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IMPROVING HYDROPHOBICITY OF NATURAL OIL SORBENTS BY MODIFICATION METHODS

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Abstract. Among the existing techniques for the removal of oil from water, the use of sorbents is generally considered to be one of the most efficient. Hydrophobicity (oleophilicity) is one of the major determinants of sorbents' properties influencing the effectiveness of oil sorption in the presence of water. In order to improve these properties, the surface of the sorbent is modified using chemical or physical treatment methods. The purpose of this study is to analyse sorbent modification methods in order to increase their hydrophobic-oleophilic characteristics for the clean-up of oil spills taking into account environmental aspects. In this research a natural organic sorbent – moss – was treated with hot water (80 °C and 100 °C), mercerized, coated with oil and oil in water emulsions with concentrations at 10% and 50%. The test of water sorption capacity was performed to compare the hydrophobic properties of modified sorbents. The results of this research demonstrate the potential of natural organic sorbents in oil spill abatement. Hot water and alkali treatments can alter the surface characteristics of plant fibers and improve absorption capacity. Sorbent coating with plant triglycerides in low concentrations of oil can be applied in order to use the modified sorbent in areas where oil is spilled into the water in small amounts due to increased water resistance and lower product absorption properties. Treating water in 80 °C can be chosen for economic purposes. Sorbents treated this way could be used to clean oil spillages not from the water surfaces, but from soil and other solid surfaces.

Keywords: oil spills clean-up, sorption, oil sorbent, organic sorbent, hydrophobicity, sorbent modification methods, environmentally friendly modification methods.

Introduction

Despite the positive development of gas and oil industry in this last decade, there are still negative side effects. One of the most popular ways of transportation of oil and petroleum products is water transport and the adverse effect of this progress in industry is oil spills. Oil spill is an accidental or intentional release of oil into water, as from a simple shipping boat, tanker, underwater pipeline or an offshore drilling rig. The world is facing a large-scale environmental problem and great attention is currently given to research of sorbent usage for oil and petroleum products spills.

The fact that natural organic fibers are cheap and available in abundance, being low density and biodegradable, has motivated many scientists to explore their potential application in different industrial sectors. After all, natural organic sorbents have some limitations like poor fire resistance, low buoyancy and one of the most crucial is high moisture absorption. While cleaning water from oil products, sorbents not only sorb the oil, but also the water.

Hydrophobicity (oleophilicity) is one of the most important characteristics which determines the efficiency of the sorbent. Hydrophobic–oleophilic properties are determined by factors such as the physical configuration and surface roughness of the fiber, porosity, the amount of the surface wax, the chemical constituent of the sorbent, the crimps and the twists. This characteristic depends on the concentration, specific gravity, temperature and the amount of the oil (Abdullah, Rahmah, & Man, 2010; Hasanzadeh, 2014).

Plant based natural organic fibers are lignocellulosic in nature and are composed of cellulose, hemicelluloses, lignin, pectin and waxy substances. The cellulose structure of the fibers is distinguished through crystalline and amorphous regions. Large numbers of strong intramolecular hydrogen bonds are formed in the crystallite region. Cellulose provides strength, stiffness and structural stability of the fiber. This creates a cellulose block and makes it difficult for other chemical penetrations. Nonetheless, oils are absorbed easily by the amorphous region. The hydrophilic hydroxyl groups (OH) are present between the macromolecules in the fiber cell wall and when moisture comes into contact with the fiber, the hydrogen bond breaks and OH groups form new hydrogen bonds with water molecules. Hemicellulose, lignin, pectin and waxy substances do normally hold these water molecules and the cross section of the fiber becomes the main access for water penetration. This makes a sorbent hydrophilic. When hydrophilicity of a sorbent decreases, oleophilicity increases simultaneously. The moisture absorption of fibers can be reduced by eliminating hydrophilic hydroxyl groups (OH) from the fiber structure through different treatments (Kabir, Wang, Lau, & Cardona, 2012; Madsen, 2004; Sidik et al., 2012).

Surface modification of sorbents can be carried out by a number of methods using physical and chemical modification. The main routes of direct cellulose modification in the preparation of sorbent materials are esterification, etherification, halogenations, oxidation, alkali, surfactant treatment, mercerization, acetylation, benzoylation, peroxide and coupling agents with or without heat are widely applied to modify the surface of fibers. Physical modification such as pyrolysis is used.

