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Gasoline absorption performance of a polymer material

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ABSTRACT

Oil spills leak dangerous chemicals into the environment, causing serious environmental pollution and damaging human health. Thus, environmentally friendly materials for remediation are urgently needed. In this study, a polymer absorbing material (PAM) with a high retention capacity (>90% at a centrifuge rate of 3,000 rpm) and high absorption capacity (7.5 g gasoline/g of PAM) was described. The pseudo-second-order absorption kinetic model was shown to accurately simulate the absorption data. The results showed that the PAM had a spherical structure and abundant functional groups. The PAM absorbed almost all of the tested liquid chemicals, including gasoline, crude oil, diesel, and kerosene. In contrast to traditional oil-absorbing materials, the high oil-retention capacity of this material prevented the volatilization of chemicals dangerous to human health and the environment. Consequently, the PAM was suitable for applications in oil-spill treatment, especially in the emergency handling of toxic and harmful substances.

Keywords: Polymer absorbing materials; Oil-retention capacity; Stable performance

1. Introduction

The unintentional discharge of oil in everyday life and frequent oil spills during exploration, transportation, storage and use damages freshwater and ocean ecosystems [1,2]. To protect the environment and human health, effective decontamination and remediation technologies are necessary. Traditional methods for remediation include dispersants [3], skimmers [4], oil booms [5], and in situ burning [6]. However, the majority of dispersants and in situ burning cause secondary pollution that is harmful to fish and other animals, while skimmers and oil booms are ineffective for the removal of trace oil from oil–water mixtures [7].

To date, oil-adsorbing materials have attracted increasing academic and industrial interest for the cleanup and collection of spilled oil. Potential sorbents for oil spill cleanup include natural fibers (such as kapok, barley straw, and wool) [8–11], cellulose-based materials [12–14], and synthetic polymers [15–18]. Although many researchers have extensively investigated natural fibers due to their high oil-sorption capacity and biodegradability [19], the oil-retention capacity also plays an important role in the selection of a sorbent material for cleanup processes.

In the present study, a specific polymer absorbing material (PAM) with both high oil-retention capacity and oil-absorption capacity was described. This PAM absorbed

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almost all of the tested liquid chemicals, including gasoline, crude oil, diesel, and kerosene. Therefore, this material is suitable for use in oil spills, oil–water separation and the emergency handling of dangerous chemicals. Due to its high oil-retention capacity and spill-free operation, this material prevents the volatilization of chemicals that are dangerous to human health and the environment. The purpose of this study was to characterize and determine the oil-absorption performance of the PAM using gasoline as an example.

2. Materials and methods

2.1. The PAM

The PAM used in this study was obtained from Anhui ChengFang New Material Technology Co., Ltd., Hefei, China. The gasoline samples were obtained from a Sinopec gas station, Hefei, China. The molecular formula of the gasoline is C_5H_{12}–$C_{12}H_{26}$, the molecular weight of the gasoline is 72–170, and the relative density of the gasoline is 0.70–0.79 g/cm^3.

2.2. Characterization of the PAM

A cold-field emission scanning electron microscopy (SEM) system (SU8010, Hitachi, Japan), in conjunction with a cryogenic system, was used to image the PAM samples. The major functional groups of the PAM were characterized using a Fourier transform infrared (FTIR) spectrometer (Nicolet iS 50+ Continuum, Thermo Fisher Scientific Corporation, USA). The FTIR spectra were collected on KBr pellets prepared by pressing a mixture of 1 mg of sample and 200 mg of spectrometry-grade KBr under vacuum conditions to decrease moisture uptake. The spectra were scanned in the range of 4,000–400 cm^{-1}. Specific surface area measurements were obtained using the single-point Brunauer-Emmett-Teller (BET) method based on nitrogen adsorption with an Autosorb-iQ Quantachrome system.

