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ORIGINAL PAPER

Application of hydrophobic polymers as solidifiers for oil spill cleanup

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Abstract
Oil spill containments are daily life problems due to inherent risks in transporting oil and diluted bitumen products via both tankers and pipelines. For oil–water separation, using a solidifier is one of the most efficient methods which triggers chemical interactions between the solidifier and the spilled oil to change the liquid phase of oil to a coherent mass, through a process called solidification. This study presents the performance of polypropylene (fibers, granule) and polyethylene granule solidifiers for oil spill cleanup by the gravimetric and spectrophotometric methods. The obtained results showed that polypropylene fibers have the highest sorption percentage (82.2%) and sorption capacity (12.5 g/g). The isothermal study reflects the Langmuir isotherm shows the good correlation coefficient ($R^2 = 0.93$) for polypropylene fibers with consistency with the experimental data.

Keywords Oil spill · Cleanup · Solidifier · Polypropylene fibers · Langmuir · Freundlich

Introduction

Spillage occurs because of the accidents of oil tankers in the seas, oil transfer deficiencies, and storage equipment (Pourrahim and Dahrazma 2009). Therefore, environmental pollution and a huge economic loss are imposed to governments and oil companies through the transportation of oil products to the waters of different parts of the world (Salehirad et al. 2013; Lv et al. 2018). Today, there are many methods for removing oil spills from water; these methods are divided into three categories including physical, chemical, and biological. Chemical methods such as those using absorbent materials and burning in place lead to higher air pollution (Zaredust and Rasouli 2012). The safest technique for immediate disposal of oil and crude oil products is to absorb thin films from the surface with the aid of solidifiers. They are attractive for applied programs in the oil cleanup, because of their ability to collect and remove more oil from the oil spill area and to facilitate the transition from liquid to semisolid phase (Tanobe et al. 2009).

There are not practical application methods and appropriate tests under various conditions and environments, and only solidifiers have the ability to convert oil into an inert state that facilitates oil recovery from the environment. Polymeric adsorbents are the most common type of solidifiers. Having empty spaces, Polymers can physically hold oil through the Van der Waals forces in the cavities. Oil can be recovered by applying pressure. The most commonly used polymeric solidifiers are styrene butadiene, polyethylene, polypropylene, and polyisobutylene. The benefits of these types of solidifiers are that they are relatively simple and cheaper, they have lower toxicity and react more slowly, and thus, they are better combined (Mohanraj and Jayselene 2010; Kutyanezhad et al. 2012; Tawousi and Shahkoei 2013; Barati et al. 2015; Motta et al. 2018).

Sundaravadivelu et al. 2016 determined the effect of temperature on the oil solidifier function as a parametric study and found that the effect and function of the solidifier agent are essentially reduced at lower temperatures, especially in lower applied amounts. Al-Majed et al. 2012 reviewed the effect of rice husk adsorbent in heavy crude oil and showed that the adsorbent of sorption capacity (g/g) is equal to (4.6–6.7).

Pablo et al. monitored the performance of five solidifiers in crude oil of Paraguay Gulf in saline in the laboratory by

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UV–Vis and GC/MS. The function of the solidifiers was determined by the UV–Vis as a function of solidifier-to-oil mass ratios (SOR) and the contact time (Rosales et al. 2010). They found that the increase in contact time reduces the residual crude oil in the solution by a slight slope; however, most solidifiers reach a constant value after 30 minutes of contact time.

As mentioned, a basic and efficient method for oil spill cleanup is adsorbents including polymeric solidifiers. In this research, the performance of three solidifiers (polypropylene fibers, granule polypropylene, and granule polyethylene) were investigated for the removal of crude oil of Isfahan refinery in the saline water from Anzali port.

Materials and methods

Materials

The saline water was supplied from Anzali port at 22 °C (pH = 8.14, alkalinity = 280, TDS = 16 mg/L, EC = 18.12 mS/cm, and salinity = 11.7 g/L). Dichloromethane was used as the extraction solvent. All solidifiers were placed in a grid to allow easy collection and removal. Crude oil was prepared from Isfahan refinery with density 0.88 g/mL.

