MOKSLAS – LIETUVOS ATEITIS
SCIENCE – FUTURE OF LITHUANIA
ISSN 2029-2341 / eISSN 2029-2252
http://www.mla.vgtu.lt

APLINKOS APSAUGOS INŽINERIJA
ENVIRONMENTAL PROTECTION ENGINEERING

2016 8(4): 397–402

http://dx.doi.org/10.3846/mla.2016.947

INVESTIGATION OF HEMP WATER SORPTION CAPACITY

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Abstract. Effective clean-up of oil spills due to their negative environmental and economic impact is of capital importance. Clean-up of oil by sorption is considered one of the most desirable choices, because oil can be completely removed without causing any secondary pollution. Natural organic sorbents had been investigated and developed to control oil products' spills. Plant biomass is a renewable resource which can be converted into various materials and energy. Hemp (USO-31), as a textile industry waste, was used as an oil product sorbent material. The present study examines hemp sorption capacity of water using different fractions of hemp raw material to be used in oil/water mixtures. The experimental research revealed that water sorption capacity depends on fraction size and sorption time. The results of water sorption capacity of 2.5 and 5.0 mm after 1440 min were 4.74 and 4.67 g water/g dry sorbent, respectively.

Keywords: oil spill clean-up, natural organic sorbent, hemp, sorption capacity, moisture content.

Introduction

The frequent occurrence of oil spills and chemical leaks in recent years exacerbated the tension regarding environmental stewardship. Angelova *et al.* (2011) note that the effective removal of oil spills is a problem of great importance and interest for the society worldwide. One of the most economical and efficient methods for combating oil spills is oil removal by sorbents. Muhammad *et al.* (2012) named preferable features of inexpensive and readily available sorbents: fast oil sorption rate, high oil sorption capacity, low water pickup, high oil retention capacity during transfer, high recovery of the absorbed oil with simple methods, good reusability, high buoyancy, excellent physical and chemical resistances against deformation, photo-degradation, and chemical attacks.

Sorbents for oil spill clean-up can be categorized into three categories of materials: inorganic, synthetic organic and natural organic. Lim and Huang (2007) noted that the inorganic mineral products (perlite, zeolite) used as oil sorbents have poor buoyancy and oil sorption capacity. Most of them sink in water and create large volumes to transport. Husseien *et al.* (2009) mentioned that among synthetic products, polypropylene and polyurethane foams are the most widely used sorbents because of their highly oleophilic and hydrophobic properties. Despite the superior oil sorption properties their poor biodegradability makes them less attractive compared to some natural oil sorbents. Most of sorbents end up in landfills or are incinerated, which either produces another source of pollution or increases the oil recovery cost. The limitations of the mineral products and organic synthetic products have recently led to a lively interest in developing alternative materials, especially biodegradable. Natural organic products have greater potential for oil spills clean-up as they are able to absorb significantly more oil compared to the commercial synthetic sorbent materials (Lim, Huang 2007) because the degree of porosity and affinity of these materials allow them to absorb an amount of oil that exceeds their own weight.

The usage of waste materials or by-products from agriculture as inexpensive alternative materials for environmental remediation had been a subject of interest among many researchers (Cojocaru *et al.* 2011; Likon *et al.* 2013; Rotar *et al.* 2014; Naval Facilities… 1999). They are relatively inexpensive and usually readily available.

Using natural organic resources for sorption of these contaminations satisfy most important criteria in oil collection direction (Baltrėnas, Vaišis 2005).

Actuality and relevance of the research. Oil spill clean-up is problematic because of the limited remediation techniques that can be applied in various environments including water surfaces. The use of natural organic sorbents to clean-up oil spills presents many advantages due to simplicity of approach and the inexpensive nature of these materials.

Therefore, to combat environmental pollution resulting from oil spill, there is a need to deepen research in the area of analyzing and developing an effective natural organic sorbent material for oil spill remediation.

The aim of this experimental research was to determine natural organic sorbent's from hemp water sorption capacity, because it is very important in oil sorption from water surfaces applications. Sorption capacity of water was performed according to the two methods using different fractions of hemp raw material.

Methodology

For experimental research in order to evaluate hemp sorption properties such as moisture content, buoyancy, water sorption capacity were used different fractions (2.5; 5; 10 mm and unsieved) of hemp. All processes are investigated under normal room temperature (20±2 °C).

