Peat as natural and industrial sorbent

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Abstract: Use of sorbents is steadily growing but at the same time it is important to advance use of sorbents based on natural and biodegradable materials. The aim of this study is to investigate the possibilities to use peat and its modification products for oil, heavy metal and nonmetallic element sorption. Peat is a prospective material for use as a sorbent because it has such advantages as high concentration of sorption centers, low cost, biodegradability and relatively high parameters of specific surface area and porosity. We have studied the sorption characteristics of natural high-moor peat with different botanical compositions and levels of decomposition for sorption of heavy metals. After use of thermal treatment or methods of peat modification increasing peat hydrophobicity (silylation, methylation and treatment with organosilicon compounds) it is possible significantly increase peat oil sorption capacity as well as buoyancy and water sorption capacity. We have determined the optimal conditions for thermal modification of peat to have an effect on hydrocarbon sorption characteristics. Peat and peat modified with iron compounds were prepared and tested for sorption of arsenic and phosphorous compounds. The highest sorption capacity was observed using peat sorbents modified with iron compounds. Sorption of different arsenic speciation forms onto iron modified peat sorbents was investigated as a function of pH, reaction time and temperature. It was established that sorption capacity increases with a rise in temperature, and the calculation of sorption process thermodynamic parameters indicates the spontaneity of sorption process, and it has endothermic nature.

Key-words: Peat, oil, sorbent, thermal treatment, chemical modification

1 Introduction
Peat is a light brown to black organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees [1]. The interest about peat properties is growing as far as peat as substance supports and influences bog and wetland ecosystems, but peat profiles can serve as an archive indicating conditions in past environments [2, 3]. In form of peat is stored significant amount of organic carbon and thus peat reserves play major role in the carbon biogeochemical cycling and is of especial role considering the ongoing climate change process [4]. Industrial and agricultural uses of peat are growing [5] and significant amounts of peat are mined industrially. Considering presence of many biologically active compounds and number of reactive functional groups in the composition of peat there is a growing interest in development of added value based products and at first – peat based sorbents. Sorbents are materials that can bind substances as a result of absorption and/or adsorption processes.

Some requirements for a good sorbent include high sorption capacity, buoyancy, porosity and high specific surface area. A significant advantage of a sorbent is its biodegradation capability [6]. Raised bog peat with a low degree of decomposition can be considered as a prospective sorbent [7], due to presence of a developed, complex pore system formed by partially decomposed sphagnum moss organic debris [8]. The porosity ratio of this material is about 95%, and the value of its specific surface area is usually more than 200 m$^2$ per g [8]. Furthermore, the biodegradation potential of peat is undeniable, and it also has other notable advantages, such as low cost and availability. Peat properties can be improved through peat modification [9]. Three major groups of substances of concern for which sorbents and sorption might be applied, to reduce environmental pollution risks are oil hydrocarbons, heavy metals and nonmetallic elements.

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 [10]. 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 [11]. One of the most effective methods for this purpose is the use of oil sorbents and peat might be considered as a good option. 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 [12, 13]. The chemical hydrophobisation 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 Ca\(^{2+}\), Mg\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\) salts with carboxymethylcellulose additive and others [14].

Sorption capacity of peat has been studied in relation to heavy metal ions (most of the studies), nutrients, as well as various organic substances, such as polyaromatic hydrocarbons [15, 16]. Peat is an effective heavy metal sorbent, because of its high cation exchange capacity. Peat components, especially lignin, contain functional groups, such as alcohols, aldehydes, acids and ethers, which can be involved in sorption of heavy metals [16, 17]. The use of peat sorbents provide many benefits, however, several disadvantages occur, such as low mechanical strength and low chemical stability of peat particles. To overcome these drawbacks, different peat modification methods have been developed [18, 19].

