Peat and Its Modification Products as Sorbents for Trace Elements

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Heavy metals or trace elements can often be found in industrial wastewater, and their discharge to the environment is a significant threat due to their acute toxicity to aquatic and terrestrial life. The common methods used for removal of toxic metals and trace elements from municipal and industrial wastewater are based on their adsorption onto insoluble compounds – sorbents. Synthetic sorbents usually are quite expensive; therefore, as a prospective approach to metal removal, the use of a natural sorbent – peat or its modification products – was tested.

Keywords: peat, heavy metals, metal sorption.

INTRODUCTION

Heavy metal ions (such as Ni^{+2}, Cr^{+3}, Cu^{+2}, Pb^{+2}, Cd^{+2}, and others) or ions of trace elements (such as AsO_4^{-3}, AsO_2^-, I^-, and others) can often be found in industrial wastewater, and their discharge to the environment is a significant threat due to their acute toxicity to aquatic and terrestrial life, including humans. The common methods used for removing toxic metals and trace elements from municipal and industrial wastewater are based on their adsorption onto insoluble compounds – sorbents, and the separation of the formed sediments. A prospective approach to removal of trace elements from wastewaters could be the use of a natural sorbent – peat or its modification products. Due to presence of organic compounds bearing polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides, peat has a high complexing capacity.

Many efforts have been made to develop effective, cheap sorbents, and several approaches have been recently suggested (Cochrane et al., 2006; Al-Faqih et al., 2008). Besides synthetic sorbents, a variety of plant species and peat have been examined for this aim (Cochrane et al., 2006; Batista et al., 2009). It was determined that better results were obtained with materials containing high concentration of polyphenol (e.g., tannins, lignin, and humic substances) to capture metal ions. Therefore, peat available in bogs has an important role in the removal of heavy metal ions from wastewater along with a role in cleaning oil spills, removing herbicide and dairy waste. Peat is a light brown to very dark organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees (Coccozza et al., 2003). Based on the nature of parent materials, peat is classified into four groups, namely moss peat, herbaceous peat, woody peat, and sedimentary peat. For the past two decades, different kinds of peat have been used especially as cost-effective adsorbents in the treatment of municipal and industrial wastewater (Ramakrishna and Viraraghavan, 1997; Fernandes et al., 2007; Kalmykova et al., 2008; Sen Gupta et al., 2009).

The aim of this study was to investigate the adsorption of Cr^{+3} and Cu^{+2} ions from aqueous solution on peat originated from a high-type bog in Latvia.

MATERIALS AND METHODS

Peat sampling. Peat was collected from the high type peat bog of Dižais Veiķenieks, Latvia. The upper profile of the peat column (from 0 to 30 cm) was taken for future experiments. At first peat was dried at 105 °C and then the sample was ground and sieved trough a 1 mm sieve.

Characterization of the studied natural organic matter. ^{14}C dating was done at the Institute of Geology of Tallinn Technical University (Estonia). Elemental analysis (C, H, N, S, and O) was carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). The ash content was measured after heating 50 mg of peat sample at 750 °C for 8 h and weighted. Cation exchange capacity (the ammonium acetate method) was determined using methods suggested for soil analysis (Tan, 2005).

Kinetic studies. The rate of metal ion uptake was measured under batch conditions using Cr^{+3} and Cu^{+2} metal solutions. For each of the sorption kinetic tests, 12.5 g of peat were suspended in 1000 ml of metal ion solution in the reaction vessel at a constant temperature (20 °C). The initial chromium (III) and cuprum (II) concentration was 25 mg/l. pH was adjusted to 5.5 ml samples were withdrawn by syringe at intervals of increasing duration up to 360 min. The concentration of equilibrium solution was determined with AAS (the Perkin Elmer AAnalyst 200).

Metal Sorption Experiment

Experiments on Cr^{+3} and Cu^{+2} sorption onto peat matter and its particle size fractions were carried out in the batch system. The solutions with different concentration of metals – 10, 50, 100, 150, 200, 250, 300, 350, 400 and 500 mg/l were prepared from the stock solution of $CrCl_3 \times 6H_2O$ and $Cu(NO_3)_2 \times 3H_2O$ with metal concentration of 1000 mg/l. One gram of peat was thoroughly mixed with 80 ml of metal solution, and initial pH 5.5 of the system was adjusted. Contact time was 24 h on a rotary shaker at 150 rpm, triplicate samples were used, and metal contents in the input and equilibrated solutions after filtration were determined with AAS.

