

Study on adsorption properties of synthetic materials on marine emulsified oil

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Abstract. As an effective measure for marine oil spill recovery, adsorption treatment can be adopted in areas where mechanical recovery is not applicable. This experiment is mainly aimed at studying the adsorption properties of synthetic materials on emulsified oil. The emulsified oil was prepared by simulating the emulsification process of marine oil spill via a wave-current flume, and the adsorption weights of synthetic materials on emulsified oil were obtained by performing a field adsorption experiment. Polypropylene, nano-polypropylene and hydrophobic melamine sponge were tested by adsorbing a variety of emulsified oils according to the Adsorption Property Test Method (Version F-726) defined by ASTM. Their adsorption weights on emulsified oil (with initial thickness of 5 mm and water content of 20.86%) are 5.42 g/g, 23.5 g/g and 82.15g/g, respectively, which, compared with that on gear oil in the initial state, are respective decreases of 46.39%, 19.88% and 11.84%, demonstrating obvious decreases in their adsorption performances.

1. Introduction

Entering the marine environment, oil will be affected by weathering processes such as evaporation, dissolution, emulsification, dispersion, biodegradation and photooxidation [1-4]. Spilled crude oil or petroleum products will disperse in water or form stabilized water-in-oil (w/o) emulsions at sea [5]. When oil spills at sea, it will form w/o emulsions rapidly [6-7]. As stabilized w/o emulsions, the minimum mass percentages of asphaltenes and resins to form mesostable emulsions are about 3%. When the latter rises over the requisite amount, the emulsion will be formed provided sufficient ocean energy. The density of the resulting emulsion can rise from the starting density 0.80 g/ml to as high as 1.03g/ml, and the viscosity typically changes from a few hundred cp to about one hundred thousand cp (centipoise, a unit of viscosity) [8].

In the final stage of oil spill emergency treatment, sorbents are used most effectively for cleaning up the shoreline and for recovering small pools of oil that are hard to be recovered using other clean-up techniques [9]. In the initial oil spilling stage where the oil slick is intact, it is not suitable to use dispersants [10]. Therefore, it is particularly important to find an effective and fast method of oil spill recovery. Under equilibrium conditions, activated carbon and hydrophobic perlite have been taken to absorb emulsified crude oil from seawater of different salinities [11].

In this experiment, medium-load gear oil and 3 kinds of adsorbents, namely, polypropylene, nano-polypropylene and hydrophobic melamine sponge were selected as the main experimental materials. This study mainly investigated the adsorption performances of the 3 kinds of synthetic adsorbents on



emulsified oils formed from the oil slick under the specific wave action, and meanwhile it explored the influence of oil spill emulsification on the adsorption performance. The goal was to provide a basis for the selection of adsorbents in the recovery process and explore new materials for the adsorption of emulsified oil.

2. Materials and methods

2.1. Experiment set-up

The experiment was carried out in the experimental flume of Tianjin Research Institute for Water Transport Engineering. The flume is 45 m long, 0.5 m wide and 1.1 m deep with a pusher-type wave maker installed at the right side and a wave absorber arranged at the other. A water pump outside can produce stable water flows. A floating boom in the middle, whose movement is limited by two mooring ropes, is composed of a floater, a skirt and a balance weight. In front of the floating boom, the initial thickness and length of oil slick are mainly controlled by flow rate. Figure 1 shows the schematic diagram of the device.

