Study on the sorption capacity of the adsorbent based on polyurethane and chitin to remove oil spills

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Abstract. Nowadays, oil and its derivatives were considered one of the major energies and they also have been one of the main sources of environmental pollution, especially for water pollution. The tendency in this time of researchers was to find new adsorption, that has high sorption capacity, economical and easy production. By accordance with the present trend, in this study, chitin was used with the dose up to 50% as a filler in the composition of adsorbents basic on polyurethane foam (PUF). The effect of the size (small size: 1-3 mm and large size: 5-10 mm) and the dose (10, 20 and 50%) of filler in the foaming composition to technological parameters of the collected adsorbent, as well as to its absorption capacity were investigated. The results showed that the adsorbents filling with a lower dose of chitin (10 and 20%) were better foaming than the one containing a higher dose of filler. At the same time, the adsorbents containing small chitin also formed the foam better than one filling large size. For 2 types of PUF, the adsorbent from elastic PUF has higher sorption capacity than the semi-elastic adsorbent with the same dose of the filler. For the results of sorption effectivity of the adsorbents presented that the adsorbent with the small size of filler observed greater the absorbency than the one with large size. In which, the elastic adsorbent containing 10% chitin with small size has the highest oil absorption capacity, which reached 13.13 g/g. To compare the sorption capacity of the adsorbent between relation to oil and water, it shown that its oil capacity is significantly higher than the sorption capacity of water.

1. Introduction

Oil and its derivatives were considered one of the major energies; on the other hand, they also had been one of the main sources of environmental pollution, especially water environmental [1-6]. They penetrated into the aquatic environment in different ways, for example: they entered into surroundings from the production, transportation and storage process; or when using oil as fuel for ship engines; either when cleaning storage tanks for oil; or even from wastewater of the refineries or possibly be caused from waterway accidents. Meanwhile, the oil pollution in the water environment has affected the sea and water transport, the economy, the health of people and living organisms. When oil came in contact with water, it has affected the aquatic organisms such as: physiological disorders, diseases, changes biological functions. On the other hands, the decomposition process of the oil in water by the microorganisms occurred very slowly, which leads to the forming the oil layer on the water surface. The oil layers on the water surface reduced the necessary supply air for microorganisms, and it also became the secondary source of pollution for the aquatic environment [7]. So, it is necessary and urgently to remove the oil from the water [8].
The wastewater containing oil and its products have been treated by various methods: mechanical, chemical, biological, or sorption method. Among these methods, the sorption method has attracted many scientists because of its simplicity and efficiency. However, the current adsorbents to remove oil spills still have many disadvantages, for instance: expensive, complicated production process, low sorption efficiency and low buoyancy, negative environmental impact [9]. Therefore, it was necessary to create a new adsorbent, which has lower cost, high adsorption and buoyancy ability in water, as well as the possibility of reusability.

Chitin is one of the inexpensive and available materials. It is produced by units of N-acetylglucosamine. This polymer is a popular polysaccharide widely distributed in nature (the second most quantity biopolymers after cellulose); it is contained mainly in the crustacean shell (shrimps, crabs) and the other aquatic animals (coral, jellyfish, squid). Chitin and its derivatives have many valuable properties, such as: antifungal and antimicrobial activity, biodegradable and biocompatible, no toxic for humans and animals. For this reason, it was considered widely renewable resource used in many fields, as an example: wastewater treatment and environmental protection, pharmacy, medicine, agriculture, industry, biotechnology. In recent years, the new functions for chitin were discovered. Hence, its production and consumption were strongly growing [10]. In the wastewater treatment and environmental field, chitin was considered a coagulant and flocculating agent for the pollutants in the wastewater such as: the suspended organic compounds and solids, amino acids [11]; it worked as an adsorbent to remove reactive dyes in the wastewater of the textile mills [12]. It also had a good adsorption ability to remove heavy metal ions [11], to remove phenols and chlorophenols in wastewater [12]. Besides, chitin removed quite high the contaminants in refineries wastewater; and so, led to improving significantly about the quality of wastewater [13]. In addition, the authors from Brazil reported that chitin and chitosan were able to remove oil spills well in seawater, nevertheless, after sorption process, this biopolymer sunk to the bottom of the sea, causing inconvenience in the removal oil spill response [14]. Moreover, in the previous studies, it can be shown that chitin has sorption capacity to remove oil spills, but after the sorption process the adsorbents not be reused. Thus, its cost was very expensive [11].

Consequently, the aim of the current study created the oil adsorbent based on polyurethane foam (PUF) and chitin, which its adsorption capacity was sufficiently high to remove oil spills. Besides, this adsorbent also had good buoyancy, can be reused and an increase of the amount recover oil after the sorption process. In the limit of this study, the influence of the size and degree of the filler on the foaming and sorption capacity of the adsorbents in two types: the elastic and semi-elastic adsorbent was investigated.

