Technologies for elimination of chemical hazards

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Hydrophobization of oil sorbent based on chitin and polyurethane foam

Tran Y Doan Trang✉, and Liubov A. Zenitova

Kazan National Research Technological University, Kazan, Russia,
e-mail: tydtrang@gmail.com

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Abstract – The rapidly-growing increase in the events of oil spills in the water environment motivates researchers to the fast development of oil sorbents. The oil pollution removal process requires a highly hydrophobic sorption material with suitable oil capacity. This study presents the results of preparing oil sorption material (PPU10C-SA) with improved hydrophobicity which is based on polyurethane foam and chitin sorbent (PPU10C) by impregnating it with the stearic acid (SA) solution. The influence of the impregnation time and concentration of SA on its content in the resulted sorbent and on its sorption capacity in relation to oil and water is studied. It is shown that the optimal conditions for obtaining the improved hydrophobized material are as follows: the concentration of SA – 0.01 g/ml and the impregnation time – 60 min. In this case, the oil capacity of the material reaches 12.54 g/g along with the water capacity of 1.44 g/g. Thus, the hydrophobicity of the modified sorbent has been increased 4 times in comparison with that of the unmodified material. The obtained results indicate that the SA-modified PPU10C-SA oil sorbent can be a promising sorbent for efficient water purification from spills of oil and oil products.

Keywords: polyurethane foam, chitin, stearic acid, hydrophobicity, oil sorption, oil pollution.

Технологии ликвидации источников химической опасности

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Гидрофобизация сорбента для нефти на основе хитина и пенополиуретана

Ч. И. Д. Чанг✉, Л. А. Зенитова

Казанский национальный исследовательский технологический университет, г. Казань, Россия, e-mail: tydtrang@gmail.com

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Аннотация – Быстрый рост случаев разливов нефти и нефтепродуктов, ведущих к загрязнению водных объектов, мотивирует быструю разработку сорбционных материалов для очистки воды от нефтяных загрязнений. Для эффективного удаления нефтяных загрязнений необходим высоко гидрофобный материал с хорошей нефтеемкостью. В данном исследовании предпринята попытка увеличить гидрофобность сорбционного материала на основе пенополиуретана и хитина (PPU10C) путем его пропитки раствором стеариновой кислоты (СК) с получением гидрофобизированного сорбента (PPU10C-SA). Исследовано влияние времени обработки и концентрации СК на ее содержание в конечном сорбционном материале и на его сорбционную способность по отношению к нефти и воде. Показано, что оптимальные условия для получения гидрофобного материала следующие: концентрация СК – 0,01 г/мл и время обработки 60 мин. При этом нефтеемкость материала достигает 12,54 г/г, а водоемкость составляет 1,44 г/г. Таким образом, гидрофобность модифицированного сорбционного материала увеличена в 4 раза по сравнению с немодифицированным материалом. Полученные результаты свидетельствуют о том, что сорбционный материал, модифицированный стеариновой кислотой, является перспективным сорбентом для эффективной очистки водных сред от их загрязнения нефтью и нефтепродуктами.

Ключевые слова: пенополиуретан, хитин, кислота стеариновая, гидрофобность, сорбция нефти, нефтяное загрязнение.

INTRODUCTION

In recent years, the water pollution caused by oil and its derivatives is increasing rapidly and has become a global challenge [1]. Meanwhile, the impact of oil pollution in the aqueous environment is extremely detrimental, since it leads to biological death of living organisms, changes in entire ecological structure, negatively affects the waterway traffic, tourism, etc. [2–5]. And what is the most serious thing, oil pollution is considered as one of the main causes of cancer, allergies, respiratory and digestive diseases in humans [6]. Therefore, the purification of water environment from oil and oil products is urgently needed [7].

Currently, various methods have been developed to remove oil pollution from water environment. In particular, the use of various types of sorbents is considered to be one of the most potent methods due to its simplicity and effectiveness [8, 9]. Recently, the combined sorbent PPU10C based on the natural polymer – chitin and polyurethane foam (PPU) has been designed as one of the sorption materials providing an effective treatment of water environments from oil pollution. It has been shown that this material has many advantages, such as high oil sorption capacity and high degree of the adsorbed oil recovery, buoyancy, reusability, applicability to various water environments, cost-effectiveness, and environmental friendliness [9–12]. However, this material has a shortcoming such as insufficient hydrophobicity. When tested in conditions of oil spills in the form of a thin layer on water, the PPU10C absorbs not only oil but also water in relatively noticeable extent. This material has a high-water sorption in a saturated state, quickly loses its buoyancy, gravitates to the bottom, and also contributes to the unwanted desorption of the adsorbed oil back into the aqueous environment. In this regard, it is necessary to increase the hydrophobicity of this sorbent.