In oil product sorption experimental research were used materials such as hemp and tap water (20±2 °C), which viscosity is 1.002 cSt and density – 0.998 g/cm^3.

Apparatus consisted of: sorption test kit with mesh basket (1 mm water/oil repellent seal) (Fig. 1), 7 vessels, volumetric cylinder, electronic balance KERN EG 4200 – 2NM (accuracy 0.01 g), heater, desiccator.

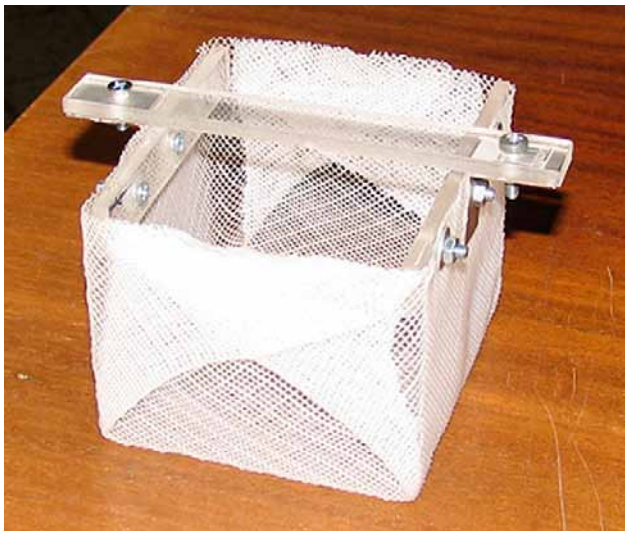

Fig. 1. Sorption test kit with mesh basket

Hemp preparation for experiments

For water sorption natural organic material hemp was used. Hemp fibers were grown in the north of Lithuania. In the experiments, the hemp species USO-31 were used. Hemp shives were obtained after initial mechanical processing.

In this study, hemp is prepared to eliminate or minimize the effect of external factors that are possible to interrupt this study. These factors are impurity and size effect.

Hemp is prepared by removing its impurity as much as possible. After mechanical processing of hemp straws, various fractions of shives and fibers were obtained. During processing, long and short fibers were separated from shives. Immediately after mechanical processing, shives' particles highly differed in terms of the size (Fig. 2). In order to ascertain properties of different size particles, hemp shives were fractioned through sieve column.

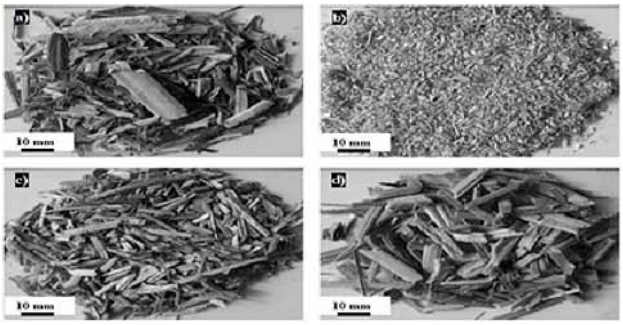

Fig. 2. View of fractioned hemp: a) – non fractioned (mixed); b) – 0–2.5 mm fraction, c) – 2.5–5 mm fraction, d) – 5–10 mm fraction

For the experiments hemp was used in normal conditions (i.e. stored in dry plastic bags to prevent additional moisture from the air). Before the experiments hemp moisture was determined.

Moisture content test

Moisture content in materials depends on environmental conditions and nature of the material (Mungasatkit 2004). In principle material that has higher moisture content absorbs less oil than the same material that has lower moisture content. In this study tested hemp is exposed in room's temperature of 20±2 °C for 24 hours before investigating its moisture content. During the procedure of determining moisture content different fractions of hemp were used which were placed in the oven at 103±1 °C until their weight remained constant. After their temperature was cooled down in a desiccator, their constant weight was determined and moisture content calculated using the following equation:

$$\text{Moisture content} = \frac{W_i - W_d}{W_d} \times 100\% , \qquad (1)$$

where:

W_i – weight of hemp sample, g;

W_d – constant sorbent weight, g.

Water sorption test

In the situation where sorbents are used to liquidate oil spill, recovering (or harvesting) of soaked materials is an important step to reduce their impact on aquatic resources.

However, it is possible that some sorbents may not be collected during the recovering process due to their sinking. This effect can be expressed by assessing the sorbent's floatation on the water surface. From ASTM: F726-99, if 10% or more of the sorbent material has sunk, then the sorbent is considered to have failed this test.