2. Detail experimental

2.1. Materials

Adsorbents - were represented polyurethane foams, were produced by mixing component A filling chitin and with component B; the components were produced by "Dow Izolan", Vladimir, Russia. Component A was used with two types: elastic and hard polyurethane foams. This choice of components PUF due to the structure of the received foams. The elastic foams had interconnection of the cells in their structure, which naturally contributed to the high absorption capacity of this foams. However, they have loosed their buoyancy and sunk when in the saturated state, which led to affect adversely on the living water organisms. On the contrary, the hard foams hard mainly the closed-cell structure, in that the cells were connected, this make difficulty to the penetration of the adsorbate; however, this adsorbent still maintains the buoyancy ability although it was saturated. When the component A with elastic PUF was used, the elastic adsorbent EPUF was obtained; and when component A was used with the hard PUF, the semi-elastic adsorbent SEPUF was obtained. The ratio of components A to B was 1: 0.6.

The chopped chitin as the filler was produced by "Chitosan Vietnam", Ho Chi Minh, Vietnam with two type of the sizes: 1-3 mm (M) and 5-10 mm (B).
2.2. Methods

- Adsorbents (PPU-X) were obtained according to the scheme in figure 2.
- Apparent density was determined according to GOST 409-77 [15].
- The oil sorption capacity of the adsorbents was calculated using the following equation:

\[
Q_0 = \frac{m_1 - m_0}{m_0}
\]  

Where: 

- \(Q_0\): the sorption capacity, g/g;
- \(m_1\): the weight of adsorbent after process sorption, g;
- \(m_0\): the initial dry weight of adsorbent, g;

In the beaker filling with 50 ml of the adsorbate (oil or water) were put about 2 grams of the chopped adsorbents. The sorption process was calculated after 1, 2, 3, 5, 8, 10, 15, 20, 30, 60, 90, 120 minutes of the sorption time [16, 17].

3. Results and discussion

3.1. Technology producing of the adsorbent based on PUF and chitin

3.1.1. The semi-elastic adsorbent
Figure 3 showed the effect of the dose and size of the filler on the foaming process of semi-elastic polyurethane foam (SEPUF). Regardless of the size of the chitin pieces, the more dose of fillers increased, the more the foaming ratio of the foam increased. However, at the dose 50% of filler, the foaming ratio decreased, the foam became denser.
Figure 3. Semi-elastic adsorbents basic on PUF and chitin
a) SEPUF; b) SEPUF-10B; c) SEPUF-20B; d) SEPUF-50B; e) SEPUF-10M; f) SEPUF-20M; g) SEPUF-50M

The piece size of the filler also affected on the foaming process and the quality of the adsorbent. Smaller pieces of chitin were distributed more evenly in the polyurethane matrix and contribute better dilation of PUF.

For the adsorbent to remove oil spills, its structure was one of the main factors affecting the sorption capacity [18,19]. Form fig. 4 observed that the addition of chitin into the composition of the elastic adsorbent give possible to forming a fairly uniform foam. In which, smaller pieces of chitin were distributed more evenly in the volume of the polyurethane matrix and gave a large number of homogeneous cells.

Figure 4. Cross-section of the adsorbents SEPUF and chitin

3.1.2. The elastic adsorbent

Figure 5. The elastic adsorbents based on PUF and chitin
a) EPUF; b) EPUF-10B; c) EPUF-20B; d) EPUF-50B; e) EPUF-10M; f) EPUF-20M; g) EPUF-50M

The results of the elastic adsorbents showed that the addition of chitin led to decreasing of the foaming. In the comparison in the degree dispersion of the filler, it was noted that in the case with smaller filler, the rise ratio of the foaming was better. The best rise ratio of the foaming was observed by the adsorbent with 10% dose of filler, for both size of the filler. Fig. 5.

The cross-sections of the elastic adsorbents were presented in fig.6. The addition of the chitin increased the pore size in the adsorbent. (Fig. 6b,c,e,f). For the adsorbent containing 50% chitin, it was seen that the pieces of chitin overlap the pores in the foam, led to reduce its absorption ability. In which,
the adsorbent filling with the smaller size of chitin gave possibly to form adsorbent with larger and more uniform the number of pores.

It was also observed that EPUF had shrinkage extent less in comparison to SEPUF. For the elastic adsorbents containing 10 and 20% chitin, it was found that the more the amount of filler in the adsorbent, the less their elasticity, which was convenient for chopping. When filling with the dose 50% of chitin, the adsorbent became hard, no elasticity.