2.3. Determination of the absorption capacity

As seen in Fig. 1, the PAM samples packaged with non-woven fabric were weighted by an analytical balance. Then, samples of known weight were inserted into a beaker containing gasoline. After 1, 3, 5, 10, 15, 20, 30, 40, 50, and 60 min, the oil-soaked PAM samples in non-woven fabric were removed and drained until no more oil was emitted. Subsequently, the samples were weighted using a weighing balance. Each experiment was repeated three times, and the average value was taken to calculate the absorption capacity. The gasoline-absorption capacity was calculated by:

$$\text{Absorption capacity} = \frac{W_t - W_0}{W_0} \tag{1}$$

where W_0 is the initial weight of dry PAM and W_t is the weight of PAM with gasoline at the end of the absorption test.

2.4. Oil-retention testing method

The oil-soaked PAM samples in the non-woven fabric were removed and drained until no more oil was emitted. Then, the weights of the samples were recorded, and the weights were measured again after the samples were centrifuged (at 1,000, 2,000, and 3,000 rpm/min) for 5 min. The oil-retention capacity of the PAM was calculated by the equation below:

$$\text{Retention capacity} = \frac{W_t'}{W_t} \tag{2}$$

where W_t' is the weight of the PAM samples after centrifugation for 5 min.

3. Results and discussion

3.1. Characterization of the PAM

The SEM image of the PAM is shown in Fig. 2. The PAM clearly showed a spherical morphology. The diameter of the polymer absorbent was approximately 240 μm, as determined by SEM. The bulk density of the PAM was 0.55 g/cm^3, and its true density was 0.96 g/cm^3. When the PAM was placed in water, the PAM could stably float. The quality of the PAM did not change after exposure to acids or bases.

The BET surface area of the PAM was determined to be 12.85 m^2/g, which is larger than traditional oil sorbents composed of raw cotton (0.665 m^2/g) [20] and expanded perlite (3.1 m^2/g) [21].

FTIR analysis was analyzed in the region of 4,000–900 cm^{-1} to observe the functional groups in the PAM. As shown in Fig. 3, the peak at 1,145 cm^{-1} was associated with C–O stretching. The bands at 1,245 and 1,378 cm^{-1} were assigned to C–O

Fig. 1. Gasoline uptake by the PAM.

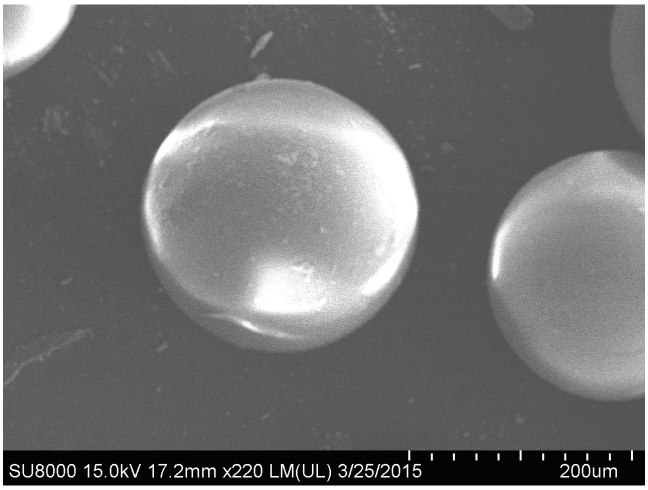

Fig. 2. SEM image of the PAM.

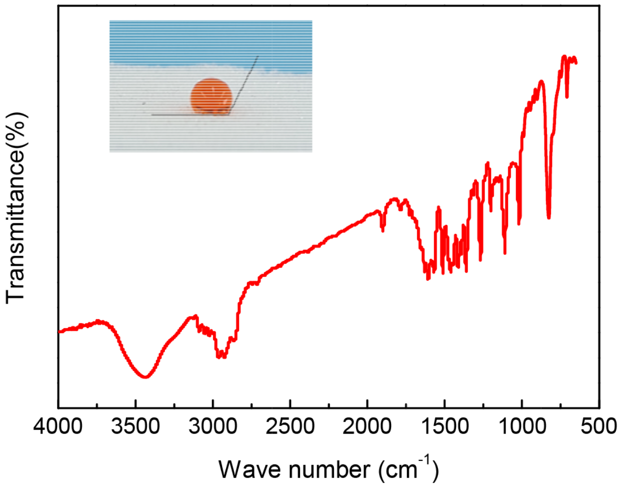

Fig. 3. FTIR spectra of the PAM (inset: contact angle of the PAM).