Although these hydrophobizing treatments are efficient, acceptable in various applications and implemented at the industrial scale, they have a negative side to them. Physical treatment methods demand a lot of time and are costly. The appropriate handling and disposal of the large amounts of hazardous chemicals that are often necessary for sorbent utilization is unattractive and incurs additional cost to the production. For that reason, surface modification of sorbents using chemical treatments can be avoided by alternative methods (Kalia, Thakur, Celli, Kiechel, & Schauer, 2013).

Environmentally friendlier methods are an excellent alternative for this. An increasing interest has been noticed in the functionalization based on eco-friendly and biodegradable reagents. While using natural and eco-friendly sorbents, improvement of their properties using eco-friendly techniques should be considered.

Methodology

For this investigation a natural organic sorbent – moss – is used to evaluate the water sorption capacity. The sorbent was treated with different solvents in order to improve its hydrophobic properties. Before use all impurities and visible lumps found in the sorbent were manually removed. Moss was grounded using a blender into 3–10 mm parts. The mix of these parts (3–10 mm) of moss was used for the experiments. The sorbent was treated with an alkaline solution, such as NaOH (5%), hot water (80 °C and 100 °C), coated with oil and oil in water emulsions with concentrations at 10% and 50%. Untreated and treated samples were air dried and then dried in the oven at 110 °C till they reached constant weight. After the treatment sorbents were placed in dry zipped bags for the water sorption capacity test.

Water sorption capacity test

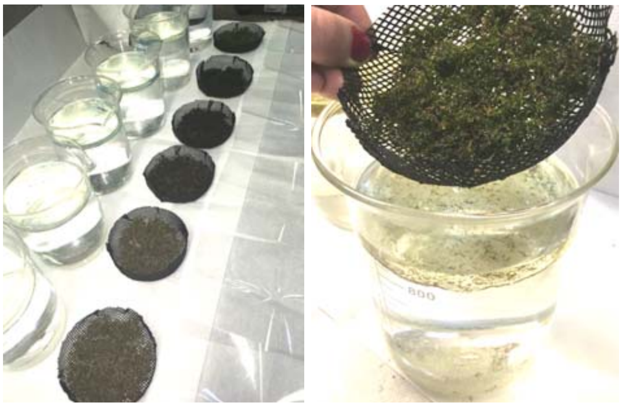
The ASTM F716-09 and ASTM F726-12 standards have been developed for absorbent/adsorbent performance and uptake capacity testing. However, most researchers do not use the procedures proposed by the ASTM when reporting their findings. Currently, the majority of the manuscripts published on oil sorbent testing do not use any uniform standard. ASTM standards have some shortcomings that make them unattractive for researchers to use.

Water sorption experiments can be done according to the Standard Test Method for Sorbent Performance of Adsorbents (ASTM F726-12). According to the method, unconsolidated and loose particulate form sorbents are classified as Type II sorbents. Water sorption experiments recommended for type II sorbents are a 15 min short test and a 24 h long test. According to the 15 min short test, at least 1 g of a sample should be weighed and put in the mesh basket and then lowered into the test cell (borosilicate 19 cm diameter, 10 cm depth) full of water. After 15 min ± 20 s, the basket should be removed and drained for 30±3 s (2 min ± 3 s for heavy oils).

Water and oil sorption capacity can be measured by hanging reading scales, top loading balances with a hook, or with normal bench top scales. First, the dry sorbent is weighed and placed in a net. Then, the net holding the sorbent is submerged into the liquid and allowed to stay for a set period of time. Next, the net is removed from the liquid and allowed to drain. Finally, after the excess liquid has been drained, the uptake capacity of the sorbent is calculated.

ASTM F726-12 is the basic method used by the researchers. Various contact times (1–1440 min), dripping times (10 s to 5 min) and sorbent dosages (0.1–10 g) were reported (Abdelwahab, 2014; Annunciado, Sydenstricker, & Amico, 2005; Wang & Zheng, 2012).