Currently, the hydrophobicity of the PPU-based sorbent materials has been improved using a variety of known methods such as sol-gel method [13], grafting the hydrophobic molecules [14, 15], or immobilization of micro- and nanoparticles on the surface of the material [16–20]. In particular, the grafting of hydrophobic molecules on the surface of the material by impregnation method is considered to be a simpler and more economical approach than other methods [21].

Stearic acid (SA) is one of the most popular hydrophobic materials which is widely used in polymer technology. Because of the long hydrocarbon chain in its molecule, stearic acid is known as the high hydrophobic fatty acid [22]. In many studies, stearic acid has been used to improve the hydrophobicity of materials by attaching nanoparticles to the surface of the material [18–20]. However, the cost of obtaining nanoparticles is quite expensive. Moreover, the process of attaching nanoparticles to the material surface is not simple. Recently, a surface coating by stearic acid without nanoparticles has been studied for such materials as cotton [23], cellulose fibers [24], and stainless steel [25]. The results show that the hydrophobicity of the modified materials is significantly improved in comparison to the original materials. In addition, coating the surface of the material with stearic acid by impregnation is the simplest and cost-effective method [21].

The aim of this work is to increase the hydrophobicity of the oil sorbent PPU10C (based on chitin and PPU) by the sorbent coating with SA using an impregnation procedure. The influence of the concentration of the used SA and the impregnation time on the oil capacity and water capacity of the sorbent is to be investigated and the optimal parameters of the hydrophobization process with the impregnation mixture are planned to be studied.

MATERIALS AND METHODS

Materials

The procedure for preparation of the PPU10C sorbent and characterization of its properties are described in our previous study [10].

Stearic acid (CAS number 54-11-4, purity grade > 98%, Alfa-Service, LLC, Kazan, Russia) – white solid, density – 0.9408 g/cm^3 (20°C), molecular mass – 284.484 g/mol.

Isopropanol (purity ≥ 99.7%, Khimprom, Russia) – transparent, molecular mass – 60.09 g/mol, melting point – 82.4°C, density – 0.7851 g/cm^3, dynamic viscosity – 0.00243 Pa·s.

Oil (Nurlat region, Tatarstan, Russia) density – 0.931 g/cm^3, dynamic viscosity – 7.8 mPa·s.

Synthesis of hydrophobized sorbent PPU10C-SA

*Preparation of the starting sorbent PPU10C***.** PPU10C containing the natural filler – chitin in an amount of 10% mass. was obtained according to the technological scheme described in [10, 11]. The obtained PPU10C is used in the form of cubes with the mean size of 1 cm x 1 cm x 1 cm.

*Preparation of hydrophobizing liquid***.** Hydrophobizing liquid with the concentration of 0.005; 0.01; 0.025; 0.05 and 0.1 g/ml is prepared by dissolving stearic acid in isopropanol at the temperature 50–55°C.

*Preparation of the hydrophobized sorbent PPU10C-SA***.** The fresly prepared material PPU10C is immersed in the hydrophobizing liquid so that the liquid covers the entire volume of cubes. The impregnation time was 5, 15, 30, 60, 90, and 120 min. Then, the sorbents are removed from the hydropholizing liquid and the sorbent is dried at the ambient temperature within 24 h. The dried material is used for the determination of its sorption capacity.

Sorption capacity determination procedure

The determination of the oil and water sorption capacity of the obtained materials is carried out by using the mass method [11]. Approximately 0.1–0.2 g of the adsorbent is added into the beaker containing 30 ml of oil or 30 ml of water. After the sorption process, materials are removed and weighted.

The amount of the adsorbed oil or absorbed water is determined by the mass method according to the difference of the mass sorbent before and after sorption. The sorption capacity is calculated as the ratio between the mass of the adsorbed oil or water and the mass of the initial sorbent.

RESULTS AND DISSCUSSIONS

Preparation of hydrophobized PPU10C-SA

The mechanism of improving the hydrophobicity PPU10C is apparently based on the adhesion of SA molecules on capillary walls of the sorption material. The use of the movable hydrophobizing liquid containing SA allows acid molecules to easily enter into the capillary pores of the material. During the drying process, the isopropanol solvent evaporates, and the SA molecules are fixed on the surface of the material, creating the hydrophobic coating of stearic acid on the surface of the material (Fig. 1).

