Liquidation of oil spills using a sorbent based on chitosan

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Abstract. The development of a sorbent for the oil spill treatment based on polyurethane foam and chitosan. Chitosan is a polysaccharide – an insoluble fiber type – derive from chitin which is found in the shells of some marine life such as shrimp, lobster and crab. It is also found in some types of edible fungi and insects.

Carry out a research into the technology of polyurethane foam filling with chitosan in the amount of 20\% and 50\% by mass. Elastic and semi-elastic polyurethane foam was used as a polymer matrix of the sorbent. Sorbents with 20\% chitosan by mass have the best oil absorbent capacity. Absorbent capacity of the sorbent based on elastic polyurethane foam, full filled with chitosan, soluble in acid, is \( \approx 12, 65 \) g / g, and the semi-elastic sorbent, full filled with chitosan, soluble in acid, is \( \approx 6.12 \) g / g. Regardless of the polymer matrix type, the sorbent has a high buoyancy (does not sink in the carbonated state), and the full saturation of the sorbent with oil occurs almost for the first 15 to 20 minutes.

1. Introduction

Crude oil is a natural fluid which consists of a complex mixture of organic molecules, mainly hydrocarbon, with various chemical and physical properties. Besides that, it is also the main raw material for the production of petrochemical products, such as solvents, chemical fertilizers, plastics, pesticides, asphalt, fuel, the remaining 12\% is used for petrochemistry.

More than 50\% of the world's crude oil is produced in the Gulf of Arabia from onshore and offshore wells. The number of oil spills registered in the Arabian Gulf was 550 cases, a total of 14,000 barrels from 1995 to 1999, and 11,000 barrels spilled from 2000 to 2003 [1].

There are various solutions to realize the removal of oil from sea surface and to prevent the coastline pollution from oil, for example, mechanical extraction and using of dispersants. However, the goal of any spill treatment is to minimize marine pollution and protect coastline from oil. For this reason, the elimination must be carried out extremely quickly in order to remove oil from the sea surface [2]. When oil spills, and penetrates the surface, consequences will extend over for a long time [3].

The main methods for the elimination of oil pollution on the water surface include 4 groups:

- The elimination of booms (booms allow you to move oil to any direction for collection);
- Chemical methods (dissolution in water or oil of surface-active substances that change the ratio of the surface energy of the interfacial boundaries in the oil-water system);
- Using special sorbents;
- Biological methods (use of destructor microorganisms) [4].

Adsorption, an efficient separation method that is widely used as an effective and economical solution to remove pollutants. Published researches have shown that chitosan is effective in removing compounds of various toxic metals, such as cadmium, mercury, molybdenum, uranium, vanadium,
platinum and palladium [5, 6]. Chitosan, a hydrophilic natural polymer obtained by alkaline dissolvent of chitin, which is contained mainly in the shells of shrimp and crab.

In addition, chitosan has promising applications such as textile manufacturing, high-quality paper production, agriculture, and even the nuclear industry [7-11].

On the other hand, polyurethane foam is also able to absorb oil and oil products [12,13]. However, it is not economically feasible solution.

The purpose of this study is to develop technologies for the production of petroleum sorbent based on polyurethane foam and chitosan as well as the study of its properties.

2. Experimental part

2.1. Materials

The object of study was a sorbent obtained on the basis of polyurethane foam and chitosan.

The sorbent components were used:

- Component A (el) manufactured by ELASTOKAM LLC, Nizhnekamsk (TU 2226-068-10480596-07) based on a mixture of polyether, catalysts, surfactants and water; Dow Izolan, Vladimir, Russia for the production of flexible polyurethane foam - PPUel, as well as the Apge component for the production of semi-rigid polyurethane foam.
- Component B for flexible polyurethane foam produced by Dow Izolan, Vladimir, Russia
- Chitosan - water-soluble chitosan (HV), acid-soluble chitosan (HC), Chitosan, Vietnam.