In this research water sorption capacity test is made according to the Standard Test Method for Sorbent Performance of Adsorbents (ASTM F726-12). Loose moss parts (size 3–10 mm) were packed inside a wire-mesh basket and immersed inside a beaker filled with water (Figure 1a). During a water sorption capacity test, a beaker was filled with 800 ml of DO water. The weight of sorbent after treatment was different due to different treatments; however, the amount of sorbents used was chosen by visible determination, i.e. it had to cover the surface area inside the beaker with liquid, not taking mass into account. The mesh with the sorbent was taken out from the beaker after 1 h, excess liquid was removed by keeping the mesh with the sorbent above the beaker for 2 min (Figure 1b). The experiment was repeated three times.



a b

Figure 1. Water sorption capacity test: a – beakers filled with liquid and sorbent with the mesh; b – excess liquid elimination

Water absorbency is the amount of liquid absorbed by 1 g of sorbent (Eq. (1)).

$$M_{H20} = \frac{(M_1 - M_2)}{M_S} \qquad (1)$$

where: M_{H20} – water absorption, g/g; M_1 – weight of the beaker with the liquid before immersion of the mesh with sorbent, g; M_2 – weight of the beaker with the liquid after immersion of the mesh with sorbent, g; M_S – weight of the sorbent, g.

The uptake capacity is referred to as the absorbency ratio, and is reported as the mass of liquid absorbed per mass of sorbent (g/g).

Water/oil absorbency tests were made in the ambient room temperature (20±2 °C). For oil sorption test diesel was used. Diesel density at 20 °C is 0.826 g/cm^3 and viscosity – 4.46 cSt. DO water density and viscosity at 20 °C is 0.998 g/cm^3 and 1.002 cSt respectively.

Results and Discussion

In order to compare the properties of untreated and treated sorbent, water sorption test was performed. In this research 7 sorbent samples were investigated. Samples are named depending on the treatment of the sorbent:

- hot water treatment at 100 °C (HW100);
- hot water treatment at 80 °C (HW80);
- coating with oil using oil-water emulsion, 10% concentration (Oil10);
- coating with oil using oil-water emulsion, 50% concentration (Oil50);
- coating with oil without water (Oil);
- mercerization (NaOH);
- untreated sorbent (Untreated).

Water sorption capacity test

Water sorption capacity test was performed with all the samples using DO water. Using the ASTM F726-12 method, water sorption capacity of each type of the sorbent was investigated and the results are shown in the table below, where M_1 is the amount of water absorbed by the sorbent mass, g; M_S – weight of the sorbent, g; M_{H20} is water absorption, g water/g sorbent. Values are shown as the mean ± standard deviation.

Table 1. Water sorption capacity of treated sorbent by type of treatment

Sorbent treatment type	M_S, g	M_1, g	M_{H20}, g/g
HW100	0.81	14.72	18.39±0.43
HW80	0.71	11.36	16.13±0.09
Oil10	2.05	12.36	6.03±0.10
Oil50	4.01	11.53	2.88±0.11
Oil	3.74	9.29	2.49±0.11
NaOH	0.81	11.09	13.53±0.05
Untreated	0.76	11.00	14.54±0.14

As seen from Table 1, the amount of water absorbed by the sorbent is lowest when moss is coated with oil. Coating with oil increased the hydrophobicity of the investigated sorbent. It can be noted that as the amount of oil on the sorbent surface increases, its water resistance increases. Coating the sorbent with oil at 10% and at 50% concentrations reduced its water sorption by 58.5% and by 80.2% respectively. The delivery of oil onto the surface of moss in the non-aqueous emulsion increased the resistance to water by 82.9%. Moss has a large surface area because its structure consists of a lot of fine hair. Oil filling and covering the surface of the moss and its pores prevents water from penetrating into the sorbent.

