Approaches for peat modification to improve oil sorption capacity

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Abstract- Oil pollution is one of the major environmental problems. The aim of this study is to investigate the possibilities to use peat and its modification products for oil sorption. Peat is a prospective material for oil sorption because it has such advantages as low cost, biodegradability and relatively high parameters of specific surface area and porosity. We have studied the sorption characteristics of high-moor peat with different botanical compositions and levels of decomposition, as well as the effect of thermal treatment on the oil sorption capacity, buoyancy and water sorption capacity of peat in comparison with the effect achieved by means of other methods of peat modification: silylation, methylation and treatment with organosilicon compounds. We have determined the optimal conditions for thermal modification of peat to have an effect on hydrocarbon sorption characteristics.

Keywords- Peat, oil, sorbent, thermal treatment, chemical modification

I. INTRODUCTION

Oil and its products are a widespread and dangerous environmental pollutant group. The growth of energy consumption and industrial production inevitably increases the volume of oil extraction, transportation and consumption and thus also the risk of oil spillage and resultant environmental pollution [1]. Since this risk is now considered as imminent, technologies and materials that help to minimise or eliminate the environmental impact caused by oil contamination are very important. If oil and its products are spilled in aquatic or terrestrial environments, it is very important to take urgent action to stop the contamination from spreading and to collect as much of the discharged products as possible. One of the most effective methods for this purpose is the use of oil sorbents. Sorbents are substances that can bind oil hydrocarbons as a result of absorption and/or adsorption processes. Some requirements for a good sorbent include high hydrophobicity, high sorption capacity, buoyancy, porosity and high specific surface area. A significant advantage of a sorbent is its biodegradation capability [2].

Raised bog peat with a low degree of decomposition can be considered as a prospective material for oil sorption [3]. This peat is characterised by a developed, complex pore system due to its main component – partially decomposed sphagnum moss organic debris [4]. The porosity ratio of this material is about 95%, and the value of its specific surface area is usually more than 200 m² per g [5]. Furthermore, the biodegradation potential of peat is undeniable, and it also has other notable advantages, such as low cost and availability. Low hydrophobicity as well as relatively low sorption capacity and sorption velocity must be mentioned as the disadvantages of peat in this context. However, these properties can be improved through peat modification [6].

There are a number of methods known for the modification of natural biopolymers to increase their hydrophobicity [7]. Since peat is composed of hydrophilic (water-soluble and easily hydrolysable) and hydrophobic (bitumen, waxes) components, its hydrophobisation can be carried out by using its own hydrophobic components condensing on the surface of material as a result of thermal treatment [3]. The chemical hydrophobilisation of peat can be achieved using water-repellent agents of organic or inorganic origin, for example, sodium salts of fatty acids, organosilicon substances, solutions of Ca²⁺, Mg²⁺, Zn²⁺, Cu²⁺, Fe²⁺ salts with carboxymethylcellulose additive and others [3]. Several known peat modification technologies include treatment at a temperature between 270° and 300°C without air access [8], treatment with tar dissolved in solvents [9] and processing with ionic and non-ionic surfactant mixture [10]. However, there is still space for improving the sorptive properties of peat.

The aim of this study is to investigate the sorption of hydrocarbons on raised bog peat with different botanical composition and levels of decomposition, to determine the optimal conditions for the thermal treatment of peat as well as to study structural changes of peat in a result of heat treatment.

II. MATERIALS AND METHODS

A. Materials

Peat was obtained from a site of industrial peat extraction at Kaigu bog (Latvia). The peat used for this study has been well characterised in the previous studies [11], and its profile consists of consecutive peat layers with significantly differing botanical composition and levels of decomposition. Information about the degree of decomposition and botanical and elemental compositions of samples used is summarised in Table 1. All peat samples were milled to a particle size 0.2-2 mm. In other experiments, only peat from sample No. 2 was used.