2.2. Methods

2.2.1. Determine the foaming technological parameters

The experiment of sorbent composition according to the technological flowsheet with free foaming was carried out in a 500ml beaker; determine the "start time" PUF (Tc, s) and "rise time" PUF (tp, s).

Determination of apparent density was carried out according to GOST 409-77.

2.2.2. Obtain sorbent

To obtain a petroleum sorbent, there are two methods as below:

The first method is to obtain a sorbent based on elastic PPU (PPUel) from component A (el) and component B for flexible polyurethane foam.

The second method is to obtain a sorbent based on semi-rigid PPU (PPUpr) from component A (r) and component B for flexible polyurethane foam.

There is an important factor for sorbents is buoyancy. Elastic foams have interconnected cells in their structure, which naturally contributes to the high absorption capacity. However, in a saturated state, they can lose buoyant property and sink, which adversely affects marine life. Rigid foams, in the other hand,
have a closed-cell structure, the cells in the foam are not communicated, so it is difficult for sorbate to penetrate into the foam, besides that, a sorbent retains its buoyant property in saturated state. Therefore, two types of sorbents were used, if PPUel tended to be “flooded,” PPUr would avoid this drawback.

Chitosan was used as filler in the amount of 20 and 50% by mass of the sum of components A and B. The ratio of components: A (el / r): B (el.) = 100: 60. After manufacturing the sorbent, it was crushed to a particle size of $D_u = 0.125 \text{ cm}^3$.

To determine the oil capacity, 50 ml of oil and a certain amount of sorbent were added to the plastic form. Oil capacity was determined by the mass difference of the saturated and initial sorbents through $1; 1.5; 2; 3; 5; 8; 10; 15; 20; 30; 60; 90$ and $120$ minutes in oil. For the oil intensity, the maximum saturation of the sorbent with oil was taken, when the oil intensity curve — the absorption time reached the plateau [14,15] according to the formula:

$$\text{oil capacity} = \frac{m_2-m_1}{m_1}$$  \hspace{1cm} (1)

Where: $m_1$ – dry sorbent mass; (g)
$m_2$ - sorbent mass after oil absorption through $1, 2 \ldots, 120$ minutes (g).

3. Results

3.1. Determination of foaming technological parameters.

| Sorbent  | $t_{s, c}$ | $t_{p, c}$ | Apparent density, kg / m$^3$ |
|----------|------------|------------|-----------------------------|
| PPUpr    | 30         | 116        | 0.0644                      |
| PPUpr - 20-HC | 32        | 121        | 0.6234                      |
| PPUpr -50-HC | 44        | 139        | 0.8380                      |
| PPUpr -20-HV | 29        | 198        | 0.0785                      |
| PPUpr -50-HV | 53        | 341        | 0.1182                      |
| PPUel    | 27         | 150        | 0.0591                      |
| PPUel -20- HC | 28       | 162        | 0.0930                      |
| PPUel -50-HC | 54        | 173        | 0.3656                      |
| PPUel -20-HV | 92        | 2075       | 0.1193                      |
| PPUel -50-HV | -         | -          | 0.3846                      |

It is seen that the temporal parameters of foaming depend both on the amount of filler, the type of PU foam and filler. Naturally, the more filler, the “harder” composition foamed. Both the “start time” and the “rise time” are lower in the case of foam filling is lower degree.

In addition, the “start time” of PPUel comes a little earlier than for PPUp sorbent. The dependence is similar for the “rise time” indicator. High temporal parameters of foaming compared to traditional – unfilled polyurethane foam – are due to the presence in composition of "heavy" filler with a large amount. The filler in large quantities makes the sorbent heavier. So in the case of unfilled PPU-sorbent, the density is lower than that of PPUel and PPUp with filler.

The indicator “start time” for the sorbent, PPUpr-50-HC comes a little earlier than for PPUpr-50-HV. The same pattern is observed for PPUel-20-HV and PPUel-20-HC. A similar pattern is observed for the indicator "time rise" foam. This result is reached probably due to the composition of chitosan.