Accumulation of moss can store water, since both living and dead plants can hold large quantities of water inside their cells – up to 16–26 times as much water as their dry weight, depending on the species (Bold, 1967). Because of this property, 1 g of unmodified sorbent absorbed high amount of water – 14.54 g. Mercerization of the sorbent decreased water absorption by almost 7%. Researchers have treated cellulose fibers with alkali in different concentrations and even at low NaOH concentrations fibres can fibrillate, resulting in a reduced fibre diameter which causes a decrease of the surface area (Wong, McGowan, Bajwa, & Bajwa, 2016). The effect of alkali on the cellulose component of fiber causes swelling; therefore, the natural crystalline structure of the cellulose I relaxes. The type of alkali and its concentration influences the degree of swelling and the degree of lattice transformation into cellulose II. Sodium oxide is commonly used because Na+ widens the smallest pores between the lattice planes for effective penetration. After removing the excess NaOH, a new Na-cellulose I lattice is formed. Meanwhile, the –OH groups of the cellulose are converted into ONa– groups. Cellulose is converted into a new crystalline structure, cellulose II, containing a lattice that is more stable than cellulose I (Weyenberg, Ruong, Vangrimde, & Verpoest, 2006).

While sorbent coating with oil and mercerization enhanced the hydrophobicity of moss, heating with water at 100 °C and 80 °C temperatures increased the hydrophilicity of sorbent. When the sorbent was modified in water at 100 °C, water sorption capacity increased by 26.5% compared with the untreated one. When the sorbent is heated at 80 °C, a less severe hydrophobicity decrease is observed – 10.9%. The external surface area of the fibers due to its swelling by immersion into hot water increases, making it more accessible to water. It also refers to the dissolving part of lignin included in the moss fibers (Amer, El-Maghraby, Malash, & Taha, 2007).

Water sorption of the treated sorbent was calculated taking into account its volume. Results are shown in Figure 2; values are shown as the mean ± standard deviation. Results of volumetric sorbent water capacity test differed from calculations according to its mass. Mercerization and coating with oil in water emulsions increased hydrophobic properties, thus coating the sorbent with oil in a non-aqueous emulsion increased water sorption.

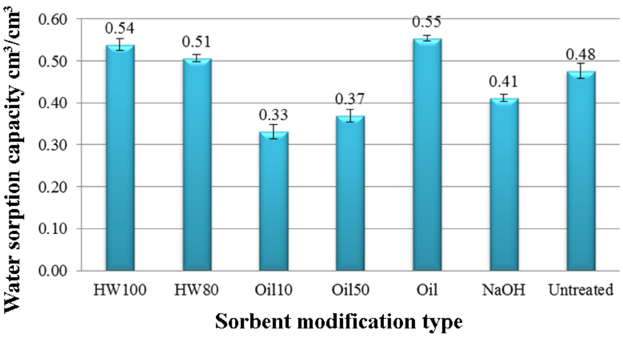


Figure 2. Graphical representation of volumetric water sorption capacity by treatment type

In conclusion, all the modifications carried out changed the water sorption properties of the investigated sorbent. Sorbent treatment with hot water reduced hydrophobicity. This could be explained by the fact that, as it has been mentioned in the literature, hot water modification process removes volatile compounds, extractives and waxy coatings from the cellulose surface, making it more accessible for the oil. Hot water also makes sorbent fibers swell, which increases the sorbent surface area. Due to these changes in the structure of the fiber, moss water sorption properties have increased. Therefore, oil uptake by the sorbent should increase in proportion to water uptake. The hot water treatment of fibers at 80 °C was more effective than at 100 °C. If the sorbent is used to clean oil products from the solid surfaces and not from the water surface, this environmentally friendly modification type can be used, because it can increase the surface area of the sorbent. Thus, treating the sorbent with 80 °C water is enough.

The oil coating on the sorbent surface has significantly improved its hydrophobicity. In this study the increase in the amount of oil coated on the sorbent resulted in the decrease in the water sorption capacity of the sorbent. The oil adheres to the surface of the sorbent and prevents the penetration of water, and the larger the area covered with oil, the lower the sorption capacity. Nevertheless, this method can also reduce the penetration of other liquids like petroleum products; however, this change in characteristics is not favorable in cleaning oil spills.

The chemical modification method – alkalization – resulted in enhanced hydrophobicity. Treatment of sorbent with alkali is a popular modification method used by scientists. Compared with the investigated environmentally friendly modification, the sorbent coated with oil showed better water resistance than the chemically treated sorbent – the sorbent treated with alkali absorbed

13.53 g/g and the one coated with oil absorbed only 2.49 g/g of water.

Sorbent coating with plant triglycerides in low concentrations of oil can also be applied. A sorbent modified this way could be used in areas where oil is spilled into water in small amounts due to increased water resistance and lower product absorption properties.

