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PEAT BASED SORBENT FOR OIL REMOVAL

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SUMMARY

Peat is a prospective material for oil sorption because it has such advantages as low cost, biodegradability and relatively high surface area and porosity. The most serious disadvantage of peat in this context is the hydrophilic character of this material
The hydrophilic properties of peat can be reduced by pyrolysis (at > 250 °C) and this process also leads to improvement of oil sorption capacity and velocity. However this method of modification only reduces the wetting ability of peat. Our results shows, that modification of thermally treated peat with organosilicon polymers causes a very significant improvement of the water repellency of its surface and ensures also high hydrocarbon sorption capacity.

KEYWORDS: peat, sorbent, hydrophobicity, low temperature pyrolysis, organosilicon polymers.

INTRODUCTION

Use of hydrocarbon sorbents is an effective way for prevention and reduction of negative environmental consequences in a case of oil spillage accidents in aquatic environments. The most commonly used commercial sorbents: synthetic organic polymers as polypropylene and polyurethane foams shows very good oleophilic and hydrophobic properties as well as high sorption capacity and other practical characteristics. However high cost of these materials and necessity of expensive utilization activities after use of them are the major disadvantages of synthetic hydrocarbon sorbents. Utilization of natural organic sorbents is much easier and cheaper; they are suitable for simple incineration or ex-situ biodegradation. One of the more prospective, widespread natural materials for oil sorption is a raised bog peat with low level of decomposition. It has such advantages as low cost, biodegradability and relatively high surface area and porosity. The most serious disadvantage of peat in this context is the hydrophilic character of this material.

Our previous studies shows that the initial sorption characteristics of peat can be significantly improved by 6-8 hours long heating in anaerobic environment at the temperature range between 230 and 280 ˚C (Klavins and Porshnov 2011). Obtained material shows good oil sorption capacity, however hydrophobic characteristics and selective action of obtained material in this case can not be considered as very good.

Another possible approach to improve hydrophobic properties of organic matter is an impregnation with hydrophobic organosilicon polymers, for example

polymethylhydrosiloxane (PMHS), which is an attractive reagent for this purpose because it is inexpensive and non-toxic (Lawrence *et al*. 1999).
The aim of this study is to compare an effect of thermal treatment and impregnation with PMHS, as well as a combination of both methods, on hydrocarbon sorption characteristics and hydrophobic properties of peat.

MATERIALS AND METHODS

Materials

The peat, used in this study, was obtained in Kaigu raised bog in Latvia. The dominant peat forming plant in used sample is *Sphagnum fuscum*. Peat was milled to a particle size 0.2-2 mm.

Crude oil with a density of 0.81 g/ml and a 42% content of volatile hydrocarbons was used for studying the interaction of modified products with hydrocarbons.

Thermal treatment of peat

Thermal treatment of peat was carried out in a laboratory oven: in a closed steel cylinder with a 5 cm diameter and 40 cm length. Before heating, samples were moistened with water, 1:1 by volume, to prevent the material from ignition. Heating was done in the temperature 240-250 °C, for 6 hours.

Impregnation with polymethylhydrosiloxane

Raw peat and thermally pre-treated peat was treated with polymethylhydrosiloxane solution (25 g/l) in acetone (1:1 by volume). After treatment peat was dried in laboratory oven in 40 °C for 2 hours.

Oil sorption experiment

4 ml (3.23 g) of pure oil and 0.25 g of peat sorbent were added into laboratory bottles (volume 100 ml) with 50 ml of MillQ water. Samples were placed on a shaker and shaken at 120 rpm for 5 hours. Then samples were filtered through filter paper. The resulting mass (peat with sorbed oil) was placed into laboratory bottles, treated with 20 ml of hexane and extracted on the rotary shaker for 30 minutes, then once again filtered though filter paper. The mass collected on the filter was washed with 20 ml of hexane. Pooled filtrate was placed in bottles with known mass and evaporated at room temperature to a constant weight. At the same time and in identical conditions, evaporated samples of oil with known mass, were dissolved in hexane. The mass content of non-volatile hydrocarbons in the oil was calculated using mass difference. The sorbed oil mass was calculated using derived factor.