Oil adsorption experiments

Determining the sorption amount of solidifiers by UV–Vis spectrophotometer

The ultraviolet–visible (UV–Vis) spectrophotometer was utilized to calculate the amount of residual oil remains in a separate solidifier after the crude oil removal (Rosales et al. 2010). Notably, the results are more consistent and reproducible with standard deviation below 5%.

Calibration curve was drawn by four standard solutions of crude oil to obtain their sorption amount by spectrophotometer. A certain amount of solidifiers was weighed in the ratio of SOR 1/4 and 1/16. To determine the residual crude oil concentration, the beaker contents were extracted by dichloromethane after the solidifier removal. The solution was extracted three times with dichloromethane, so that the final amount of oil and dichloromethane solution was adjusted to 50 mL (Rosales et al. 2010). The crude oil was diluted after re-extraction with dichloromethane. All measurements were recorded at $\lambda_{max} = 260$ nm (Fig. 1).

Crude oil (0.5 mL, 0.4887 g) was added to beaker containing 80 mL water. Volumes of crude oil and saline water were kept constant, while the solidifier mass varied depending on the SOR ratio. Each solidifier was added to an oil spill (0.5 mL) in the water in various SOR ratios, and the mixtures were stirred by a magnetic stirrer for 60 min.

Evaluating the effectiveness of solidifiers by gravimetric method

To calculate the solidifiers swelling, a specific weight of solidifier was collected in beakers containing 80 mL water; the solidifier was gathered and weighted after one hour, enough time for the data to reach a balanced state (Rosales et al. 2010); this experiment was repeated three times. A grid containing three polymers was used to calculate the swelling and oil sorption amount. The grid was immersed in a beaker of water and a beaker of oil separately. Then, certain weight of three solidifiers was picked up to determine the sorption of solidifier, and they were put in beakers containing 80 mL distilled water and 0.5 mL crude oil. Then, they were gathered and weighted. The initial

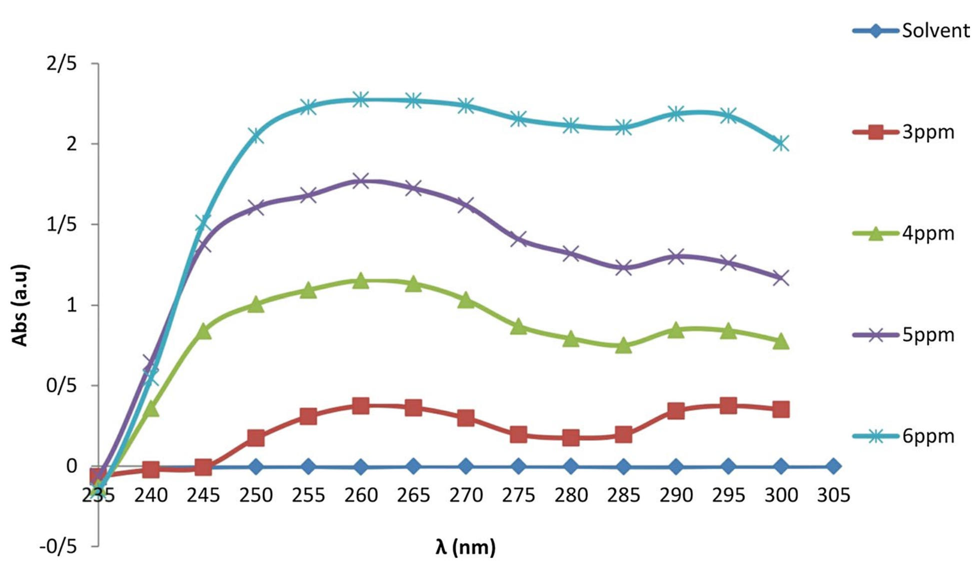

Fig. 1 UV–visible absorption of crude oil at different concentration

weight of all solidifiers was calculated in SOR ratios of 1/4, 1/8, and 1/16.