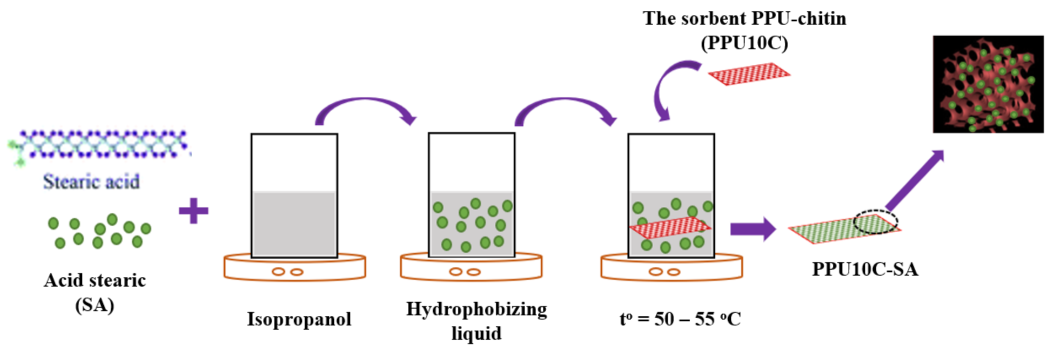

Fig. 1. Synthetic scheme for preparation of hydrophobized sorbent PPU10C-SA.

Effect of SA concentration on hydrophobicity of PPU10C-SA sorbent

The data in Table 1 show that increasing concentration of SA in the hydrophobizing liquid leads to an increase in the SA content in the obtained material.

Table 1. Effect of SA concentration on sorption capacity of obtained sorbent

Concentration of SA, g/ml	Content of SA,%	Oil capacity, g/g	Water capacity, g/g
0	0	13.13(*)	5.66(*)
0.005	5.06	12.85	2.92
0.010	6.67	12.54	1.44
0.025	22.11	11.31	1.12
0.050	34.13	9.22	0.81
0.100	35.03	7.83	0.63

(*) – results of the previous study [10]

For oil sorbents, the oil sorption capacity is one of the most important parameters. The results indicate that when increasing the concentration of SA from 0.005 g/ml to 0.01 g/ml, the oil adsorption capacity of the obtained materials practically does not change. The increase in the concentration of SA to 0.1 g/ml decreases the oil capacity of the material, since the SA molecules fill the pores and reduce their total volume [21]. Therefore, the entering of oil molecules in the capillary pores of the modified material is becoming limited. Eventually, it leads to a reduction in the oil sorption capacity. So, the oil sorption capacity of the obtained sorption material is inversely proportional to the SA content in it (Fig. 2).

To evaluate the hydrophobicity of the modified material, its water sorption capacity has been studied. The data in Fig. 2 and Table 1 show that the use of low concentrations of SA leads to incomplete filling of the surface with molecules SA to create the hydrophobic coating. Consequently, the lower the SA concentration, the higher the water capacity of the material.

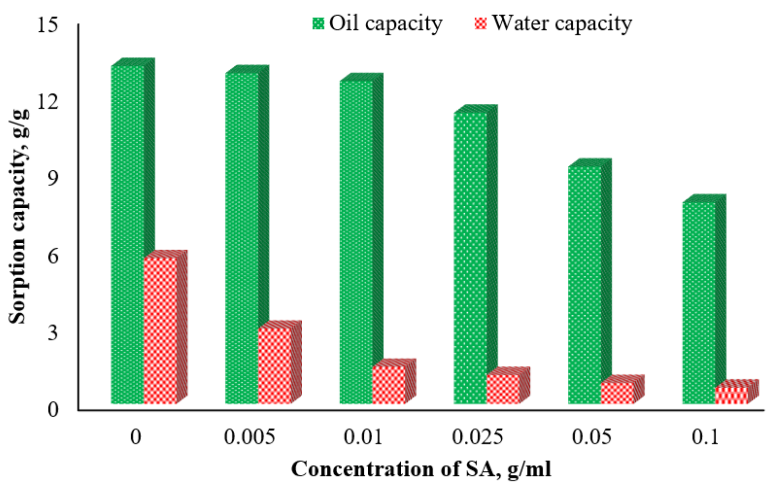

Fig. 2. Effect of SA concentration on oil and water sorption capacity of PPU10C-SA.