![Figure 6. Cross-section of the elastic adsorbents based on PUF and chitin](image)

### 3.2. Technological parameters in the foaming of the adsorbents based on PUF-C

For the foaming process of the adsorbent, the main parameters were the “start time” and “rise time” of the foam. The data of table 1 presented that the both “start time” and “rise time” of the foam were higher when the dose of filler in both types of adsorbent increased. Especially, the “start time” and “rise time” of the foam 50% of the filler increased in comparison to the unfilled adsorbents. The influence of the size of filler was evaluated, the results showed that the adsorbent containing filler with smaller size affected less on the foaming parameters; for the dose of filler 10 and 20%, they were commensurate with the initial ones. The large size of the filler impeded the interaction of the components of PUF [20].

For the adsorbent to remove oil spills, the apparent density was one of the main parameters. The higher the apparent density, the heavier the adsorbent, this led to reduced its buoyancy. The purpose of this study created the adsorbent with high buoyancy, which prevented the sinking and ensured to remove it easily at the saturated state. From the data in table 1, it is shown that the addition of chitin into the adsorbent led to the increase of its apparent density. The larger sizes of chitin pieces affected more on increasing the density of adsorbents. Because the higher the quality of foam, the less its apparent density and its structure were more porous.

| Table 1. Technological parameters of adsorbents based on PUF-C |
|-----------------------------|-----------------------------|-----------------------------|
| Adsorbent       | Start time, s | Rise time, s | Apparent density, kg/m3 |
| SEPUF           | 33            | 110           | 64.39                    |
| SEPUF-10M       | 33            | 112           | 72.37                    |
| SEPUF-20M       | 34            | 132           | 67.53                    |
| SEPUF-50M       | 52            | 197           | 141.46                   |
| SEPUF-10B       | 34            | 138           | 98.35                    |
| SEPUF-20B       | 40            | 166           | 88.69                    |
| SEPUF-50B       | 111           | 249           | 148.71                   |
| EPUF            | 29            | 156           | 59.10                    |
| EPUF-10M        | 29            | 156           | 77.78                    |
| EPUF-20M        | 40            | 160           | 91.86                    |
| EPUF-50M        | 87            | -             | 220.29                   |
| EPUF-10B        | 30            | 161           | 86.65                    |
| EPUF-20B        | 43            | 170           | 132.21                   |
| EPUF-50B        | 90            | -             | 138.30                   |

*: can’t determinate
3.3. Oil adsorption capacity of the adsorbents

Sorption process is the process of movement of absorbed substances through the capillaries in the holes and on the surface of porous solids [6]. To evaluate the effect of the sorption process, the sorption capacity was one of the important factors. The sorption capacity of the adsorbent was the higher, its efficiency for removing oil spills was the greater. The results of the oil sorption capacity of the received adsorbents were shown in fig.7.

Figure 7. The relationship between oil absorbency and time sorption of the adsorbent PUF-C

The results from fig.7 presented that the sorption process of oil divided into three main steps:

Step 1: the speed adsorption process increased significantly in the first 15 - 20 minutes of the sorption process. Initially, the porous contained only air, so the oil got into the foam unhindered.

Step 2: the sorption process was slow down in the period from the 20th to 60th minutes.

Step 3: the sorption process came to the balance from the 60th minutes.

3.3.1. The sorption capacity of the adsorbents

a. The semi-elastic adsorbent

The adsorbent containing small chitin had greater oil absorption capacity than the one with the large size of chitin. It was previously noted that the adsorbents containing smaller chitin formed a better foam with the uniform distribution of pores in comparison to the foam containing the larger size of chitin; obviously, this led to the higher sorption capacity of the adsorbent (fig.3-6).

The semi-elastic adsorbent containing 20% chitin reached the highest oil sorption capacity, was 4.9 g/g. Also, the density of this adsorbent was compared to the density of the unfilled foam, it was indicated the higher buoyancy than the unfilled foam.

b. The elastic adsorbent

The oil sorption capacity of the elastic adsorbents also occurred similarly to the semi-elastic adsorbent. Fig.7b. The oil absorbency of the elastic adsorbents containing chitin with small size was presented higher than the elastic adsorbents with the large size of chitin. The adsorbent EPPU-10M with dose 10% of filler reached the greatest absorption ability, was 13.13 g/g, it had the absorption capacity higher when comparing with the analogues containing 20 and 50% chitin.

When comparing the sorption capacity of adsorbents, it was found that the elastic adsorbents had significantly higher oil sorption capacity than the semi-elastic adsorbents (fig.7a,b). This is obvious because the absorption capacity of the adsorbent depended on two factors: the number of pores and their sizes [18]. Meanwhile, the elastic adsorbent contained mainly the open-cells structure in comparison to the semi-elastic adsorbent, in which the number of closed-cells was significantly smaller.
3.4. The water sorption capacity of the adsorbents

For the adsorbents to remove oil spills, the water absorbency was an important factor. The results of the sorption capacity in relation to the water were shown in fig.8.