Results and discussion

Determining the sorption capacity and sorption percentage

In order to determine the sorption capacity (SC g/g), Eq. (1) was used, where Mo is the weight of the adsorbed oil and Mi is weight of the solidifier (Wu et al. 2014; Liu et al. 2015).

$$SC(g/g) = (Mo)/Mi \quad (1)$$

The sorption percentage (SP%) was determined by Eq. (2), where M_{Oil} is the initial mass of 0.5 ml oil spill (0.4887 g), M is the weight of the sorbent after sorption of crude oil, M_{oil} is the weight of crude oil, and M_0 is the weight of the sorbent before sorption (Razavi et al. 2014).

$$SP\% = \left(M - M_0/M_{oil}\right) \times 100 \quad (2)$$

As shown in Table 1, polypropylene fibers with SOR 1/4 has the highest SP% and polyethylene with SOR 1/16 has the lowest SP%. Moreover, polypropylene fibers with SOR 1/16 has the highest SC (g/g) and polyethylene granule with a SOR 1/4 has the lowest SC (g/g). It can be attributed to the higher surface-to-volume ratio in polypropylene fibers. The obtained results show a higher SC% and SP% for spectrophotometry analysis compared to its weight analysis due to higher accuracy.

The maximum sorption capacity of Propylene fibers was compared with the others reported in the literature for crude oil adsorption (Table 2) (Motta et al. 2018). It was found that the sorption capacity of the propylene fibers is higher than most of the inorganic adsorbents.

Table 1 SP% and SC (g/g) calculated by UV–Vis spectrophotometer and gravimetric method

Solidifier	SOR	Gravimetric method		UV–Vis spectro-photometer	
		SC (g/g)	SP%	SC (g/g)	SP%
Polypropylene fibers	1/4	8.8	79.2	3.4	86.2
	1/16	15.1	74.5	12.5	82.2
Polypropylene granule	1/4	3.1	73.6	2.7	83.9
	1/16	9.6	59.8	8.2	64.1
Polyethylene granule	1/4	1.9	49.4	1.6	55.3
	1/16	4.8	29.4	3.7	36.8

Table 2 Comparative adsorption capacities of various adsorbents for diesel adsorption

Adsorbents	SC (g/g)	References
Polypropylene fibers	15.1	This study
Jute fiber modified via the sol–gel method	8.48	Teli and Valia (2013)
Magnetic polyurethane sponge	12.3	Yu et al. (2016)
Durable and modified Magnetic polystyrene foam	17.4	Lv et al. (2018)

Adsorption isotherm experiment

Langmuir adsorption isotherm

Langmuir equation for a solid–liquid system is as follows:

$$q_e = \left(k_1 C_e\right)/\left(1 + bC_e\right) \quad (3)$$

where q_e is the solved material amount on the adsorbent weight (mg/g), C_e is the absorbed material concentration after the completion of adsorption in solvent and in equilibrium state (mg/L), K_L (the Langmuir constant) is the amount of solved material as surface adsorption on the adsorbent weight in monolayer form (single layer) on the surface (mg/g), and b is the constant energy or pure enthalpy for adsorption. Langmuir linear form is calculated as follows (Songsaeng et al. 2019; Motta et al. 2019):

$$\left(C_e/q_e\right) = \left(1/K_L\right) + \left(b/K_L\right)C_e \quad (4)$$

Thus, the drawing of C_e/q_e in terms of C_e represents a straight line with the slope b/K_L and y-intercept as $1/K_L$. The main advantage of Langmuir isotherm is the separation factor or equilibrium parameter R_L (separation factor) defined in the following equation:

$$R_L = 1/\left(1 + \left(bC_0\right)\right) \quad (5)$$

In this equation, C_0 is the initial concentration of adsorbent (mg/L) and b is Langmuir constant related to the sorption energy. The value of R_L shows the nature and feasibility of adsorption process (Table 3) (Motta et al. 2019).

The equilibrium data for the sorption of polypropylene fibers with Langmuir isotherm model illustrated more matching because the highest R^2 correlation coefficient (0.93) was found in this model (Fig. 2).

Langmuir equilibrium parameter R_L for polypropylene fibers was between 0 and 1 indicating appropriate adsorption (Table 4). Regarding the equilibrium parameter R_L, solidifier with the lower initial weight has better absorption because it is closer to one. The results show that polypropylene fibers have the highest adsorption capacity (K_L) in Langmuir isotherm model, while polyethylene granule has the lowest.