Arsenic contamination of waters is one of the most important problems [20]. Drinking water supplies in polluted areas contain dissolved arsenic in excess of 10 \(\mu g/l\) which is the maximum level recommended by the World Health Organization [20]. Arsenic enters waters through a combination of natural processes as well as through a range of anthropogenic activities. As previously mentioned; sorption as an approach and sorbents as materials have found widespread application in different areas of production and everyday life. However, still new areas of sorbent application are arising, and thus new types of sorbents are needed. Among the chemically modified adsorbents, the solid phases loaded with iron species are particularly efficient to remove As (III) and As (V) ions from contaminated waters due to the formation of stable inner and outer sphere surface complexes [20]. One way of developing new sorbents is working at sorbents based on natural materials as far as they are cheap, recyclable or they can be utilized in an environmentally friendly way, but their efficiency is similar to synthetic sorbents. In this respect, a prospective matrix for sorbent development is peat. Search for peat based sorbents is topical also considering available significant peat resources in Latvia.

The aim of this study is to investigate the possibilities to use raised bog peat with different botanical composition and levels of decomposition and its modification products for oil, heavy metal and nonmetallic element sorption, to determine the optimal conditions for the peat modification and sorption.

2 Materials and methods

2.1. Materials

Peat was obtained from a site of industrial peat extraction at Kaigu and Dizais Veikniex bogs (Latvia). The peat used for this study has been well characterised in the previous studies [21], and its profile consists of consecutive peat layers with significantly differing botanical composition and levels of decomposition. All peat samples were milled to a particle size 0.2-2 mm.

2.2. Oil sorption study

All studied peat samples were heated for 2 hours in at 200°C. Then 10 ml (9.1 g) of 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.

2.3. Modification of peat with Fe compounds

Modified peat I. Method was based on peat impregnation with iron hydroxide. 0.25 mol (67.55 g) FeCl\(_3\)·6H\(_2\)O were dissolved in 250 mL distilled water, added 250 mL 3M NaOH, and left for 2-4 hours. Then reaction mixture was rinsed, and decanted in 1 L vessel. A dispersion of Fe(OH)\(_3\) were mixed in 100 g of homogenized peat. After filtration, reaction product was rinsed with approximately 0.5 L distilled water and thermal treated for 4 hour at 60 °C temperature. After that iron content was determined in the modified peat I. Modified peat II. Method was based on peat impregnation with iron salts. 0.25 mol iron chloride hexahydrate was dissolved in 540 mL water. 100 g homogenized peat was mixed with 540 mL iron chloride hexahydrate and left overnight. Then mixture was filtered, wet peat was poured with 500 mL 1.5 M NaOH and left for one hour. Reaction mixture was filtered, rinsed with distilled water till pH ~ 7. Product was thermally treated treated for 4 hour at 60 °C temperature.

2.4. 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.

2.5. Metallic and non-metallic element sorption study

Sorption experiments were carried out using peat and modified peat sorbents. Two inorganic speciation forms of arsenic - As (V) and As (III), and organic form – cacodylic acid (C₁₂H₇AsO₂) were used. Arsenic solutions were prepared dissolving necessary amount of arsenic compound (Na₂HAsO₄·7H₂O, AsNaO₂ and C₁₂H₇AsO₂) in distilled water so that concentrations of arsenic were 300, 200, 100, 50, 25, 10 and 5 mg/L. In 100 mL glass vessels 0.5 g of peat was poured with 40 mL of necessary arsenic solution. Vessels were shaken for 24 h at room temperature. After that suspension filtered, and total dissolved arsenic analyses of samples were carried out using a Perkin-Elmer AAnalyst 200 atomic absorption spectrophotometer (AAS) with flame atomization.

In order to investigate the obtained sorption isotherms Langmuir, Freundlich and Dubinink- Radushkevich sorption models were analyzed. The obtained data fitted to the Langmuir model.

2.6. 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.

3 Results and discussion

Oil sorption onto peat depends on peat botanical composition and highest sorption capacity is typical for Sphagnum fuscum peat with decomposition degree ≤10%.

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.

The curves of oil sorption kinetics on the modified materials as well as on raw peat are shown in Figure 1. 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, 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.
Five peat samples from two industrially mined peatlands have been tested as sorbents for the removal of Cu\(^{2+}\) from single-component aqueous solution. The effect of metal concentration, pH and contact has been studied in batch mode. The Cu\(^{2+}\) uptake by peat in respect to different initial metal concentrations is shown in Figure 2. It was found that the difference between sorption capacity of Cu\(^{2+}\) can be up to three times when peat from different peatlands was used, suggesting that the sorption capacity strongly depends on the physical and chemical properties of the peat. Peat from Kaigu bog (depth of 45-70 cm) showed the highest sorption capacity – 28 mg/g at initial Cu\(^{2+}\) concentration of 1000 mg/L. Lowest sorption capacity by showed by peat from Kaigu bog (depth of 95-125 cm). Both peat samples from Mazais Veikenieks showed equal sorption capacity of 22 mg/g.