Buoyancy evaluation

Sorbent samples (0.5 g) were placed into bottles (volume 100 ml) with 50 ml of distilled water. The samples were left for 72 hours. Visual assessment of buoyancy by the criteria described below was made after 24, 48 and 72 hours. Criteria for the assessment of buoyancy:

5 points: All the material remains buoyant, part of the material is dry and floating; 4 points: A small portion of the material sunken, the remaining part is buoyant, mixed with water; 3 points: A significant part of the material sunken; 2 points: The most part of the material sunken; 1 point: All the material sunken.

Water sorption experiment

Sorbent samples (0.5 g) were placed into laboratory bottles (volume 100 ml) with 50 ml of distilled water, put on a rotary shaker and shaken at 120 rpm for 5 hours. Then the samples were filtered through filter paper and weighed on analytical scales. The mass of sorbed water was calculated.

FTIR spectroscopy

Fourier transform IR spectrometry was carried out with Perkin Elmer Spectrum BX spectrometer. Infrared transmission spectra were taken as follows: peat samples were rubbed through a 0.25 mm sieve. 250 mg of potassium bromide and 2.5 mg of sample were weighed on the analytical scales. Then the sample was thoroughly mixed with potassium bromide, 50 mg of mixture was pressed in a special press into about a 1-mm-thick tablet. The tablet was inserted into the sample holder and the infrared spectrum was obtained.

RESULTS AND DISCUSSION

As we can see in Table 1, and Figures 1-2, both methods: thermal treatment and impregnation with PMHS improves sorption characteristics of peat. Heating is more effective for modification of oil sorption characteristics and buoyancy, while treatment with PMHS is more effective for reduction of water sorption, however assessed by all properties, effects of both methods can not be considered as very good, because hydrophilic properties in both cases are still well-expressed, that means a lack of selective action in oil-water systems.

Table 1. Buoyancy of obtained peat samples

Sample	Evaluation of buoyancy		
	24 h	48 h	72 h
Raw peat	3	2	2
Impregnated peat	4	4	4
Heated peat	5	5	5
Impregnated heated peat	5	5	5

Different situation can be observed if both methods are combined as far as material obtained in this case is characterized by very good buoyancy, high oil sorption capacity, and low water sorption. It means that combination of 6 hours long thermal treatment and impregnation of obtained material with PMHS leads to very significant improvement of the hydrophobic properties of peat and ensures also higher hydrocarbon sorption capacity.