Sorbent water sorption was defined as follows: a sorbent charge with a weight of 5 g and 7 samples of the same hemp fraction were placed into the beakers of 150 ml in volume filled in with tap water (Fig. 3). The sorbent layer thickness in the glasses were 5–7 mm. The sorbent residence time in water was 15, 30, 60, 120, 180, 240 and 1440 (varied time).

Fig. 3. Water sorption capacity determination test

As the time passed, the sorbent was percolated and weighted. Then, taking the weight difference, it was possible to determine the amount of the sorbent waterlogged and sunk according to Equation 2.

$$W = \frac{(M_1 - M)}{M}, \tag{2}$$

where:

W – water sorption capacity, g water/g sorbent;

M_1 – a weight of the sample taken out from water, g;

M – a weight of the sample prior to be put into water, g.

Hemp sorbent's water sorption capacity determination test

Water sorption capacity is the amount of water being absorbed by 1 g of sorbent (Eq. (3)):

$$\begin{aligned} Water\ sorption\ capacity &= \frac{M_{water} - M}{M} \\ \frac{Water}{Diesel}\ absorbency &= \frac{M_{water/diesel} - M}{M} \end{aligned}, \tag{3}$$

where:

M_{water} – a weight of the sample taken out from water, g;

M – a weight of the sample prior to be put into water, g.

Material used as the oil spill clean-up sorbent should absorb minimum of water and it should be less water absorptive than oil products in oil/water mixture. Some additional methodology suggested by Sek *et al.* (2015) will be applied with intend to obtain more accurate test results. This method allows us to investigate sorption capacities without sorbent's take out for weighting. Water sorption of materials is determined using experimental equipment shown in Figure 4.

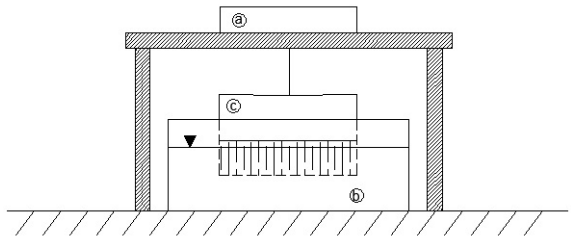

Fig. 4. Experimental sorption test scheme: (a) balance, (b) vessel with investigative liquid, and (c) basket with sorbent

For the water sorption test 2.5, 5, 10 mm and unsieved hemp sorbents fractions were used. The amount was chosen to keep constant 1 cm^3 high of sorbent in the mesh basket. Sorbent amount varied from 11 to 13 g. The basket was placed in 1 L vessel with investigative liquid and results were recorded every minute for 60 min, 120, 180, 1440 min till the sorption became constant. All the results were taken using electronic balance (KERN EG 4200-2NM) with 0.01 g accuracy.

Results

Determined hemp moisture content

The results of the moisture content of different sorbent fractions after sample preparation and estimation using gravitational method were recorded. After statistical analysis of 7 tests of each fraction to find moisture content of 5 g primary hemp material, average results with standard deviations are presented in Table 1.

Table 1. Moisture content determination of room-dry hemp results

Sorbent fraction, mm	Moisture content, %
2.5	9.04±1.11
5.0	8.17±0.99
10.0	7.69±1.88
Unsieved	7.40±1.03

As we can see from Table 1 results, there is a moisture content dependence on particle size of hemp sorbent. The highest moisture content of 9.04±1.11% is determined in 2.5 mm fraction of sample. Other fractions of 5 mm and 10 mm of hemp fractions were 8.17±0.99% and 7.69±1.88%, respectively. Unsieved hemp sorbent samples had the lowest moisture content from investigated – 7.40±1.03%.

Smaller fraction samples absorbed more moisture from the environment, because there are less of air between

pores and capillaries. Also bigger surface area and bulk density had an effect on increase of the moisture content in the samples. According to Cigasova *et al.* (2014), dependent on porous structure of hemp fiber, materials with higher bulk density have higher moisture content.

Water sorption capacity using loose hemp sorbent

The effect of water sorption in different fractions of the sample of sorption time (15–1440 min) is shown in Figure 5.