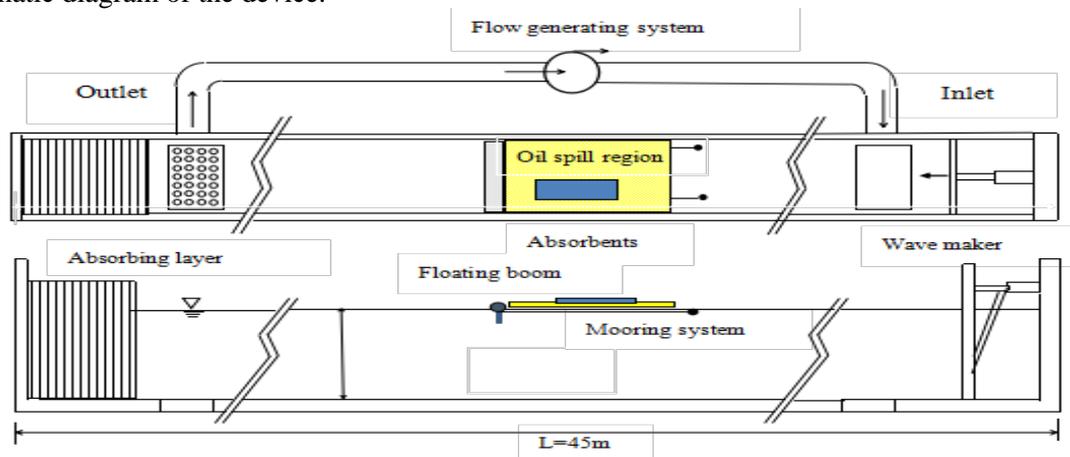


Figure 1. Sketch of the experimental set-up (Top: top view; Bottom: front view).

2.2. Experimental methods

According to ISO 21072-1-2009 [12], for conducting performance test of oil skimmers, different oil slick thicknesses should be set based on different properties of the oil. Adsorbents are mainly applied to thinner oil slicks in the final stage of oil spilling emergency, so the thickness is set to be smaller than the usable range of the skimmer. In the experiment, the thickness was set to be 3 mm, 5 mm and 10 mm, respectively.

First, hydrophobic melamine sponge, polypropylene and nano-polypropylene were cut into 3 cm×3 cm small pieces as backup materials. In the experiment, factors that need to be controlled include the amount of oil, the extraction and weighing of materials, the wave and the current. The experimental phenomena, including the geometric changes, emulsification and adsorption process of oil slick in the experimental area, were recorded and observed by a monitoring camera. The fresh water whose surface temperature and pH value was around 30 °C and 7.12, respectively, was adopted with the outdoor temperature ranging from 26 °C to 37 °C. The wave parameters are listed in Table 1.

Experiments were carried out according to the following steps:

1. An appropriate amount of oil was slowly poured into the experimental area, and meanwhile the flow rate was adjusted to enable the initial thickness of oil slick to meet the experimental requirements and the length of oil slick to remain over 0.8 m.

2. A specific wave was selected from Table 1 to be spread in the flume for 5 minutes, after which the oil sample was extracted immediately and put into 50 ml and 5 ml sample tubes, respectively.

3. According to ASTM F-726 [13], the adsorbents were put into the flume to freely adsorb the oil slick, so that their oil absorption rates can be measured.

4. Step 2 and 3 were repeated till oil spilled under the wave condition for 30 minutes (namely, to repeat for 5 times).

5. The remaining oil was removed from the flume and to proceed to the next step.

6. Viscosity and water content of the emulsified oil can be acquired by analyzing all of the oil samples obtained. On the day of sampling, dynamic viscosity of the emulsified oil sample was measured by a rheometer (Brookfield DV3T type, the indoor temperature was about 30 °C). Meanwhile, according to ASTM D95 [14], the emulsified oil sample was processed into distillation solvent by using petroleum spirit to achieve the separation of oil and water after removing the water. In this way, the water content of emulsified oil was figured out.

Table 1. Wave parameters .

Wave	W1	W2	W3	W4	W5	W6	W7
Wave height H (m)	0.06	0.06	0.06	0.08	0.04	0.04	0.08
Period T (s)	1.2	1.7	2.2	2.2	2.2	1.3	1.2
Wave steepness H/L	0.027	0.015	0.011	0.015	0.007	0.016	0.036

3. Results and discussion

3.1. Changes of oil slick under the action of wave and current

The geometric changes of oil spill controlled by a floating boom are demonstrated in Figure 2. Spilled oil moves towards the boom with the increase of current velocity, leading to the growth of slick thickness. By adjusting the water flow, the initial thickness can rise from 3 mm to 10 mm or even thicker. After the action of W7 for 30 minutes, the initial thickness rises from about 11.2 mm to about 15.4 mm (even if part of the emulsified oil has been extracted). Stable emulsions contain 55%-85% of water, so the volume of spilled oil is expanded to 2 to 5 times the original volume [8]. Changes in the shape of the slick affect the effective contact surface between the adsorbent and the crude oil spill.