The evaluation of the parameters of water capacity and oil capacity shows that despite the fact that the material when impregnated with SA at 0.005 g/ml has the high oil capacity, at the same time its water absorption is also quite significant. Meanwhile, the material when impregnated with SA at 0.01 g/ml has the oil capacity close to the modified material in the concentration of SA 0.005 g/ml. At the same time, its water uptake is significantly reduced. So, the optimal concentration of SA in the hydrophobizing liquid 0.01 g/ml.

Effect of impregnation time on hydrophobicity of PPU10C-SA sorbent

It is obvious that the longer the impregnation time of the material in the hydrophobizing liquid, the higher will be the content of SA that covers the sorbent surface (See Table 2). However, the significant increase in SA content the surface of the sorbent occurs within the first 60 min of the immersion process. After 60 min of contact with the hydrophobizing liquid, no significant difference is observed in the SA content on the material surface.

The increase in the impregnation time results in an increase in the content of SA on the material surface. The sorption capacity of the impregnated material with respect to both oil and water decreases (Fig. 3). It has been found that with an impregnation time of 60 min, the obtained material has oil sorption values comparable to those corresponding to the shorter impregnation time, but significantly higher than that with a longer impregnation time. At the same time, the water capacity of the material with the impregnation time of 60 min is significantly reduced and is practically comparable to higher values of the impregnation time.

Table 2. Effect of PPU10C impregnation time on sorption capacity of obtained sorbents

Impregnation time, min	Content of SA,%	Oil capacity, g/g	Water capacity, g/g
0	0	13.13(*)	5.66(*)
5	1.79	13.10	5.06
15	2.19	12.79	3.22
30	5.93	12.61	2.17
60	6.67	12.54	1.44
90	6.76	10.84	1.30
120	6.83	10.29	1.19

(*) – results of the previous study [10]

Thus, the optimal immersion time for obtaining the hydrophobized sorbent is 60 min.

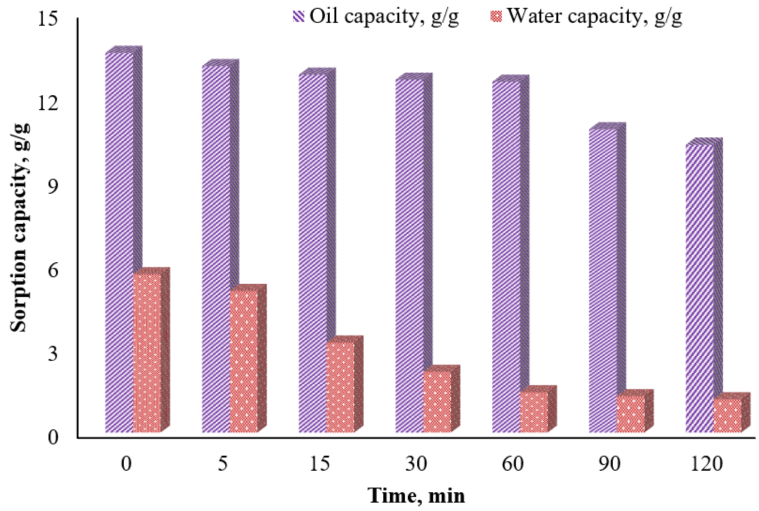

Fig. 3. Effect of impregnatiom time on oil and water sorption capacity of PPU10C-SA.

At the same time, the oil sorption capacity of the obtained material reaches 12.54 g/g, and the water capacity – 1.44 g/g. Thus, the hydrophobicity of the modified sorbent has been improved 4 times compared to that of the non-modified PPU10C material.

CONSLUSIONS

The hydrophobization of the oil sorbent based on chitin and polyurethane foam (PPU10C) by modifying it with stearic acid has been studied. The method for obtaining hydrophobized oil sorbent (PPU10C-SA) has been developed. The effect of the concentration of stearic acid in the composition of the hydrophobizing liquid along with the effect of the impregnation time on the SA content in the obtained materials and their oil uptake and water uptake are evaluated. The optimal conditions for obtaining the hydrophobized material are the following: concentration of stearic acid – 0.01 g/ml and the impregnation time – 60 min. The oil sorption capacity of the obtained optimized sorbent reaches 12.54 g/g with the simultaneous 4-fold decrease in its water sorption capacity (1.44 g/g) compared to that of the original material PPU10C. Thus, the stearic acid modified sorbent can be considered as a promising hydrophobic material for use in water purification from spills of oil and oil products.

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