and C–H bending vibrations, respectively. The band at approximately 1,405 cm^{-1} was due to bending vibrations of the O–H bond, and the triplet at approximately 1,530 cm^{-1} and the doublet with a maximum at 1,640 cm^{-1} were related to the elastic vibrations of the C=O bond in the carboxyl groups. The band at approximately 2,968 cm^{-1} belonged to the stretching vibrations of the C–H bond in CH_3 and CH_2 groups of aliphatic or aromatic hydrocarbons. The broad band at 3,600–3,100 cm^{-1} was attributed to stretching vibrations of the O–H group. The results from FTIR analysis showed that the PAM contained a variety of functional groups, which is in accordance with traditional oil sorbents, such as rice husk [22], kapok fibers [23], and milkweed fibers [24]. In addition, the contact angle of the PAM was 141.3°, which indicates that the PAM was hydrophobic.

3.2. Gasoline absorption capacity of the PAM

Fig. 4 shows the variation in the absorption capacity of PAM over time at 25°C. The absorption capacity was observed to increase significantly within 0–15 min. Over the following 15–30 min, the absorption capacity increased slightly until reaching the maximum capacity of 7.5 g gasoline/g of PAM at an absorption time of 30 min. The results revealed that the absorption capacity was related to the time, as with an increase in the contact time, a larger number of gasoline molecules can fully contact the absorption sites and pores in the PAM, resulting in an increase in the absorption rate. However, after reaching a certain value (such as 7.5 g/g), the absorption capacity remained almost constant, regardless of the reaction time. Considering the oil-absorption capacity, a reaction time of 30 min was adequate and favored.

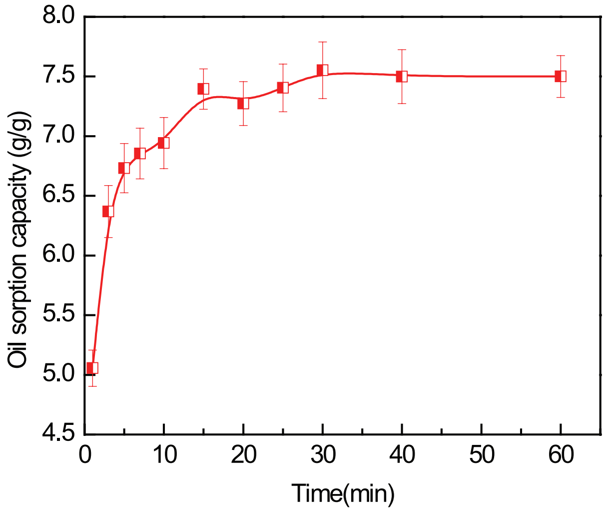

Fig. 4. Absorption capacity with respect to gasoline of the PAM.

The PAM exhibited a fast absorption rate, reaching 6.4 g/g in the first 5 min and achieving a maximum value of 7.5 g/g within 30 min. After 30 min, the oil-absorption capacity did not increase with time. This observation is in agreement with the findings of Thompson et al. [25]. The fast absorption rate and high absorption quantity most likely resulted from the high specific surface area of the PAM (12.85 m^2/g), which was favorable for absorbing a large number of gasoline molecules. After saturation, the PAM surface sites were difficult to occupy due to repulsive forces between oil molecules [26].

Moreover, to study the mechanism of absorption and obtain the absorption rate constants, the experimental data were further analyzed using the pseudo-first-order and pseudo-second-order kinetic models, which are represented in their linear forms in Eqs. (3) and (4) [27,28], respectively.

Pseudo-first-order rate equation:

$$\log(q_e - q_t) = \log q_e - \mathrm{k}_1 t \tag{3}$$

Pseudo-second-order rate equation:

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t are the absorption capacities (g/g) at equilibrium and a certain time (min), respectively, and k_1 (min^{-1}) and k_2 (g/g min) are the rate constants for the above two equations.