Similar to the oil adsorption process, the largest amount of water is absorbed in the first 20 minutes. Then, the speed of the sorption process slows down and finally, from 60th minutes of the sorption process, the sorption curve reached the equilibrium status.

In much the same way of the oil sorption process, the adsorbents containing chitin with smaller size, their water absorbency were higher than of adsorbents with a larger size of chitin. However, for the semi-elastic adsorbent filled with 20% chitin, the water absorption reached the highest 4.96 g/g. Meanwhile, the elastic adsorbent with a dose of filling of 10% showed better water adsorption capacity - 5.79 g/g than with the filling of 20 and 50% chitin.

![Figure 8. The relationship between water absorbency and the adsorption time of the adsorbents PUF-C](image)

Because the removal to oil spills was often carried out on water surfaces, thus the oil adsorption more than water adsorption of the adsorbent was necessary. The selectivity of the adsorption was characterized by the coefficient "a" and was calculated by the formula:

\[
\alpha = \frac{\text{Water sorption capacity}}{\text{Oil sorption capacity}}
\]

From the formula (2) indicated that if the coefficient “\( \alpha \)" of the adsorbent was low, then its oil sorption capacity was higher than the water sorption capacity; on the contrary, if the coefficient “\( \alpha \)" was high, then the water sorption capacity of the adsorbent was higher than its oil sorption capacity. In this study, the coefficient “\( \alpha \)" of the adsorbents was calculated at sorption times 120 minutes (the table 2).

| Adsorbents | Coefficient “\( \alpha \)" |
|------------|--------------------------|
| SEPUF-10M  | 0.90                     |
| SEPUF-20M  | 1.01                     |
| SEPUF-50M  | 0.80                     |
| SEPUF-10B  | 1.01                     |
| SEPUF-20B  | 0.99                     |
| SEPUF-50B  | 0.92                     |
| EPUF-10M   | 0.44                     |
| EPUF-20M   | 0.56                     |
| EPUF-50M   | 0.60                     |
| EPUF-10B   | 0.56                     |
| EPUF-20B   | 0.63                     |
| EPUF-50B   | 0.52                     |

From the data of table 2 can be observed that the elastic adsorbents had greater oil sorption capacity. And the semi-elastic adsorbents reached absorption capacity related to water higher than to oil.
Chitin was structurally polysaccharide built from chains, which was containing amine N-acetyl-D-glucosamine (β(1–4)-linked) (fig. 9). This chains formed a layered structure. Polysaccharide chains are interspersed with layers of protein. Besides, chitin has two hydroxyl groups, one of which at C-3 is secondary, and the second at C-6 is primary. The presence of functional groups in chitin structure on the one hand are the reason of its polarity and hydrophilicity; and on the other hand, the structure of chitin provided the possibility of interaction between functional groups that provide various chemical modifications.

![Structure of chitin](image)

**Figure 9.** Structure of chitin

It would seem that, due to the hydrophilicity of chitin, led to the water sorption degree was greater than oil sorption. But because of the presence of hydroxyl and N-acetyl groups in the structure of chitin, it caused strong hydrogen interactions, including with the structural components of oil, which contributes to its good oil sorption ability.

In both EPUF and SEPUF, the same dose of chitin is used to filling. Therefore, the PUFF adsorbent have a greater oil capacity than SEPUF adsorbents due to the nature of PUF foam. Apparently, when comparing with the SEPUF adsorbents, the EPUF adsorbents had presence of a larger number of open pores; this affected the increased oil sorption capacity.

Therefore, the use of elastic adsorbents PPU-C was more preferable. The elastic adsorbent with a dose 10% of chitin had the highest oil sorption capacity, reached 13.13 g/g and it also had the highest selectivity “a” equal to 0.44.

**Conclusions**

The adsorbents based on polyurethane with filling chitin have been developed and investigated, it presented the high sorption efficiency. The elastic adsorbents based on PUF and chitin had higher sorption capacity than the semi-elastic adsorbents. A significant amount of oil was absorbed in the first 15–20 minutes of the sorption process, then the rate of absorption decreased, and after 60 minutes of the sorption process, it occurred saturation state. Adsorbents with chitin pieces size 1-3 mm had greater absorption capacity than the ones with size 5-10 mm of chitin. The highest selectivity of sorption for the water and oil system was presented by the elastic adsorbent based on polyurethane foam containing 10% chitin with size 1-3 mm and its oil sorption capacity reached 13.13 g/g.

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