The effectiveness to cleanup oil spills from the water environment of the combined sorbent on the basic of PUF and chitin

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Abstract. This study provides information about evaluating the parameters (density, buoyancy, sorption capacity) of a combined oil sorbent based on polyurethane foam filled with chitin (PPU10M). In comparison with the original chitin, the developed sorbent has better buoyancy, and commensurate with the pure polyurethane foam (PUF). The effect of the contact time, the type of the water, the thickness of the oil layer and the adsorbent dosage are studied. The results show that the optimal contact time of the sorption process is 60 minutes. In which, the oil capacity of the sorbent PPU10M in artificial seawater reaches 13.6 g/g and in artificial river water 13.2 g/g. The sorbent dose depends on the thickness of the oil layer on the water surface. For a thin oil layer, the use of 1g of adsorbent reaches higher oil capacity but the oil removal percentage lower in comparison to the dose of 2g sorbent. For an oil layer thickness equal to or greater than the height of the sorbent cube, the efficiency of oil removal is observed better when using 2g of sorbents. Thus, it is considered that the use of 2g sorbents is optimal. A generalization of the research results indicates the prospects of the developed combined sorbent based on chitin and polyurethane for oil spill treatment.

1. Introduction

Nowadays, because of the quick development of industry and transport, leading to an increase in oil demand [1]. Mostly oil is transported by waterways such as through rivers, seas, and oceans. It is one of the main reasons that lead to accidents and the spill of oil into the sea and river environment. These accidents can not only cause serious pollution in the water environment but also negatively affect the surrounding environment, and these are also one of the causes of the significant loss of valuable resources [2]. Therefore, it is urgent to remove oil spills from the water environment [3]. To treatment the oil spills problem, commonly used methods include on-site burning, mechanics method, chemistry method and the use of sorbents [4]. Each method has its advantages and disadvantages.

The sorbent method can be considered one of the most effective methods for the cleanup of oil spills and regeneration of oil after the process adsorption [5]. A good sorbent should include criteria such as high sorption capacity, selectivity for oil adsorption, the possible reusability, good oil regeneration, high buoyancy and a moderate cost [6, 7]. There are three main types of oil adsorbents: inorganic mineral absorbents, organic natural absorbents, and synthetic absorbents. Among them, the most potential and promising method is the use of synthetic absorbents, because their absorption capacity is significantly higher than other groups. However, they have a fairly high cost and decompose very slowly.
Furthermore, the effects on the environment of these sorbents are still not clear. Therefore, it is important to develop environmentally-friendly oil absorbents with high adsorption capacity, reasonable cost and high ability to recycle process and reuse [2].

Recently, polyurethane foam (PUF) is one of the synthetic sorbents that has attracted the attention of many scientists, because of its high oil capacity, the reusability, and high buoyancy. However, its cost is quite high. Reducing the cost of this synthetic adsorbent by the use of fillers from natural materials with low density is considered a viable method [8]. For this aim, it is recommended to use chitin - an available natural material that has many advantages, such as low cost, low density, environmental friendliness, and biodegradability. However, chitin has a not high adsorption capacity and hydrophobicity in comparison to the synthetic materials [8]; more its reusability is impossible. To resolve these disadvantages of both materials, in this work, the polyurethane foam is combined with a natural sorption material - chitin.

The adsorption capacity of the sorbent PPU10M for oil spilled on the surface of seawater and river water is studied.

2. Materials and methods

2.1. Materials
To produce the PUF, components A and B from the company "Dau Izolan" (Vladimir City, Russia) are used. Component A has the density - 1.02 g/cm³ and the viscosity - 1200 MPa.s; component B has the density - 1.20 g/cm³ and the viscosity - 50 MPa.s. The filler is chitin obtained from shrimp shells with a particle size of 1-3 mm, with moisture content - 2.54%, ash content <0.1%. Chitin is purchased from the company "Chitosan Vietnam" (Ho Chi Minh City, Vietnam).

As a pollutant, oil is purchased from the Vereisky region (Tatarstan republic, Russia) with a density at 20°C - 0.984 g/cm³, and a kinematic viscosity at 20°C - 55.7 MPa.s. Artificial seawater has been used according to ASTM D1141-98 [9] and artificial river water according to the method described in the work [10] for simulating oil spills in river water and seawater.

2.2. Synthesis of the combined sorbent PPU10M
For the synthesis of the combined sorbent PPU10M, component A is mixed with chitin by using the high-speed agitator, then component B is added to this chitin-component A mixture, and continue to mix them. The ratio between the components A and B by weight is 10:6. In the previous study, it is showed that the sorbent containing 10% chitin with the crushed size of 1-3 mm (PPU10M) has the highest oil capacity [11]. After the preparation process, the material is left in 24 hours at room temperature. Next, it is cut into particles with a size of 10×10×10 mm.

