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Removal of oil from water using polyurethane foam modified with nanoclay

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HIGHLIGHTS

- Nanocomposite of polyurethane foam with nanoclay was used as a novel oil sorbent.
- Different amounts of nanoclay in the foam were used to optimize its performance.
- Removal capacity and efficiency were improved up to 16% and 56%, respectively.
- Reusability feature of the prepared sorbent was investigated.

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ABSTRACT

To enhance the removal of oil contaminants from water, polyurethane foam structure was modified by integrating cloisite 20A nanoclay into it. Pure and modified polyurethane foams (nanocomposite adsorbents) were then characterized using scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy tests. Optimum weight fraction of the added cloisite 20A to the foam structure was 3 wt%, improving the sorption capacity up to 16% and oil removal efficiency up to 56% in water–oil system. The reusability feature of blank polyurethane and nanocomposites with 3 wt% and 4 wt% of cloisite 20A nanoclay was studied through chemical regeneration by toluene and petroleum ether. In the case of structurally modified polyurethane foams with nanoclay (nanocomposites), chemical regeneration reduced the oil removal efficiency, but improved the adsorption capacity in the range of low to medium oil initial concentration and reduced it in high oil initial concentrations. A comparison between the obtained adsorption data and adsorption isotherm models, including Langmuir, Freundlich and Redlich–Peterson, showed a good agreement with Langmuir and Redlich–Peterson models.

1. Introduction

Oil discharge into the natural environment and aquatic ecosystems can cause serious global, ecological, and environmental problems [1]. Industrial development has increased oily wastewater discharge to the environment [2]. Petroleum transportation with a yearly average of about 5 million tons across seas poses a great risk of pollution to the marine ecosystem [3]. Oil industry, especially oil refining processes and transport, has a major role in this problem. However, increasing oil consumption and establishing more refineries near the cities and populated regions have caused severe pollution in the underground and surface waters [4]. Oily contaminants in polluted water may be detected in different forms like fats, lubricants, cutting liquids, heavy hydrocarbons (tars, grease, crude oils and diesel oil), and light hydrocarbons (kerosene, jet fuel and gasoline) [2]. So, the removal of in situ oil and other types of organic pollutants is crucial to prevent them from migrating and to reduce their disastrous effects on the ecosystem [1].

Different techniques have been developed for the removal of oil contaminants from water. They are classified into chemical, biological and physical methods [5]. These include different types of filters [6], chemical dosing, reverse osmosis [7], gravity separation [8], ultra-filtration [9], micro-filtration [10], biological processes [10], air flotation [11], membrane bioreactor [12], chemical coagulation, electrocoagulation and electroflotation [13]. Adsorption is among the most profitable methods for the removal of oil contaminants as it can effectively remove or recover oil from the water [14].

Oil sorbents are divided into three basic types: natural organic, natural inorganic and synthetic adsorbents [15]. Some examples of natural sorbents used for the adsorption of oil are sugar cane bagasse [16], vegetable fibers [17], sawdust bed [18], bentonite, chitosan, activated carbon [19], vermiculite [20], chrome shavings

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[21] and peat [22]. Synthetic sorbents used for oil contaminants adsorption include rubber powder [23], expanded perlite [24], polymeric material based on butyl rubber [25], high-silica zeolites [26], carbonized pith bagasse [27], wool-based nonwoven [28], hydrophobic aerogels [29], acetylated rice straw [30], exfoliated graphite [31], inorgano clays [32], polypropylene [33] and oleophilic polyurethane foams [34].

Polyurethane (PU) in the form of foam provides a large specific area and enough space for adsorption. Polyurethane foams (PUFs) have shown the noticeable capability of oil adsorption due to their special features such as low density, open-cell, high porosity, and industrial production. Nanoclay is one of the possible materials that can modify the polyurethane foam structure. The presence of cloisite 20A nanoclay in the structure of PUF has been found to enhance the foam strength [35] and open its cells [36]. Furthermore, nanoclay itself is an oil adsorbent, but it needs structural modification.

The main objective of this study is to investigate the effect of cloisite 20A nanoclay presence within the PU foam structure on the removal efficiency of oil. The effect of chemical regeneration of the foam and its performance are also investigated. The isotherm of the oil adsorption is also studied using this sorbent.

2. Materials and methods

2.1. Materials

NIXOL AM-313 polyether polyol was provided from KPX chemical CO. (South Korea) and methylene diphenyl diisocyanate (MDI) was obtained from Daeyang International CO. (South Korea). 1,1-Dichoro-1-fluoroethane (HCFC 141b) was purchased from Liñan E-COOL Refrigeration Equipment CO. (China). Cloisite 20A nanoclay was purchased from Sigma Aldrich (USA). Light crude oil was obtained from Isfahan refinery feed stream (Iran). Toluene and Xylene were supplied by Isfahan petrochemical complex (Iran) and petroleum ether with the boiling range of 30–60 °C was obtained from Pars Chemie Co. (Iran).