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Table 1. All peat samples were milled to a particle size 0.2/2 mm. In other experiments, only peat from sample No. 2 was used.
**Table I:**

**Characteristics of peat samples used**

<table>
<thead>
<tr>
<th>No</th>
<th>Average embedding depth (cm)</th>
<th>Botanical composition</th>
<th>Age (years)</th>
<th>Degree of decomposition (%)</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>Cotton-grass – sphagnum peat</td>
<td>810</td>
<td>33</td>
<td>48.26</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>Sphagnum fuscum peat</td>
<td>1200</td>
<td>10</td>
<td>49.31</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>Narrow-leaf sphagnum peat</td>
<td>1790</td>
<td>33</td>
<td>48.53</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>Narrow-leaf sphagnum peat</td>
<td>1970</td>
<td>7</td>
<td>48.53</td>
</tr>
<tr>
<td>5</td>
<td>135</td>
<td>Sphagnum fuscum peat</td>
<td>2260</td>
<td>9</td>
<td>41.75</td>
</tr>
</tbody>
</table>

Crude rapeseed oil with a density of 0.91 g/ml was used as the hydrocarbon model substance to study the hydrocarbon sorption capacity on peats with different botanical compositions. 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.

**B. Oil sorption capacity on peat with different botanical composition**

All studied peat samples were heated for 2 hours in at 200°C. Then 10 ml (9.1 g) of rapeseed oil and 1 g of peat were added into bottles filled with 50 ml of MilliQ water. Samples were shaken (120 rpm) for 24 hours and filtered. The resulting mass was extracted 3 times with 20 ml of acetone. Combined extracts were evaporated to a constant weight and the mass of the remaining oil was weighed.

**C. TGA analysis of peat**

The peat and thermally treated peat was studied using thermogravimetric analysis. The thermal analysis was performed with SII EXSTAR 6300 TG / DTG derivatograph within the temperature range of 25-550°C and heating rate of 10°C/min. The recorded curves were thermogravimetric (TG) and differential thermogravimetric (DTG). Thermograms were used for identifying the temperature region related to a rapid weight loss of the material (thermal degradation of peat structure).

**D. Thermal treatment of peat**

Thermal treatment of peat was carried out heating with unlimited air access or heating with limited air access (in a closed steel cylinder). 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. Heating times and sorption characteristics are given in Table 3.

**E. Oil sorption experiment**

4 ml (3.23 g) of oil and 0.25 g of peat sorbent were added into bottles with 50 ml of water. Samples were shaken at 120 rpm for 5 hours, then samples filtered. The resulting mass (peat with sorbed oil) was extracted 3 times with 20 ml of hexane then again filtered though paper. Pooled filtrate was 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.

**F. 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.
G. Water sorption experiment

Sorbent samples (0.5 g) were placed into laboratory bottles (volume 100 ml) with 50 ml of distilled water and were 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.

H. Study of sorption kinetics

4 ml (3.23 g) of oil and 0.25 g of sorbent were added to bottles (volume 100 ml) with 50 ml of water. The samples were shaken at 120 rpm and removed after 2.5, 5, 10, 20, 30, 60, 120, 180, 240 and 300 minutes, filtering each sample afterwards. The sorbed oil was extracted with hexane, as described above. Finally, the mass of the sorbed oil was calculated.

I. Characterisation of structural changes in the modified peat

Fourier transform IR spectrometry was used for the characterisation of structural changes in the modified peat samples. It 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 25 mg of testable sample were weighed on the analytical scales. Then the sample was thoroughly mixed with potassium bromide and 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.

III. RESULTS AND DISCUSSION

A. Assessment of oil sorption capacity on peats with different botanical compositions:

The results of oil sorption experiment on peats with different botanical composition are presented in Table II. As we see, a better sorption capacity is typical for Sphagnum fuscum peat with decomposition degree ≤10%. So, the peat from sample No. 2 (sphagnum fuscum peat, with degree of decomposition 10 %) was chosen for further experiments.

<table>
<thead>
<tr>
<th>№</th>
<th>Botanical composition</th>
<th>Degree of decomposition (%)</th>
<th>Sorbed oil (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cotton grass, sphagnum</td>
<td>33</td>
<td>3,48</td>
</tr>
<tr>
<td>2</td>
<td>Sphagnum fuscum</td>
<td>10</td>
<td>5,98</td>
</tr>
<tr>
<td>3</td>
<td>Narrow-leaf sphagnum</td>
<td>33</td>
<td>3,52</td>
</tr>
<tr>
<td>4</td>
<td>Narrow-leaf sphagnum</td>
<td>7</td>
<td>4,17</td>
</tr>
<tr>
<td>5</td>
<td>Sphagnum fuscum</td>
<td>9</td>
<td>5,16</td>
</tr>
</tbody>
</table>

B. Conditions of the thermal treatment of peat

Figure 1 shows the results of thermogravimetric analysis of raw peat. After the evaporation of water at a temperature range around 100°C, the DTG curve shows a significant reduction of the mass loss, and this fact indicates that no significant changes in the structure or composition of the studied peat samples have taken place at the temperature range between 100 and 200°C. The increase of mass loss is observed at the temperature range between 200 and 250°C, and this process cannot be associated with the destruction of aromatic structural units of peat, which occurs at much higher temperature [12].