Bound loads of metal were calculated as a difference from initial and equilibrium metal concentration in solution per mass unit of peat, and the results were presented as equilibrium mass isotherms.

RESULTS AND DISCUSSION

To study the possibilities to use peat as a sorbent, a raised bog peat of industrial importance was used. The botanical composition of the deepest layers of peat in the studied bogs is mostly high-type cotton-grass-sphagnum peat and high-type fuscum peat, but in the upper layer it is high-type fuscum peat. The age of the samples varies from 400 to 2260 years, and their decomposition degree (on the von Post scale) varies from H_2 to H_6. The metal concentration in the peat mass is comparatively low, indicating low levels of contamination. An example of the studied peat materials is given in Table.

Table. **The physicochemical characteristics of the studied peat of the Dižais Veiķenieks Bog**

Characteristics		Parameters	
Peat type		High-type fuscum peat	
pH		3.01	
Age, years		400	
Elemental composition			
C, %	45.67	S, %	0.69
H, %	5.65	O, %	46.87
N, %	0.73	Ash, %	1.08
Metal content in peat, µg/g			
Na	124	Fe	392
Mg	741	Cu	1.14
K	114	Zn	11.6
Ca	1860	Cr	1.02
Mn	5.6	Pb	6.6
Cation exchange capacity, µg/g			
Na	94	K	142
Mg	605	Ca	1370

The adsorption properties of peat have been studied batchwise and in a dynamic regime. The adsorption of ions onto peat increases with increasing time and reaches a maximum value within 150 min, thereafter it remains constant

(Fig. 1). However, significant differences exist between sorption kinetics of divalent Cu^{+2} ions and trivalent Cr^{+3} ions (in the case of the latter, the equilibrium is reached much slower).

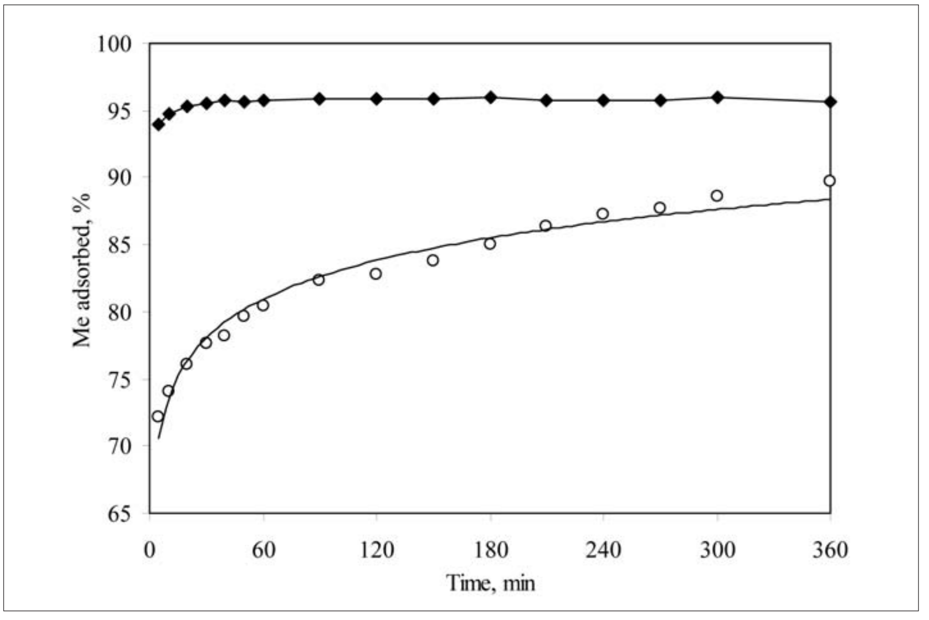

Figure 1. **Kinetics of the adsorption process of Cu^{+2} (♦) and Cr^{+3} (○) onto peat**