2.3. Characteristics of the sorbent
To determine the apparent density of materials, method GOST 409-77 is used [12]. The buoyancy of sorbents is evaluated by method ASTM F 726-99 [13].

2.4. Sorption capacity of the sorbent
The experiments are carried out in the oil-water system. To simulate accident spilled oil on the water, 250 ml of the artificial seawater or artificial river water is placed in a glass with a volume 500 ml, and then an amount of oil is added until it forms a layer on the surface of the water. Next, an amount of the sorbent is weighed and placed in this system. The sorption process is carried out within 120 minutes. Then the sorbents are removed and drained for 2 min and the total mass of the sorbents after sorption process is determined on the analytical balance. The remaining oil-water after adsorption are separated by 100 ml toluene. This obtaining mixture is separated by the separatory funnel to obtain the remaining water after adsorption. It is weighed and the result is recorded to calculate the mass of absorbed water. The oil capacity of the sorbent – (q, g/g) calculate by the formula (1).

\[ q = \frac{m_a - (m_w + m_o)}{m_0} \]
where: \( m_s \) – the mass of saturated sorbent (water, oil and initial sorbent), g; \( m_w \) – the mass of the adsorbed water, g; \( m_0 \) – the initial mass of the dry sorbent, g.

The degree of oil removal – \((P, \%)\) is determined according to the formula (2).

\[
P = \frac{m_r}{m_n} \times 100 \tag{2}
\]

where \( m_r \) – the mass of the adsorbed oil, g; \( m_n \) – the initial mass of oil, g.

The efficiency of oil adsorption by the sorbent PPU10M – \((E, \%)\) is determined by the ratio between the mass of adsorbed oil \((m_r, \text{g})\) and the total mass of the sorbent after sorption process \((m_s, \text{g})\) (formula 3).

\[
E = \frac{m_r}{m_s} \times 100\% \tag{3}
\]

2.4.1. Effect of the contact time on the sorption capacity

About 50 g of oil is added to 250 ml of the water (artificial seawater or artificial river water) in the glass beaker, then 2 g of the sorbent PPU10M is placed into this oil-water system. Sorption capacity is measured after 5, 15, 30, 60, 90 and 120 min respectively.

2.4.2. Effect of oil layer thickness and sorbent dose on adsorption capacity

Oil is added to a glass beaker with 250 ml of water until it creates a layer with a thickness of 3, 5, 7, 9, 11, and 13 mm, respectively in the surface of the water. Next, 1, 2 or 3 g of sorbent, respectively, is placed into these simulate oil spills system. The contact time of the adsorption process is 60 minutes.

3. Results and discussion

3.1. Characteristics of the materials

Evaluation of the density of sorbents is necessary because it affects the buoyancy of the sorbents. As can be seen from the data in table 1, the density of chitin is lower than the density of the sorbents. Therefore, its presence in the sorbent PPU10M doesn’t affect the density of the sorbent. But in view of the fact that foaming of PPU filling with chitin is somewhat difficult, the density of the combined sorbent with chitin is higher than the blank PUF.

| Characteristics                  | PUF     | Chitin  | PPU10M  |
|----------------------------------|---------|---------|---------|
| Density, kg/m³                   | 59.10   | 13.12   | 69.91   |
| Buoyancy in the saturated state, | 95%     | 55-60%  | 95%     |
| Description of the buoyancy      | Floats (100% mass) | > 70% of the mass submerged in water | Floats (100% mass) |

The sorbent with good buoyancy leads to reducing the negative effects on the organisms living in the aquatic environment [7]. The research results about the buoyancy of materials show that the buoyancy of the combined sorbent PPU10M is not different from the original PUF, but it is significantly higher than in comparison to the chitin. The loss of buoyancy of chitin at the saturated state not only affects the oil recovery process and the removal process of the solid waste after adsorption, but it is also one of the causes of secondary pollution and negative influences on aquatic organisms. Due to the high buoyancy of the sorbent PPU10M, after the adsorption process, it is easily removed by using the simple and cheap mechanical methods, for example, the use of nets. This contributes to the significant reduction in the cost of the oil spill removal process.

3.2. Adsorption capacity of the sorbent PPU10M

3.2.1. Effect of the contact time
With the purpose to establish the optimal contact time for maximum oil absorption, the adsorption process is studied within 120 minutes. It is noticed that the oil sorption of the sorbent PPU10M increases with the increase of contact time (figure 1a). For both types of water, the speed of oil sorption increases significantly in the first 30 minutes due to the high oil concentration. In the next 30 minutes, the oil concentration decreases, leading to the reduction gradually of the speed of the oil sorption. After 60 minutes the oil sorption reaches the equilibrium state, so the oil capacity hardly increases. The oil sorption on the sorbent PPU10M can be explained because of the large number of capillary pores in its structure, that provide a sufficient volume to absorb oil through intermolecular interactions [14-16]. Next, the oil continues to enter into the capillary pores of the PPU10M. It leads to a low speed of the oil adsorption process and after 60 minutes the equilibrium state is setup.

