mechanism.

A comparison of the curves of the equilibrium data with the classification proposed by (Giles et al. 1960) indicates the similarity of the L curves and the depicted curves of the present study. The L curves are the best-known pattern of sorption data, and the initial curvature shows that as the more sites are occupied, it becomes difficult for the other molecules to find free sites and that the adsorbed molecules are probably adsorbed flat.

Conclusion

The impregnation of the PUF has been performed through the reaction of the chemical groups existing on the surface of AC particles and those belonging to the unreacted PUF polyol with MDI functionalities. The experimental

Table 6 Predicted parameters of Langmuir, Redlich–Peterson and Freundlich isotherm by nonlinear regression method through minimizing the HYBRID and MPSD error functions

Isotherm	Blank PUF	0.5 wt% AC surface-modified PUF	1 wt% AC surface-modified PUF	2 wt% AC surface-modified PUF	3 wt% AC surface-modified PUF
Langmuir					
$q_m (g\,g^{-1})$	20.38	23.5	26.38503	25.08328	24.24982
$K_L (L\,g^{-1})$	0.95742	1.441049	2.589171	2.139087	1.796086
HYBRID	29.28886	12.13017	93.73207	60.89002	42.5577
Sum of normalized HYBRID	6.470238	7.260028	5.735964	6.099829	5.805036
$q_m (g\,g^{-1})$	20.38	23.5	26.64115	25.3	24.49424
$K_L (L\,g^{-1})$	0.820633	1.341253	2.031706	1.732866	1.53379
MPSD	17.48253	8.855496	30.67121	23.9068	20.32865
Sum of normalized MPSD	6.271849	6.685061	5.767429	6.159723	6.274002
Redlich–Peterson					
g	1.108433	1.112438	1.236579	1.205715	1.147492
$K_R (L\,g^{-1})$	15.03223	23.5	27.15	25.3	25.1
$a_R (L\,g_R^{1-1/K})$	0.481097	0.673704	0.463631	0.512426	0.633087
HYBRID	15.92245	5.869236	199.1734	133.4575	62.84631
Sum of normalized HYBRID	6.312063	7.836284	4.710827	2.564682	7.328421
g	1.136828	1.12646	1.259608	1.235422	1.162458
$K_R (L\,g^{-1})$	13.53567	23.5	27.15	25.3	25.1
$a_R (L\,g_R^{1-1/K})$	0.389818	0.644229	0.428448	0.465083	0.603691
MPSD	14.42758	8.103472	43.19673	32.67488	25.13489
Sum of normalized MPSD	2.814804	3.691628	2.62146	2.434915	4.161529
Freundlich					
$K_F (g\,g^{-1})(L/g)^n$	9.010921	10.8895	13.01478	12.06515	11.51052
n	4.248957	4.588896	5.230367	5.035781	4.897463
HYBRID	141.8959	170.8041	298.5617	247.6416	215.8103
Sum of normalized HYBRID	2.239558	2.174227	3.683705	3.372295	3.513399
$K_F (g\,g^{-1})(L/g)^n$	7.561714	9.338805	10.71831	10.05669	9.683561
n	3.502567	3.814125	4.138535	4.026093	3.975359
MPSD	34.18453	34.29186	44.85461	41.42543	38.86507
Sum of normalized MPSD	3.159314	3.00494	4.308983	6.36899	4.954346

data have shown that the presence of 1 wt% of AC on the surface of PUF increases the sorption capacity up to 33.2 % in comparison with the blank PUF. Furthermore, the sorption efficiency has increased in all amount of AC on the surface of PUF as less water and more oil have been adsorbed. The reusability feature of the 1 wt% AC surface-modified sorbent has been investigated through four cycles of chemical regeneration and reuse. The investigation of the best-fitting isotherm model through minimization of various error functions using linear method has proposed the Langmuir as the best fit, while the nonlinear method has suggested that for the blank and the 0.5 wt% surface-modified PUFs, Redlich–Peterson is the best fit while for the 1, 2 and 3 wt% surface-modified PUFs, the Langmuir model is the best fit of the sorption data.

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