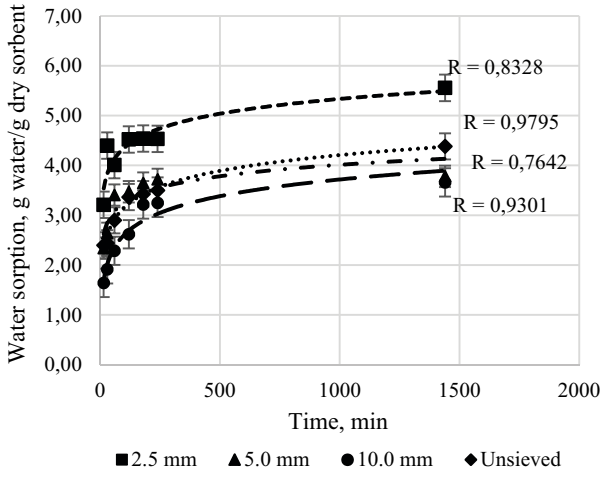

Fig. 5. Water sorption capacity of different hemp fractions by time

Hemp can hold significant amounts of water due to hydrogen bonding between hydroxyl groups existing in the material, water molecules and small amount of wax which is water repellent. It is obvious that water sorption capacity increases over time. Water sorption by hemp of 2.5 mm fraction increases over time and reaches a saturation point at 5.56 g water/g of dry sorbent. On the other hand, after 240 min 5.0 mm of the sample almost reaches its water sorption capacity which is 3.78 g water/g of dry sorbent. Despite the fact that unsieved hemp shives consist of different fractions, which are not extensively investigated, they have showed highest water sorption after 240 min and reached a saturation point at 4.38 g water/g of dry sorbent after 1440 min. 10.0 mm fraction with 3.66 g water/g of dry sorbent showed the lowest water sorption capacity during this experiment. During the test less than 10% of hemp sorbent sunk. This means that the material has good buoyancy during the time of experiment equal to 1440 min.

This test method is not very accurate, because sample was every time been percolated and weighted, which leaves a possibility that some water or material was lost during measurements' evaluation. To investigate water sorption in hemp sample the other batch method with test kit attached to electronic balance was used (Sek *et al.* 2015).

Water sorption capacity using test kit

For water sorption capacity determination of natural organic sorbent from hemp a batch method was used. During the experiment a mesh basket was attached to electronic balance and results were recorded at different times from immersion into water till 1440 min of sorption. The amount of tested different fractions of hemp (i.e. 2.5, 5, 10 mm and unsieved) varied between 11 to 13 g to keep constant 1 cm^3 height of sorbent in the mesh basket. The results were counted for mass of water absorbed by 1 g of dry sorbent. Graphical expression of water sorption capacity using test kit are shown in Figure 6.

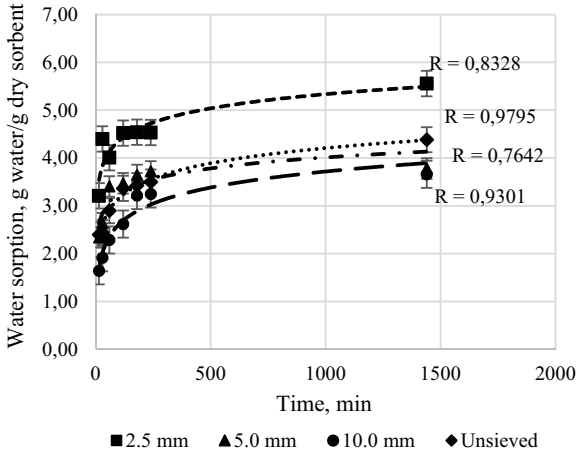

Fig. 6. Water sorption capacity of different hemp fractions by time

The results showed (Fig. 6) that fractions of 2.5 and 5.0 mm absorb the highest amount of water comparing with other fractions (i.e. 10.0 mm and unsieved). Water sorption capacity of 2.5 and 5.0 mm after 1440 min were 4.74 and 4.67 g water/g dry sorbent, respectively. It showed that larger fraction particles had smaller sorption capacity, such as 10 mm – 4.11 and unsieved – 4.53 g water/g dry sorbent because of higher bulk density and smaller surface area in contact with water. According to the results (Figs 5 and 6), it is obvious that the sorption time has an effect on water sorption capacity of hemp with different particle size. The time required to reach natural organic sorbent's maximum sorption capacity depends on the particle size. As the particle size increases, the time required for maximum sorption rises (Husseien *et al.* 2009). This can be related to the fibrous form of the hemp, which causes the shives with different fiber lengths and equal diameter to pass through the sieves during the mechanical sorbent preparation for the experiments. This can result in the formation of heterogeneous particles in large sieves. The ones which are unsieved have a higher bulk density, therefore, the interfacial area/volume becomes smaller. Although, when the particle size

is smaller, then more homogeneous particles have higher interfacial area for water sorption.