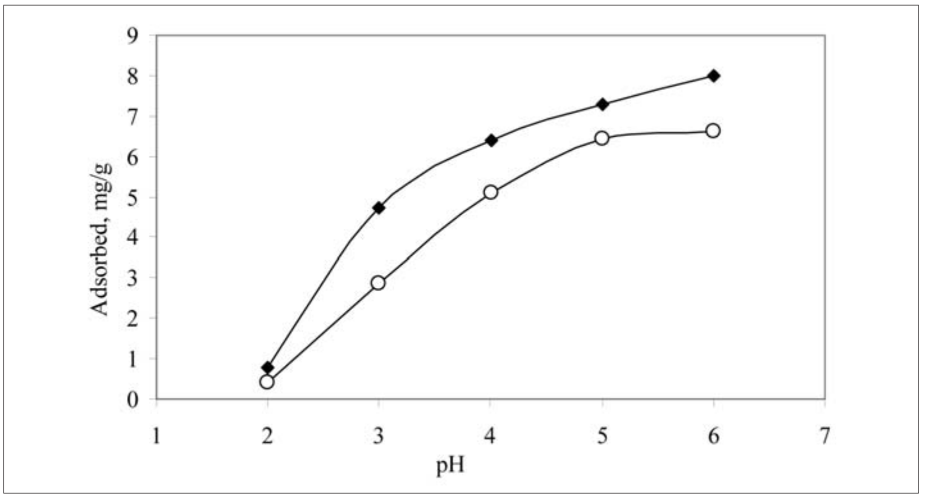

Figure 2. **Effect of pH on sorption of Cu^{+2} (♦) and Cr^{+3} (○) onto peat**

Adsorption of the studied ions onto peat largely depends on pH and on ion activity in the studied solutions (Fig. 2, 3). Sorption is the lowest in acidic environment, but the character of dependence on pH is similar in Cu^{+2} and Cr^{+3} ions. However, high sorption capacity can be reached within concentration ranges common for wastewaters and wastewaters of galvanic industry. Also, the ionic strength of the adsorption media can influence the sorption capacity of the studied peat samples; however, the dependence on the ionic strength is not very high in a comparatively large interval of concentrations, and the sorption capacity is relatively stable in concentration intervals common to wastewaters.

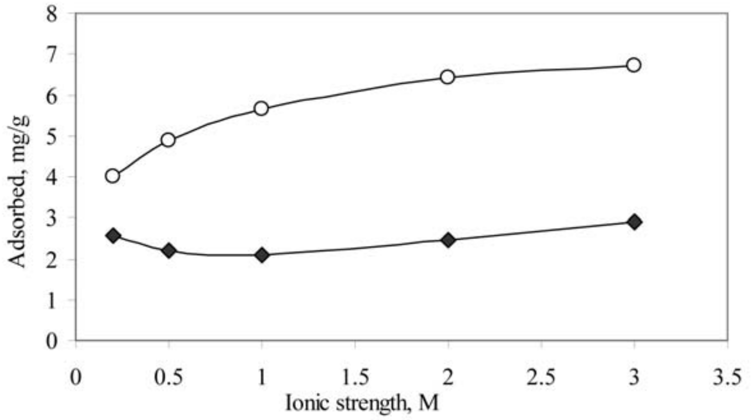

Figure 3. **Effect of the ionic strength on sorption of Cu^{+2} (♦) and Cr^{+3} (○) onto peat**

As shown in Fig. 4, when the initial concentrations of aqueous solutions are changed from 1 mg/l to 400 mg/l, the absolute number of ions adsorbed per gram of peat increases from 0.7 mg/g to 13 mg/g at 20 °C and pH 5.5. Furthermore, the percentage of adsorption decreases with increasing concentration. The maximum percentage of removal by peat was about 95% in the range of concentrations investigated above and at a liquid-to-solid ratio of 50 ml of solution to 0.5 g f adsorbent. The adsorption isotherms of Cu^{+2} and Cr^{+3} on peat (Fig. 4) demonstrate the level of sorption capacity of the studied peat samples: despite the numbers of the sorbed metal increasing from 6 mg/l to 8.5 mg/l (in the case of Cr^{+3}) and from 8 mg/l to 13 mg/l (in the case of Cu^{+2}), we could assume that starting from the metal ion concentration level of 100 mg/l in an aquatic solution the sorption capacity of the peat sorbent is reached.