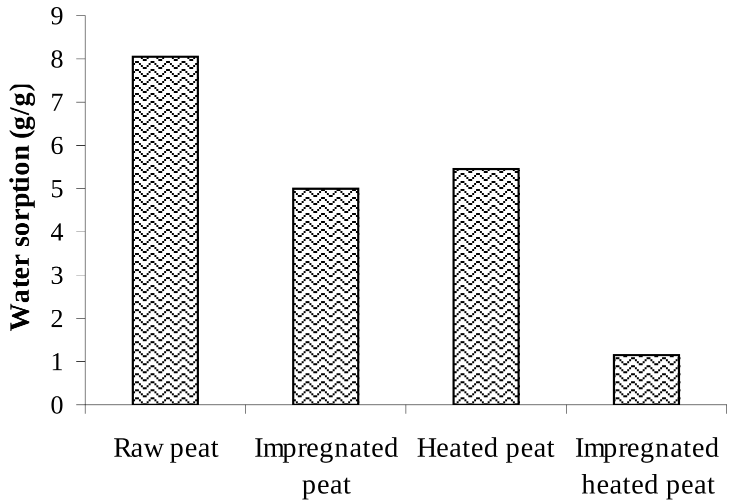

Fig. 1. Sorption of water on obtained peat samples

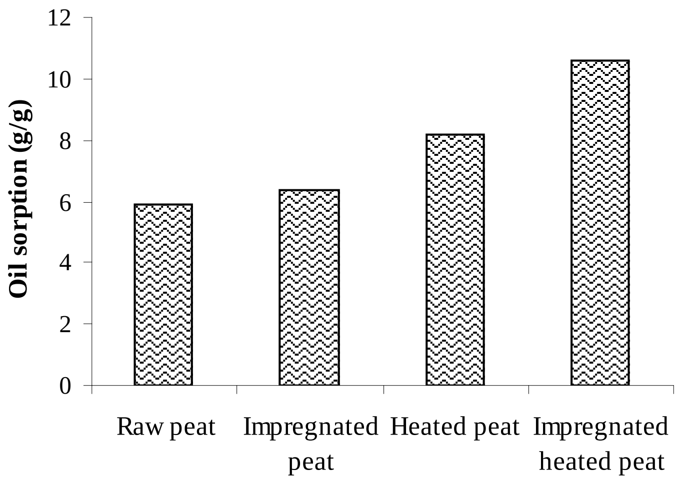

Fig. 2. Sorption of crude oil on obtained peat samples

FTIR spectra of samples (Figure 3) shows that very serious changes after thermal treatment can be observed in 3300-3400 cm^{-1} region that displays a presence of hydrogen bonded OH group. Reduction of this pike after thermal treatment shows sharp dehydration of peat matter. In our opinion, directly dehydration is a process that leads to better bonding between PMHS and peat.

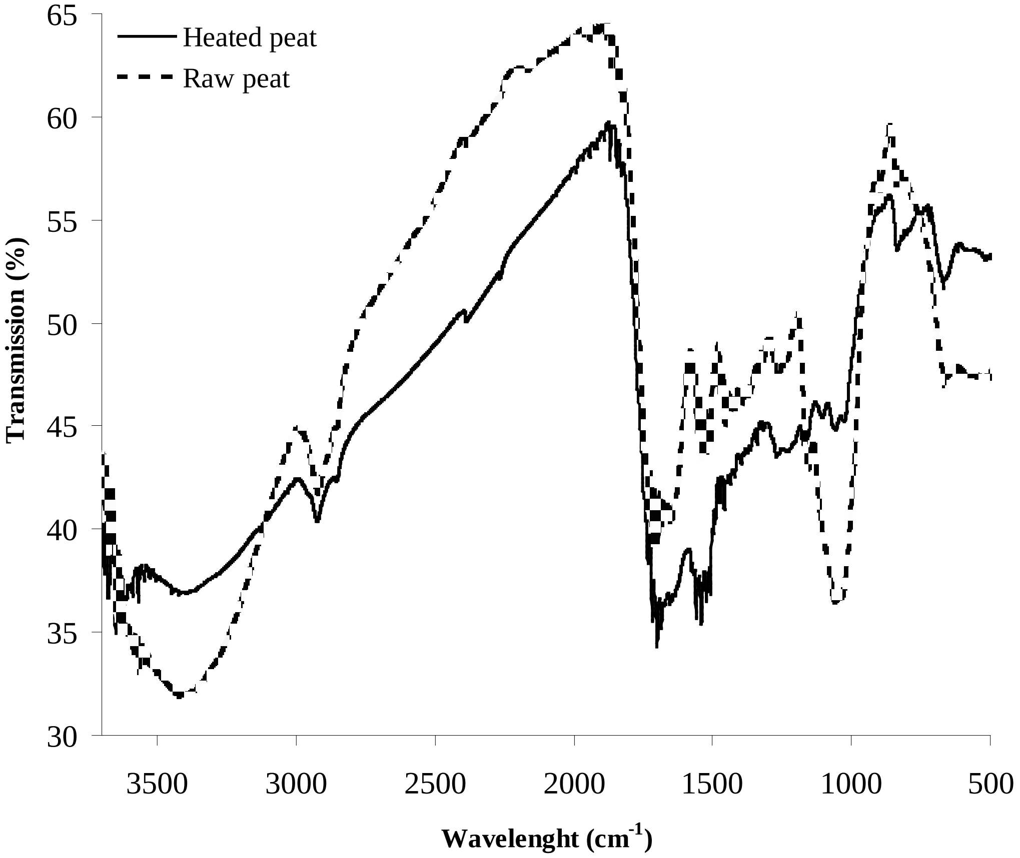

Fig. 3. FTIR spectra of raw and thermally treated peat

CONCLUSIONS

Combination of low temperature pyrolysis and impregnation with PMHS can be recommended as good approach for the modification of peat, to produce a highly selective hydrocarbon sorbent, for usage in oil – water systems. Obtained product is characterized by high oil sorption capacity, good hydrophobic properties and buoyancy. Selective action of obtained product allows an application of it not only in water surface treatment in a case of oil spillage, but also as a sorbent for column filtering of hydrocarbon containing waste waters.

REFERENCES

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