2.2. Synthesis of polyurethane foams

Deionized water was used as the chemical foaming agent while HCFC 141b was used as the physical foaming agent. For the synthesis of open-cell PUF, at first, 10 g of polyol was fully mixed with 0.1 g of deionized water and 1 g of HCFC 141b. Then, 4 g of MDI was added to the homogeneous mixture from the previous step, and it was completely mixed using a mixer at 1000 rpm. Immediately after mixing, the mixer blade was taken out and the final mixture was left for 30 min to provide enough time for the foaming reaction. It should be noted that the amount of added MDI to a definite quantity of polyol depends on the stoichiometric reaction, but because of the net structure of polyol, this amount is higher than that required by the stoichiometry. The whole procedure was performed under ambient temperature (22 ± 3 °C).

2.3. Synthesis of nanocomposite

For the synthesis of nanoclay-polyurethane foam (NCPUf) naonocomposite, nanoclay (NC) should be completely dispersed in the polymeric structure in order to obtain nanostructured foam based on nanoclay and polyurethane foam where polymeric chains diffuse into the silicate layers of nanoclay. Nanoclay was dried in an oven under the temperature of 100 °C for 24 h, and then mixed with polyol by means of a mixer at 1000 rpm for 24 h. Then, the obtained mixture was mixed by an ultrasonic for 25 min (by 10 min rest between each 5 min), and again the mixture was mixed by a mixer at 1000 rpm for 2 h. After that, the foaming agents including 1 wt% deionized water and 5 wt% HCFC 141b were added while mixing to have a homogeneous mixture and then 35 wt% MDI was immediately added and was mixed for 20 s. At the end, the final mixture was left for 30 min to provide enough time for the foaming reaction. Synthesized foam was cut into 1-cm^3 cubes to be used in the sorption experiments.

2.4. Adsorption determination method

The method developed for the measurement of oil and water sorption capacity of the sorbent was based on the Standard Test Method for sorbent performance of adsorbents (ASTM F726-99). All of the sorption experiments were performed in water–oil system with different initial weight of oil. In water–oil system test, crude oil was poured into a 600 ml beaker containing 250 ml of deionized water with the thickness of oil layer being about 2–4 mm. Then, 1.0 g of the adsorbent cubes was added to the system and the beaker was placed on a shaker at 100 rpm for 5 min ± 20 s. The content of the beaker was allowed to settle for a period of 2 min. Then, adsorbent cubes were removed and put into glass beaker using forceps and weighted accurately using balance to determine the total weight of adsorbed oil and water. Weight of the adsorbed water was determined according to the Standard Test Method for Water in Crude Oil by Distillation (ASTM D4006). Adsorbent cubes after the sorption stage, were completely washed by 400 ml of xylene to extract the adsorbed oil and water. Then, the extracted mixture was boiled in an azeotropic distillation apparatus, and distilled water was collected in a trap connected to the distillation apparatus. Finally, the collected water was weighted to determine the adsorbed water. Finally, the oil sorption capacity of the sorbent was calculated using the following equation:

$$S = \frac{S_s - S_w - S_0}{S_0} \tag{1}$$

where S is the oil sorption capacity (g/g), S_s is the weight of saturated sorbent (water + oil + sorbent), S_w is the weight of adsorbed water (g) and S_0 is the initial dry weight of sorbent (g). Oil adsorption percentage of sorbent was determined by the following equation:

$$P_a = \frac{O_a}{O_t} \times 100 \tag{2}$$

where P_a is the oil sorption percentage (oil removal percentage), O_a is the weight of adsorbed oil (g) and O_t is the initial weight of oil (g).

Oil removal efficiency of the sorbent is defined as the ratio of adsorbed oil to the total weight of adsorbed materials. It is calculated by the following equation:

$$R = \frac{M_o}{M_t} \tag{3}$$

where R is the oil removal efficiency, M_o is the weight of adsorbed oil (g) and M_t is the total weight of adsorbed materials. All of the tests were performed at ambient temperature (22 ± 3 °C) and in duplicate. If the value of any results deviated over 15% from the arithmetic mean of the two runs, the sample data would be rejected and the test would be repeated.

2.5. Adsorbent regeneration method

Regeneration of the adsorbents was performed through chemical regeneration method. Toluene and petroleum ether were used for this purpose. To do this, the used adsorbents were immersed in 150 ml of toluene in a 250 ml beaker and then mixed by a mixer. After that, adsorbent cubes were taken out and washed by