Probable it can be assumed that, at this temperature interval, the volatile peat components evaporate, while the less volatile compounds start to condensate. At the temperature range between 250 and 275°C, we can observe a decrease in weight loss, which is indicative of an active condensation process of hydrocarbons on the surface of the material. At a temperature higher than 275°C, we can observe a rapid mass loss, indicating a rapid destruction of hydrocarbons and substances forming the structure of peat. These results show that the temperature for thermal condensation of hydrocarbons without the loss of material structure in aerobic conditions should definitely be higher than 200°C, but should not exceed 275°C.

It is possible that in anaerobic conditions the optimal temperature for thermal treatment could be higher than 275°C because of the reduced impact of oxygen and weaker oxidative destruction. This confirms the information provided in [10], i.e. that temperature for thermal hydrophobisation of peat in anaerobic conditions can be within the range of 270-300°C; however, in our opinion, the lower limit of this temperature range should be slightly lower, and the optimal temperature range for thermal hydrophobisation of peat is from 230 to 300°C. A temperature range between 240 and 250°C was chosen for our experiments.

C. Thermal treatment of peat and characterisation of resulting structural changes

Structural changes resulting from thermal treatment of peat have been studied using FTIR spectroscopy. FTIR
spectrograms of raw peat and heated peat samples are showed in Figure 2. As we can see, the spectrum of raw material contains absorption peaks that are typical for peat:

- The peak at a wavelength within the range 3300-3400 (centred at 3360) indicates the stretching of O-H bonds and the presence of the hydroxyl groups in phenols, alcohols and carbohydrates;
- The peak at a wavelength within the range 2490-2900 (centred at 2890) indicates the stretching of C-H bonds and the presence of aliphatic CH chain fragments in the macromolecular structure of the material;
- The peak at a wavelength within the range 1720-1725 (centred at 1721) indicates the stretching of C=O bond and the presence of carbonyl functional groups;
- The peak at a wavelength beyond the range 1600-1620 (centred at 1602) indicates the stretching of cyclic C=C bonds and the presence of aromatic rings;
- The peak at a wavelength within the range 1170-950 (centred at 1025) indicates the stretching of C=O bonds in carbohydrates and the presence of polysaccharides.

IR spectra of the modified samples show the degradation of oxygen-containing material in the peat structure as a result of heat treatment. OH\textsubscript{3360}/C=H\textsubscript{2890} and OH\textsubscript{3360}/C=O\textsubscript{1602} factor indicates a slight increase in the content of hydrogen-bonded OH groups after a 4-hour long heating period with limited air access. This phenomenon can most likely be explained with the influence of water vapour, and its occurrence is related with experimental conditions. Later on, a significant decrease in the content of hydroxyl groups was observed. In the spectra of samples heated with unlimited air access, we can see the disappearance of the OH\textsubscript{3360} peak after 4 hours of heating, indicating complete removal of hydrogen-bonded hydroxyls. The increase in OH\textsubscript{3360}/C=O\textsubscript{1602} together with the increase of C=O\textsubscript{1602}/C=O\textsubscript{1025} taking place after 6 hours of heating with limited air access indicates the thermal destruction of hydrophilic polysaccharides, while the increase of OH\textsubscript{3360}/C=O\textsubscript{1602} value together with the increase of C=O\textsubscript{1602} points at the destruction of COOH functional groups.

The decrease of C=H\textsubscript{2890}/C=O\textsubscript{1602} value after a 4-hour long heating period with limited air access indicates an increase in the relative amount of aliphatic chains in the material as well as the condensation of hydrocarbons on the surface of the material. However, when the heating time exceeds 4 hours, we can observe a rapid increase of C=H\textsubscript{2890}/C=O\textsubscript{1602} value, which is common in the case of oxidation of hydrocarbons under the influence of atmospheric oxygen. The impact of oxygen on the destruction of aliphatic chains is also observed in the spectra of peat heated with unlimited air access, where the C=H\textsubscript{2890} peak disappears already after 4 hours of heating.

In our opinion, the inconsequence in the increase of value of C=H\textsubscript{2890}/C=O\textsubscript{1602} indicates that the condensation and degradation of aliphatic compounds take place simultaneously.