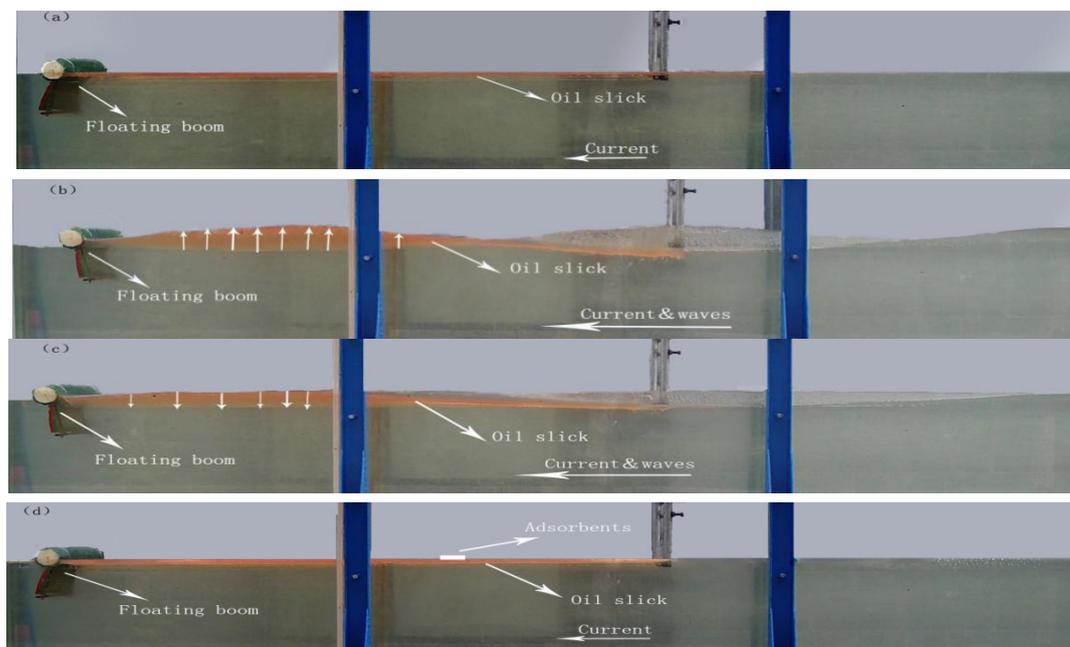


Figure 2. Schematic diagram of oil slick changes under the action of wave and current.

With the marine oil slick extending and contracting repeatedly under the wave action, hydrophilic substances in the oil adsorb on the surface of water droplets immediately and stabilize them through combination. Afterwards, a more viscous oil slick is formed at the interface between the free-flowing seawater and the repeatedly expanding and contracting oil slick [15].

After entering the ocean, oil mostly exists as an emulsion which is difficult to dissipate due to its high viscosity and content of seawater. After performing a flume experiment imitating the actual wave-current environment to prepare the emulsified oil, the adsorption properties of synthetic adsorbents are analyzed.