The results of volumetric sorbent water capacity differed from calculations according to its mass. In terms of water absorption by 1 cm^3 of sorbent, treatment with alkaline solution (NaOH, 5%) and with oil in water emulsions can enhance the hydrophobicity.

Conclusions

1. Coating with oil increased the hydrophobicity of the investigated sorbent. It can be noted that as the amount of oil on the sorbent surface increases, its water resistance increases. Delivery of oil on the surface of moss in the non-aqueous emulsion increased the resistance to water by 82.9%. Oil filling and covering on the surface of the moss and its pores prevents water from penetrating into the sorbent.

2. Mercerization of the sorbent decreased water absorption by almost 7%. The effect of alkali on the cellulose component of fiber causes swelling. Sodium oxide is commonly used because the –OH groups of the cellulose are converted into ONa– groups and it reduces hydrophilicity of the sorbent.

3. Heating with water at 100 °C and 80 °C temperatures decreased the hydrophobicity of the sorbent. The external surface area of the fibers increases due to its swelling when immersed in by hot water increases, making it more accessible to water. Therefore, oil uptake by this kind of way treated the sorbent treated this way should increase in proportion to water uptake.

4. Results of volumetric sorbent water capacity by differed from calculations according to its mass. In terms of water absorption by 1 cm^3 of sorbent, treatment with alkali and with oil in water emulsions can enhance hydrophobicity.

5. The results of this research demonstrate the potential of natural organic sorbents in oil spill abatement. Sorbent coating with plant triglycerides in low concentrations of oil can be applied and such modified sorbent could be used in areas where oil is spilled into water in small amounts due to increased water resistance and lower product absorption properties. Treating water in 80 °C can be chosen for economic purposes. Sorbents treated this way could be used to clean oil spillages not from the water surfaces but from soil and other solid surfaces.

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NATŪRALIŲ ORGANINIŲ SORBENTŲ SIEKIANT PAGERINTI JŲ HIDROFOBINES SAVYBES MODIFIKAVIMO METODAI

E. Anužytė, V. Vaišis

Santrauka

Tarp esamų naftos ir jos produktų valymo nuo vandens paviršiaus būdų, sorbentų naudojimas paprastai laikomas vienu iš efektyviausių. Hidrofobiškumas yra viena iš pagrindinių sorbento savybių, kuri nusako sorbento efektyvumą šalinant naftos produktus nuo vandens paviršiaus. Siekiant pagerinti hidorfobiškumą, sorbento paviršius gali būti modifikuojamas cheminiais ar fizikiniais metodais. Šio tyrimo tikslas – išanalizuoti sorbentų modifikavimo metodus, siekiant pagerinti jų hidrofobines-oleofilines savybes valant dyzeliną nuo vandens paviršiaus atsižvelgus į aplinkosauginius aspektus. Šiame tyrime natūralus organinis sorbentas – samanos buvo modifikuotas karštu vandeniu (80 °C ir 100 °C), merserizuotas, padengtas aliejumi ir aliejaus vandenyje emulsijomis (10 % ir 50 % koncentracijomis). Siekiant palyginti modifikuotų sorbentų hidrofobines savybes, buvo atliktas vandens maksimalios sorbcinės įgerties tyrimas. Šio tyrimo rezultatai rodo, kad sorbento paviršiaus veikimas šarmo tirpalu (NaOH 5 %) gali pagerinti jo hidrofobines savybes. Sorbento paviršiaus padengimas aliejaus vandenyje emulsijomis (10 % ir 50 % koncentracijomis) pagerina hidrofobines sorbento savybes, kartu mažindamos dyzelino įgertį. Modifikavimas karštu vandeniu (80 °C) didina sorbento paviršiaus plotą, o tai didina jo vandens ir naftos produktų sorbcinę gebą, todėl tokiu modifikavimo būdu gali būti apdoroti sorbentai, naudojami naftos produktams valyti iš dirvožemio arba kitų kietų paviršių.

Reikšminiai žodžiai: naftos produktų išsiliejimo valymas, sorbcija, natūralūs organiniai sorbentai, sorbentų modifikavimo būdai, hidrofobiškumas, aplinkai nekenksmingi sorbentų modifikavimo būdai.