The data in both Table 1 and Fig. 5 indicate that the pseudo-second-order expression produced a better regression

Table 1
Absorption parameters of the pseudo-first-order and pseudo-second-order absorption kinetic models for the PAM

q_e (experiment) (g/g)	Pseudo-first-order			Pseudo-second-order		
	q_e (first) (g/g)	k_1 (min^{-1})	R^2	q_e (second) (g/g)	k_2 (g/g·min)	R^2
7.55	7.02	0.0278	0.822	7.58	0.209	0.999

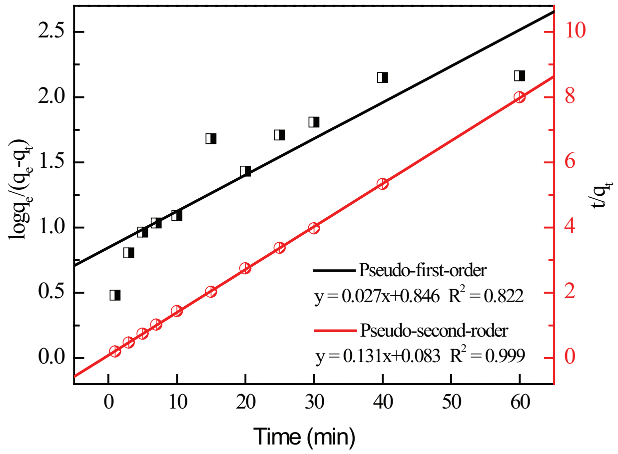

Fig. 5. Pseudo-first-order and pseudo-second-order rate equation models for absorption capacity of the PAM.

coefficient ($R^2 = 0.9999$) than the pseudo-first-order kinetic model ($R^2 = 0.822$). In addition, the value of q_e estimated from the pseudo-second-order kinetic model (7.58 g/g) was very close to the experimental value (7.55 g/g). The results are in good agreement with the results of other oil sorbents [26,27]. Therefore, the pseudo-second-order kinetic model was more suitable for describing the sorption equilibrium of gasoline on the PAM. The results indicated that oil was first transported from the aqueous phase to the surface of the PAM, and then, the oil quickly diffused into the interior of the porous particles [28,29]. This implied that oil penetration into the pores of the material was more predominant than surface sorption.

3.3. Oil-retention capacity of the PAM

As displayed in Fig. 6, the oil-retention capacity of the PAM barely decreased with an increase in the centrifuge rate. The trace amount of loss may be due to the volatilization of gasoline itself. This observation can be justified by the fact that the PAM can combine with the gasoline molecules as closely as possible, rather than by loose surface absorption, as in the case of sponge sorbents [30]. The high oil-retention capacity was likely due to the presence of abundant functional groups (Fig. 3), which also contributed to the pseudo-second-order absorption kinetic model accurately simulating the absorption data (Table 1; Fig. 5). These results indicated that the PAM was resistant to harsh environments, such as that in transfer and handling operations. Obviously, a high oil-retention capacity is an important parameter for evaluating the oil-absorption ability, especially during transport. More importantly, a high oil-retention capacity can prevent secondary pollution caused by the volatilization of poisonous and harmful materials (e.g., methylbenzene). Therefore, this PAM, with its excellent retention capacity, has great promise in practical applications.

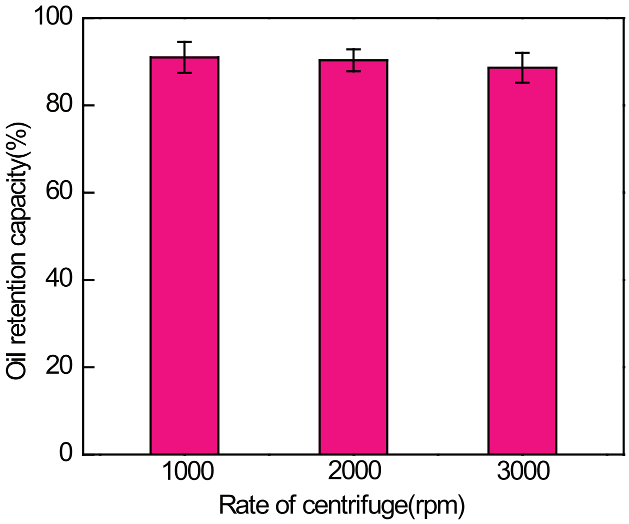

Fig. 6. The oil-retention capacity of the PAM at different centrifuge rate.