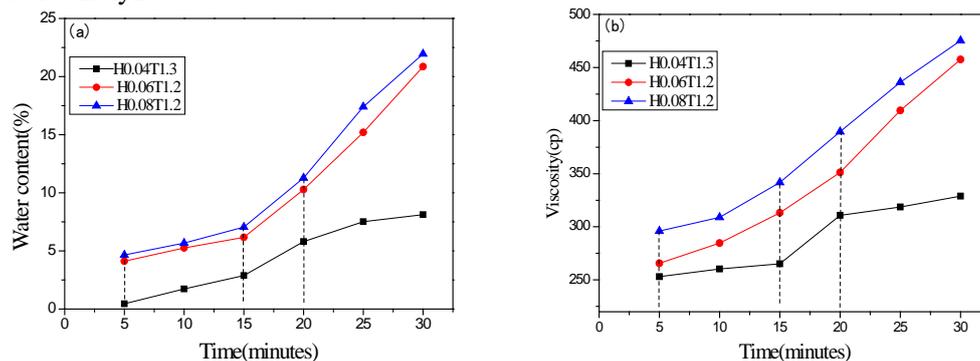


Figure 3. Changes in water content (a) and viscosity (b) of 5 mm oil slick under the action of waves (Wave: W1, W3 and W7).

Under the action of low height wave W1, the water content of oil slick increases to 2.88% at 15 minutes and to 5.80% at 20 minutes, which is twice as much as its previous water content. In this case, the maximum growth rate of water content is 0.58. Under the action of medium and high height waves W3 and W7, they show similar change laws. That is, their water contents reach 4.11% and 4.65% at 5 minutes, rise to just 6.16% and 7.05% at 15 minutes and then soar to over 10% at 20 minutes. In the two cases, the growth rates are up to 0.82 or more higher after 15 minutes. The results in the literature suggest that the energy requirement is variable, and that some oils will form emulsions at apparently moderate ocean energy, while others at higher turbulent levels [8]. As shown in Figure 3a, within the same period, the larger the wave height, the greater the water content of oil. As illustrated in Figure 3b, under the action of W1, the viscosity of oil increases from the initial value 233.7 cp to 265.2 cp at 15 minutes and to 310.7 cp at 20 minutes with a low overall growth rate. The viscosities of oil slick also have resemblance in the change regularities under the action of W3 and W7. For instance, the growth rates of viscosities are low in the period of 5-15 minutes, but they reach about 0.74 and 0.68 respectively after 15 minutes. The variations of water content and viscosity agree with each other, reflecting the direct relationship between the increasing viscosity of w/o emulsified oil and its rising water content. Literature reveals that the formation of emulsion is relatively rapid, and it is fully completed in 0.1-3 h in the laboratory (under moderate energy conditions) [8].

The wave W3 with medium height and high frequency was selected as the main wave parameter to observe and analyze change laws of oil slicks. The changes in water content (a) and viscosity (b) of oil slicks of 3 kinds of thicknesses are presented in Figure 4. The water content of 3 mm oil slick is higher than those of 5 mm and 10 mm oil slicks. Among them, the changes of 5 mm oil slick are the same as the ones in Figure 3, while the 10 mm oil slick exhibits slowly growing water content and viscosity rate. Under the action of the same wave W3, the thinner the oil slick, the larger the water content and viscosity change. The 5 mm oil slick with more notable water content and viscosity change was selected as the main research object in this study.

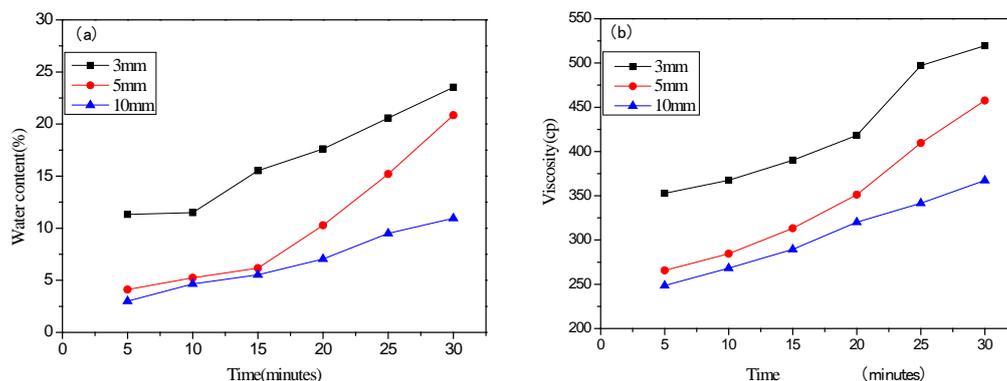


Figure 4. Changes in water content (a) and viscosity (b) of emulsified oil slicks under the action of W3 (Thickness: 3 mm, 5 mm and 10 mm).