Table 3 Nature of adsorption isotherm

R_L^a value	Adsorption process
$R_L > 1$	An undesirable adsorption that how much it is closer to one, sorption is better
$R_{L=1}$	Linear
$0 < R_L < 1$	A suitable and desirable adsorption
$R_L = 0$	Adsorption is unchangeable

[a]Separation factor

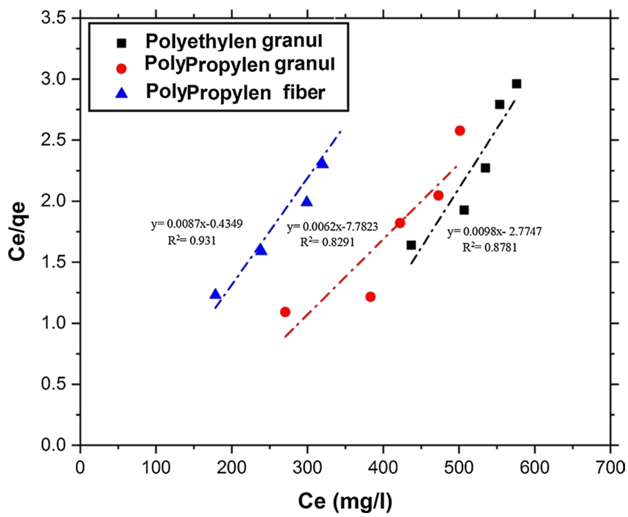

Fig. 2 Langmuir sorption isotherms for oil sorption by solidifiers

Table 4 Displaying the results of gravimetric test for oil sorption by adsorbents and used parameter for calculation of Langmuir model

Solidifier	C_0 (ppm)	R_L^a	R^2	K_L^b (L mg^{-1})
Polypropylene fibers	6108	0.3863	0.93	10.5943
Polypropylene granule	6108	1.0126	0.6538	0.5998
Polyethylene granule	6108	1.1206	0.88	0.1058

[a]Separation factor

[b]The Langmuir constant

Freundlich isotherm

Freundlich isotherm is used for abnormal adsorption on a heterogeneous surface, e.g., a multilayer surface with the following equation:

$$q_e = k_f C_e^{(1/n)} \tag{6}$$

The linear form of the equation is as follows:

$$\text{Log } q_e = \text{Log } K_f + (1/n)\text{Log } C_e \tag{7}$$

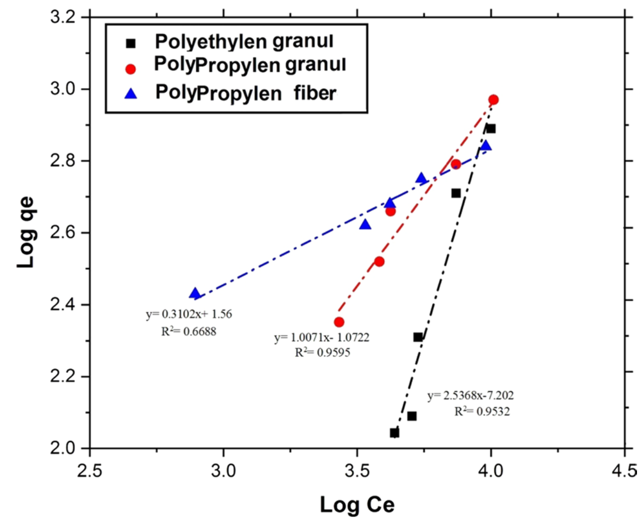

Fig. 3 Freundlich sorption isotherms for oil sorption by solidifiers

K_f is Freundlich equilibrium constant which shows the adsorption capacity, and n is Freundlich constant which indicates the dependence of the absorbed material on the adsorbent surface. q_e is the solved material amount on the adsorbent weight (mg/g), and C_e is the concentration of the absorbed material after completion of the adsorption in the solvent and in the equilibrium state (Motta et al. 2019). The matching of sorption equilibrium data with Freundlich model expresses the inhomogeneity of the adsorbent surface and heterogeneity of the sorption position on the absorbent surface. Also, when $n > 1$ in Freundlich model, the adsorption process is desirable (Bazargan et al. 2015).

Drawing charts and calculating Langmuir and Freundlich equations for solidifiers

The equilibrium data of the sorption of polypropylene granule and polyethylene granule indicated more matching with Freundlich isotherm model because the highest correlation coefficient was obtained in this model (Fig. 3, Table 5).