Correlation coefficients of two methods' experimental results are 0.980, 0.960, 0.979, and 0.979, respectively. It shows strong relation between two methods. However, in the first method used for water sorption capacity determination we can see that for 2.5 and 5.0 mm fraction sorbents determination coefficient R^2 is 0.83 and 0.76. It indicates that experimental data does not fit statistical model very well. Although, in Figure 6 experimental water sorption in the sorbent data is from 0.96 to 0.99 of R^2 and fits well statistical model. According to the results it is suggested to use the second sorption test method in further researches. Comparing water sorption capacities between hemp and commercial sorbents: Oil Sponge (4.15 g/g), Absorbent W (7.56 g/g), Fiberperl (3.14 g/g), Spill dri (4.32 g/g), SPC SXT (1.05 g/g) and Spilftr Oil (blue) Loose Mat. (0.95 g/g), we can see that hemp water sorption capacity is close to commercially used sorbents, although some of them repel water and are hydrophobic (Quinones, Scholze 1999).

After performing moisture content and water sorption capacity experiments it is known that hemp as a natural organic sorbent is hydrophilic and in order to use this sorbent in commercial applications investigation on the modification of the sorbent and its oil sorption capacity has to be made.

Conclusions

The present study of natural organic sorbent from hemp and it's water sorption capacity detemination is an important step in investigation of oil products sorption on water surfaces.

The moisture content was found to be decreasing by fraction size of hemp sorbent: 2.5 mm – 9.04±1.11%, 5 mm – 8.17±0.99%, 10 mm – 7.69±1.88% and unsieved fraction moisture content was 7.40±1.03%.

Water sorption capacity was investigated according to two methods: with loose particulates and test kit. The previous method was easier performed and showed more precise test results – 2.5 and 5.0 mm after 1440 min were 4.74 and 4.67 g water/g dry sorbent.

After 1440 min of static water sorption experiment, less than 10% of hemp sorbent settled down and it showed good buoyancy properties.

Experimental results showed that water sorption capacity depends on particles fraction size and sorption time: the larger is the size of fraction and the more heterogeneous particles are in it, the more time is needed to reach maximum water sorption capacity.

Acknowledgments

We are much obliged to the Vilnius Gediminas Technical University Thermoisolation institute for the help during this study.

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NATŪRALIŲ ORGANINIŲ KANAPIŲ SPALIŲ SORBENTO NAFTOS PRODUKTAMS ŠALINTI TYRIMAS

E. Budriūtė, V. Vaišis, D. Mikulskis

Santrauka

Labai svarbu efektyviai likviduoti išsiliejusius naftos produktus dėl jų neigiamo poveikio aplinkai ir ekonomikai. Naftos produktų valymo metodas pasitelkiant sorbentus yra laikomas vienu iš geriausių pasirinkimų, nes produktai yra absorbuojami sorbentų, nesukeliant jokios antrinės taršos. Natūralūs organiniai sorbentai buvo tiriami ir tobulinami, siekiant kontroliuoti naftos produktų išsiliejimus. Augalų biomasė yra atsinaujinantis išteklis, kuris gali būti naudojamas įvairioms medžiagoms ir energijai išgauti. Kanapių spaliai (USO-31), tekstilės pramonės atlieka, buvo tiriami kaip naftos produktų sorbentas. Buvo išnagrinėta kanapių vandens sorbcija naudojant įvairias šios medžiagos frakcijas. Eksperimentinis tyrimas parodė, kad vandens sorbcija priklauso nuo frakcijos dydžio ir sorbcijos laiko. Tyrimų metu buvo nustatyta vandens sorbcijos geba – 4,74 ir 4,67 g vandens/g sauso sorbento 2,5 ir 5,0 mm pavyzdžiams po 1440 min atitinkamai.

Reikšminiai žodžiai: išsiliejusių naftos produktų šalinimas, natūralus organinis sorbentas, kanapių spaliai, sorbcijos geba, drėgmės kiekis.