The experimental data fitted equally well both the Freundlich and Langmuir equation. According to Ringqvist and Oborn, the pH of the solution can significantly affect the sorption performance. When peat is used in wastewater treatment, higher efficiency is expected at higher pH values [22]. Our research shows that in the pH interval 2–9, the removal of Cu\(^{2+}\) from the solution increased from 30% to 97%. Results of kinetic experiments showed that removal of Cu\(^{2+}\) is very rapid – in the first 5 minutes 95 % of Cu\(^{2+}\) had been sorbed. Equilibrium was reached in 10 minutes – 96 % of Cu\(^{2+}\) sorbed. This rapid uptake is in accordance with results obtained by other authors, for example Lui and coworkers observed that sorption of Cu\(^{2+}\) by Irish peat was so rapid that equilibrium was reached in 20 minutes [23].

Raw peat did not bind phosphate ions; therefore peat has been modified with iron compounds to improve the sorption effectiveness. Iron based materials have been used as effective sorbents for the removal of phosphorus from different types of wastewater [24]. The maximum sorption capacity of modified peat reached 10 mg/g at 20 °C and initial phosphate concentration of 250 mg/L (Figure 3). Sorption capacity was found to be pH dependent and maximum uptake occurred at pH 2. Kinetic data revealed that 50 % of phosphate ions had been sorbed in the first 5 minutes. Equilibrium was reached after 8 hours with 99.5 % phosphate sorbed.

Sorption experiments of arsenic indicated that sorption onto modified peat is much higher in comparison with peat from peat bog. Modification of peat managed to enhance sorption capacity. The reason is formation of As-O-Fe bond for Fe modified sorbents. The obtained results indicate that the modification method has a great impact on sorbent sorption capacity. As the iron content in both modified peat sorbents are almost equal, it supposedly is affected by the form of iron present in sorbent. Wherewith different is binding ability of iron containing sorbent to arsenic.
To compare sorption isotherms of As (V), As (III) and cacodylic acid (As(org.)), it can be suggested that arsenites has a larger sorption capacity on iron modified peat sorbents (Figs. 4, 5). Therefore, such modified peat samples could be very useful for removing arsenites from polluted areas.

Fig. 4. Arsenic sorption isotherms using modified peat I.

Fig. 5. Sorption of arsenites using iron modified sorbents.

To understand the fate and behavior of arsenic in the environment, it is important to comprehend its interaction with natural environment components under a variety of physicochemical conditions; for example, pH. As (V) maximum binding at pH ~ 7 was observed for both types of modified peat samples. The obtained result indicates that the optimal arsenate uptake occurs between pH 6 and pH 8, when HAsO$_4^{2-}$ and H$_2$AsO$_4^-$ are the predominant species in solution. Our results were in good agreement with the results found in the previous studies [25, 26, 27, 28], where different kind of sorbents to remove As (V) from aqueous solutions were used.

The results of arsenate sorption onto modified peat I at 275, 283, 298 and 313 K showed that sorption capacity increased with temperature. The calculated thermodynamic parameters indicated that the sorption process was spontaneous ($\Delta G^\circ$<0) and endothermic, ($\Delta H^\circ$ = 41.43 kJ/mol). Positive values of standard entropy ($\Delta S^\circ$ = 214 J/mol K) showed increasing randomness at the solid/liquid interface during the sorption of arsenic ions onto modified peat.

4 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.
- Arsenic sorption onto the peat from Dizais Veikenieks peat bog and the modified peat sorbents indicated that using modified peat and also synthetic sorbents sorption is much higher in comparison with peat from a peat bog.
- Arsenate sorption capacity increases with increasing temperature. Calculation of sorption process thermodynamic parameters indicates the spontaneity of sorption process, and it has endothermic nature.

References:


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