Due to the amount of n in Freundlich model for polypropylene fibers which is more than one, the sorption process is physically more favorable. The Freundlich constant (n) shows the sorption intensity and indicates optimal sorption from 0.1 to 1. Therefore, polyethylene granule and polypropylene granule have an appropriate sorption. It can be attributed to the heterogeneous adsorption sites that are not similar to each other in respect of adsorption phenomenon. The multilayer adsorption occurs at heterogeneous surfaces with different adsorption energies and characteristics leading to spontaneous and favorable solidification.

In Fig. 4, we can see SEM micrographs of propylene fiber before and after oil removal. There are spaces between propylene fibers that can adsorb oil. Oil in water attached to

Table 5 Displaying the results of gravimetric test for oil sorption by adsorbents and used parameter for calculation of Freundlich model

Solidifier	$Y = mX + c$		R^2	K_F^a (mg g^{-1}) (L mg^{-1})$^{1/n}$	n^b
	M	*C*			
Polypropylene fibers	0.1537	3.0792	0.67	1200.051	6.5061
Polypropylene granule	1.4697	− 1.703238	0.96	0.0198	0.68
Polyethylene granule	2.6917	− 7.1535	0.95	7.022 × 10-8	0.3706

[a]Freundlich constant

[b]The adsorption intensity

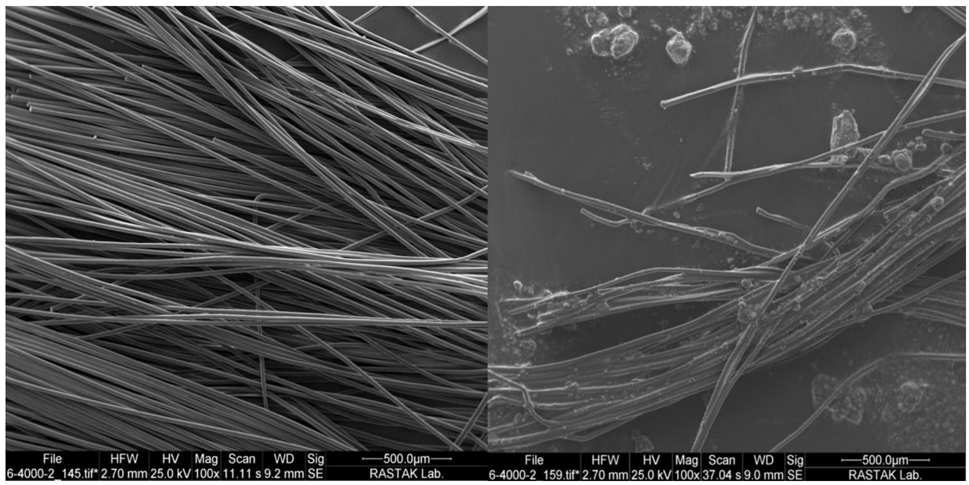

Fig. 4 SEM images of propylene fiber **a** before **b** after oil

sorbents through absorption, adsorption, and\or a combination of both mechanisms with no chemical bond formation or dissociation. Van der Waals forces, *p*-electron interactions, and hydrophobic effects are at play in the adsorption and absorption due to the oleophilicity and hydrophobicity of sorbents. Absorption (a bulk phenomenon) is related to the liquid oil assimilation in the whole sorbent, while adsorption (surface phenomenon) is concerned with the accumulation of liquid oil components on the surface instead of the bulk of the sorbent (Bazargan et al. 2015; Songsaeng et al. 2019).

Conclusion

The efficiency of oil cleanup by commercial solidifiers depends on the test conditions. It was observed with lower SOR that less solidification occurred for polypropylene granule and polyethylene granule. The equilibrium data for the sorption of polypropylene fibers with Langmuir isotherm model ($R^2 = 0.93$) have shown more matching because of homogeneity of the sorption surface. However, the sorption propylene granule and polyethylene granule were more consistent with Freundlich isotherm model due to the non-uniformity of the sorption position and heterogeneous surface for these two solidifiers. Consequently, the propylene fiber presented in this study is a promising alternative oil sorbent for oil spill cleanup in the ocean.

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Compliance with ethical standards

Conflict of interest There is no conflict of interest to declare in this study.

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