D. Characterisation of application possibilities of the modified peat samples

The results of experimental evaluation of raw peat and the modified peat samples are summarised in Table III. The curves of oil sorption kinetics on the modified materials as well as on raw peat are shown in Figure 3. As we see, sorption properties of peat can be significantly improved by heating.

Heating with unlimited air access can improve the hydrophobic and oleophilic properties of peat after a 4-hour period long treatment, whereas longer heating deteriorates the characteristics achieved by heating the material for up to 4 hours. As we can see in Figure 2, the improvement of characteristics in this case can be explained by the destruction of oxygen-containing polysaccharides and carboxyl groups within the structure of the material. This process can reduce the polarity of substance and improve its oleophilic properties accordingly. However, as we can see in Table 4, such treatment is associated with a rapid, irreversible loss of mass and, accordingly, the structure of peat. In our opinion, despite the fact that our results indicate the possible effectiveness of 4-hour long peat heating with unlimited air access for the improvement of its oil sorption characteristics, this method is not the best for this purpose. As we see, much better results can be obtained by heating with limited air access. In this case, a sufficient improvement of properties can be observed after 4-hours long heating, while the best results can be obtained by 6-8 hours long heating. In our view, all changes of properties in this case can not be explained only with condensation of aliphatic hydrocarbons. As we can see, the sample with the lowest value of C=H\textsubscript{2890}/C=O\textsubscript{1602} factor shows only the lowest value of water sorption, but not the best result in oil sorption. Later on, we can observe a continued increase in the oil sorption capacity in spite of the decrease in the C=H\textsubscript{2890}/C=O\textsubscript{1602} factor. It can be explained with the destruction of oxygen-containing structural fragments of the material. Figure 3 (A) shows that thermal treatment affects the sorption capacity of peat as well as oil sorption kinetics. This phenomenon can also be explained with the depletion of oxygen-containing structural fragments and the resultant changes in the polarity of material.

![Figure 2: Curves of oil sorption kinetics on raw and heated peat](image-url)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss (%)</th>
<th>Water sorption (g/g)</th>
<th>Evaluation of buoyancy (g/g)</th>
<th>Oil sorption (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw peat</td>
<td>10.5</td>
<td>3 2 2 5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat samples heated with unlimited air access</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 30 minutes</td>
<td>No data</td>
<td>8.9 3 2 2 6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 1 hour</td>
<td>No data</td>
<td>9.6 4 3 5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 2 hours</td>
<td>No data</td>
<td>7.8 4 3 5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 4 hours</td>
<td>48</td>
<td>7.9 5 5 8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 6 hours</td>
<td>72</td>
<td>7.6 4 4 7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat samples heated with limited air access</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 2 hours</td>
<td>No data</td>
<td>6.0 4 3 2 5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 4 hours</td>
<td>23</td>
<td>6.2 5 5 7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 6 hours</td>
<td>29</td>
<td>6.2 5 5 8.2</td>
<td></td>
<td></td>
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<tr>
<td>Heated for 8 hours</td>
<td>40</td>
<td>6.5 5 5 8.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated for 10 hours</td>
<td>52</td>
<td>6.7 5 5 8.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: FTIR spectra of raw and heated peat samples. A: samples heated with limited air access, B: samples heated with unlimited air access.
The destruction of oxygen-containing compounds, in contrast to the destruction of aliphatic compounds, is not related to the presence of oxygen. It means that complete prevention of oxygen access in the process of heating may be the optimal solution for thermal production of peat sorbents.

IV. CONCLUSIONS

- This study has confirmed that the initial sorption characteristics of peat can be significantly improved for the production of peat-based oil sorbents. Sphagnum fuscum peat with low (10%) degree of decomposition showed the best initial sorption capacity in our study. We have found that the optimal heating conditions for thermal modification of peat are 6-8 hours long heating in anaerobic environment at the temperature range between 230 and 280°C.
- Our study demonstrated that the improvement of peat sorption characteristics as a result of heat treatment can be explained not only with the condensation of hydrocarbons on the surface of the material but also with the destruction of oxygen-containing fragments in the macromolecular structure of peat. Furthermore, we have found that the condensation of aliphatic hydrocarbons affects the water sorption capacity more than other characteristics, while the increase in oil sorption capacity and sorption velocity are induced by the depletion of oxygen-containing compounds.

REFERENCES