It is obvious that HV’s structure components influence the process of foam formation. Indeed, chitosan contains methylol and hydroxyl groups capable of interacting with the isocyanate groups in the component B. Figure 1.
During the synthesis of polyurethane foam, there are series of reactions:

$$\text{OCN} - \text{R} - \text{NCO} + \text{HO} - \text{OH} \rightarrow \text{O} - \text{C} - \text{NH} - \text{R} -$$  \hspace{1cm} (1)

$$-\text{NCO} + \text{H}_2\text{O} \rightarrow -\text{NH}_2 + \text{CO}_2$$  \hspace{1cm} (2)

$$-\text{NCO} + -\text{NH}_2 \rightarrow -\text{NH} - \text{C} - \text{NH} -$$  \hspace{1cm} (3)

$$-\text{NH} - \text{C} - \text{NH} - + -\text{NCO} \rightarrow -\text{N} - \text{C} - \text{NH} - + -\text{NCO}$$  \hspace{1cm} (4)

$$-\text{O} - \text{C} - \text{NH} - + -\text{NCO} \rightarrow -\text{N} - \text{COO} -$$  \hspace{1cm} (5)

The main reaction is urethane formation between the hydroxyl-containing component (component A) and the isocyanate groups of the isocyanate component (component B) (reaction 1). Since water is present in component A, the isocyanate groups of component B will react with water to create carbon dioxide, which is a chemical foam blowing agent (reaction 2). In addition, the isocyanate groups of component B react with amines presented in component A to create urea groups (reaction 3), then, interacting with the isocyanate groups of component B, produce biuret groups (reaction 4). These components are responsible for branching and stitching polymer chains latter. Urethane groups formed by reaction 1, when interacting with the isocyanate groups of component B, according to reaction 5, create allophanate groups, as like as the biuret groups, cause branching and cross-linking of polymer chains. In the case of the prevalent reaction rate of polymer chains formation (reaction 1.3-5), the foaming process by reaction 2 is difficult or does not occur. In the case of the predominant interaction rate of isocyanate groups with water, the foam grows rapidly, but at a certain moment it coalesces without creating the polymer network. In order to equalize the speed of these reactions, catalysts are given into the PUF system, namely in component A, so that the elongation and cross-linking of the polymer chains occur simultaneously.

Water-soluble chitosan in the process of obtaining PPU may partially dissolve in the water of component A and is able to react with the isocyanate of component B, competing with the hydroxyl groups of component A. Thus, component B becomes insufficient for full foaming of the PPU composition.

For acid-soluble chitosan, this process is impossible due to its water resistance.

3.2. The effect of exposure time on its oil capacity
From the shown in Figures 3 and 4, it is clear that in the first 15-20 minutes there is a rapid absorption of oil for all sorbents. After 30 minutes the sorption PPUel reaches an equilibrium state. The balance of sorption PPUpr is achieved in 60 minutes.

The most effective among PPUel is PPUel-20-HC sorbent. Its absorption capacity in relation to oil is ~ 12.65 g / g. Figure 3

Among the sorbents PPUpr the most effective is PPUpr-50-HC sorbent. Its absorption capacity in relation to oil is ~ 6.12 g / g. Figure 2

When comparing chitosan HC and HV, it was found that chitosan, soluble in acid, has a greater oil capacity than chitosan, which is soluble in water.

Both types of sorbent retain their buoyancy in the saturated state.

4. Conclusions

Thus, an effective sorbent is the one based on flexible polyurethane foam, filled with 20% by mass of chitosan, soluble in acid. Its absorption capacity in relation to oil is ~ 12.65 g / g. The advantages of this sorbent are that it has a high rate of retrieval per litre of absorbed oil, does not sink even in saturated state, has a high sorption rate (90% absorption in 15-20 minutes), easy to operate, allows to remove the absorbed substance, non-toxic, be manufactured on the basis of available renewable materials.

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