In the treatment of oil spills, the degree of oil removal and the efficiency of oil adsorption are two important parameters for evaluating the sorbent. Figure 1b shows that the oil removal percentage of the sorbent PPU10M increases significantly from 5 to 60 minutes, after 60 minutes there is almost no difference in the process of oil removal. Similarly, when the contact time is longer than 60 minutes, the efficiency of oil sorption also significantly reduces. Therefore, the optimal contact time of the oil adsorption by the sorbent PPU10M is 60 minutes with oil capacity reaches 13.6 g/g for artificial seawater and 13.2 g/g for artificial river water.

The difference in adsorption capacity between artificial river water and artificial seawater of the combined adsorbent PPU10M is explained by the presence of various salts in the composition of these types of water. It leads to the changes in the electrical double layer between the sorbent and the adsorbate, which affects the sorption ability of the sorbent in different aqueous environments [17, 18]. But generally, the difference in oil adsorption capacity of the sorbent PPU10M is small, it ranges 0.19-0.35 g/g. This indicates that the chemical composition of the aqueous phases does not significantly affect the capacity to remove oil spills by the combined adsorbent based on polyurethane foam and chitin. Therefore, the sorbent PPU10M can be used widely to treatment oil spills both on the rivers and in the sea.

3.2.2. Effect of oil layer thickness and adsorbent dose

The dose of sorbent and the thickness of the oil layer are two factors that significantly affect the effectiveness to clean up oil spills. Three different dosages of the sorbent (1, 2 and 3g, respectively) and the various thicknesses of the oil layer (3, 5, 7, 9, 11 and 13 mm, respectively) are investigated.

Due to an increase in the thickness of the oil layer leads to an increase in the contact area between the adsorbent and adsorbate, at the same time, it leads to the decrease of the contact between the absorbent particles and the water surface (figure 2). Therefore, with an increase in the thickness of the oil layer in the limit of this study, the oil capacity of the PPU10M increases for all three cases of the adsorbent dosage (figure 3a).
The research results show that the use of adsorbent dosage depends on the thickness of the oil layer. With a thin layer of oil, the increased dose of the sorbent leads to a decrease in oil capacity and the efficiency of oil adsorption. Because a large amount of absorbent leads to contact of the adsorbent not only to the oil but also to the water. Therefore, the water capacity increases, while the oil capacity reduces. But the low dose of adsorbent (1g) reaches the lower significant degree of oil removal in comparison to the higher dose (2g and 3g) (figure 3b). With the oil layer thickness commensurate with the height of the sorbent cube ($d_{oil} = 9-11$ mm), the increase of adsorbent dosage from 1g to 2 g significantly increases oil capacity. When the use of the sorbent increases from 2g to 3g, the degree of oil removal and the efficiency of oil sorption are not significantly different. In the case the thickness of the oil layer exceeds the size of the cubes PPU10M ($d_{oil} \geq 11$ mm), the more the adsorbent dosage increases, the more the oil capacity and the degree of oil removal increases. In general, in comparing the parameters: oil capacity, removal percentage and efficiency of the oil sorption show that the optimal dose of the sorbent is 2g. At a dosage of 2g PPU10M, its oil capacity reaches about 5.2–13.4 g/g, the degree of oil removal is in the range 56–90%, and the efficiency of oil absorption is relatively high about 44–92%.

**Figure 3.** The dependence of the oil capacity of the PPU10M (a), the degree of oil removal and the efficiency of oil sorption (b) on the thickness of the oil layer on the surface of water.

**Conclusion**

The oil adsorption capacity of the combined adsorbent based on chitin and polyurethane foam was studied in this paper. It is showed that the fill of chitin to the component PUF doesn't significantly change the density of the combined adsorbent PPU10M in comparison to blank PUF, it reaches 69.91 kg/m$^3$. The buoyancy of the combined sorbent is also higher compared to the original chitin and corresponds to the buoyancy of the blank PUF. The study of the effect of sorption time on the efficiency of oil sorption on the adsorbent in artificial river water and artificial seawater shows that the optimal contact time of the oil sorption process is 60 minutes; the oil capacity at 60 minutes reaches 13.6 g/g for seawater and 13.2 g/g for river water. At the same time, the chemical composition of the aqueous environment does not significantly affect the efficiency to remove the oil spill of the material PPU10M. The initial thickness of the oil layer on the water surface affects the use of the adsorbent dosage. In detail, for the thin oil layer, the use of 1 g of adsorbent reaches better oil capacity but the oil removal percentage is not high as the dose of 2g; for the oil layer thickness equal to or exceeding to the size of the sorbent cube, then the use of 2g PPU10M is most effective. In general, the optimal adsorbent dosage is 2g.

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