3.4. Practical application tests of the PAM

Developed PAMs are mainly used in emergency environmental protection, for example, the absorption of offshore oil spills and oil industrial wastewater treatment. A test for the practical application of the PAM to remove gasoline (colored red with oil) from water is demonstrated in Fig. 7. When a piece of the PAM packaged with non-woven fabric was immersed into the gasoline layer on the water surface, the gasoline was quickly absorbed by the PAM. The PAM swelled after absorbing the gasoline and continued to float. The gasoline-loaded PAM was easily removed from the water, after which the water contaminated by gasoline returned to its original appearance, to achieve the goal of complete oil removal.

The PAM was also tested in the absorption of crude oil, diesel, and kerosene. The absorption capacity increased until it reached a maximum capacity of 3.8 g/g, 5.9 g/g, and 7.1 g/g of PAM, respectively, after an absorption time of 30 min. Once the organic compounds were absorbed, the PAM did not leak even when squeezed, showing the effective prevention of secondary pollution. When absorbed, the organic chemicals became part of the PAM for easy handling and safe storage. Generally, the fully oil-loaded PAM can be disposed by burning (this product is flammable) or by deep land filling to minimize contamination.

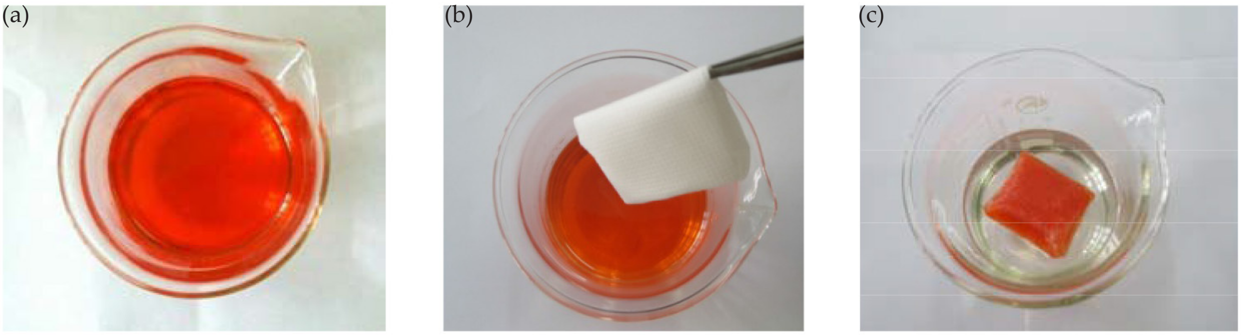

Fig. 7. Pictures for the cleanup of gasoline (colored with oil red) from water by the PAM: (a) gasoline was floating on water surface; (b) the PAM packaged with non-woven fabric was put into the beaker (0 min), and (c) gasoline was absorbed by PAM (2 min).

4. Conclusions

In this study, the characteristics, absorption capacity, absorption kinetics, retention capacity, and practical applications of a PAM were analyzed and described. The spherical structure and large specific surface area (12.85 m^2/g) of the material led to a high oil-absorption capacity (7.5 g/g). The pseudo-second-order absorption kinetic model accurately described the absorption data. Compared with other oil-absorbing materials, the PAM has a higher retention capacity (>90% at a centrifuge rate of 3,000 rpm), retains absorbed oil during transfer and handling operations, and avoids the volatilization of dangerous chemicals that cause environmental pollution and damage human health. Therefore, the described PAM has the advantages of both high oil-absorption capacity and oil-retention capacity, making it a promising candidate for applications in the treatment of oil spills and especially in the emergency handling of toxic and harmful substances.

Acknowledgments

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