3.2. Emulsified oil adsorption experiment

Emulsified oil can be formed in a short period of time. Thus, it is necessary to evaluate the adsorption and recovery performance of the existing adsorbents on emulsified oil, so as to develop a technology for effective recovery. In this experiment, the variations of adsorption properties of adsorbents on medium-viscosity emulsified oil were studied.

Adsorption weights of hydrophobic melamine sponge, polypropylene and nano-polypropylene on 5 mm oil slick under the action of W3 are presented in Figure 5. At the third time, the adsorption weight of hydrophobic melamine sponge decreases by 2.23% due to the small rise of oil spill viscosity. After the third time, its adsorption weight keeps decreasing, as the oil spill viscosity rises rapidly. At the fifth and sixth times, its adsorption weight is stable, with the adsorption loss being 11.84%. The adsorption weight of nano-polypropylene shows oscillatory changes. It maintains good adsorption properties on the emulsified oil in different states, with the maximum adsorption loss being 21.57%. Moreover, the effective contact area between the adsorbent and the oil slick also affects the adsorption weight. As the oil spill property changes continuously, the adsorption weight of polypropylene keeps falling, which is much lower than its initial property, with its adsorption loss being as high as 46.39%.

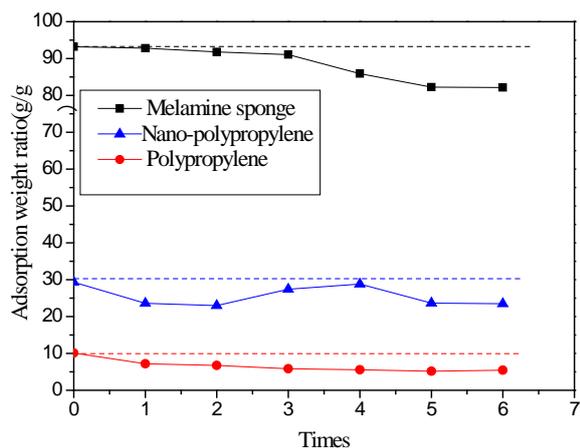


Figure 5. Adsorption weights of 3 kinds of materials on 5 mm oil slick under the action of W3 (a: melamine sponge, b: Nano-polypropylene, c: Polypropylene; Abscissa means the adsorption experiment times).

The adsorption weights of the 3 kinds of materials all fall to varying degrees with the increase of oil slick waving time. Oil with high viscosity can cause two opposing effects, either increasing or decreasing oil adsorption. The increased adsorption happened due to the adherence of the oil to the fibre's surface whereas the decreased sorption occurred when oil is inhibited from penetrating the interior of the fibre[16-18].According to the viscosity changes of oil slicks of different thicknesses and

the adsorption weights on 5 mm oil slick shown in Figure 5, it can be inferred that under the same wave condition, the thinner the oil spill, the higher the emulsification degree of oil, and thus the more intense the changes in adsorption weights of the 3 kinds of materials. In general, the emulsification of oil spill has significant influence on the adsorption properties of materials.

4. Conclusions

The emulsification of oil spill occurs in a short period of time. Under the continuous action of waves, the water content of oil slick keeps increasing, and the viscosity of emulsified oil soars after 15 minutes. By comparing the adsorption weights of the 3 adsorbents, it is found that adsorption property of polypropylene decreases by 46.39% and its adsorption weight is small, suggesting that it is not suitable for the treatment of emulsified oil. Possessing excellent compatibility of emulsified oil in different states, the nano-polypropylene maintains a good adsorption property, with a minimum adsorption weight of 22.98 g/g and an adsorption property decreasing by 21.57%. The adsorption weight of hydrophobic melamine sponge is stabilized at about 82 g/g at the fifth and sixth times, indicating that it retains a good adsorption property. Hydrophobic melamine sponge has a strong adsorption property on the emulsified oil, which is worth further study.

Acknowledgment

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