One of the major obstacles in the way of industrial use of peat as a sorbent is the significant heterogeneity of peat as a natural material (Gondar et al., 2005), especially in comparison with synthetic sorbents. To assess the impact of peat composition heterogeneity, sorption of Cu^{+2} and Cr^{+3} onto peat from a bog profile (0–118 cm) was studied (Fig. 5, 6). The adsorbed amounts of the studied metals do not change randomly with the depth of peat location and demonstrate the impact of peat heterogeneity on the metal sorption capacity.

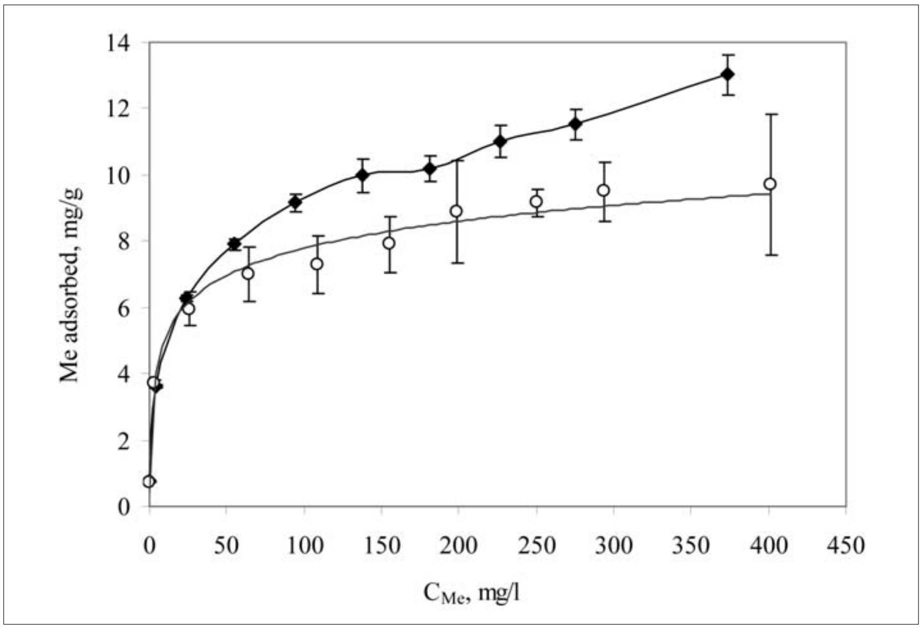

Figure 4. **The adsorption isotherms of Cu^{+2} (♦) and Cr^{+3} (○) on peat**

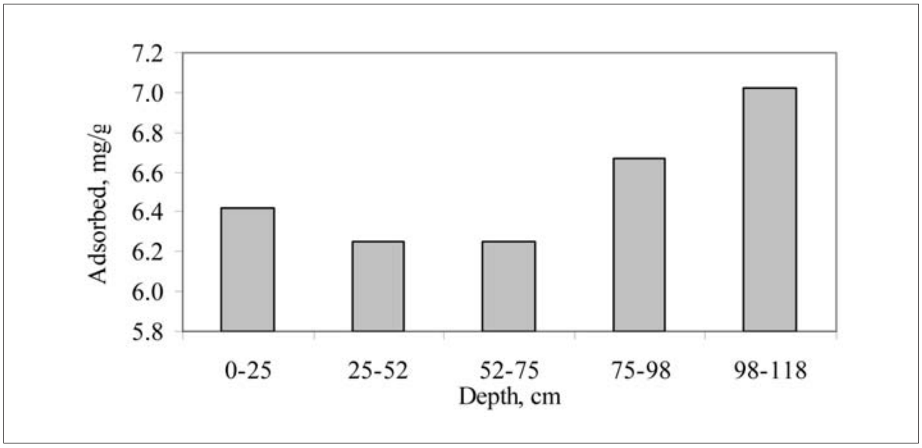

Figure 5. **Adsorption of Cu^{+2} onto peat depending on the depth of the peat column**

However, the variability of the amount of the adsorbed metal is not high in the studied peat profile and does not exceed 15%. It is possible to state that, in general, the sorption character of metal ions onto peat is similar in all the studied peat samples.

The cation exchange capacity of peat can be considered to be the main factor determining peat sorption capacity – not so much the number of acidic and complex-forming functional groups, rather the availability of sites capable to adsorb metal ions, characterized by the cation exchange capacity (Fig. 7).

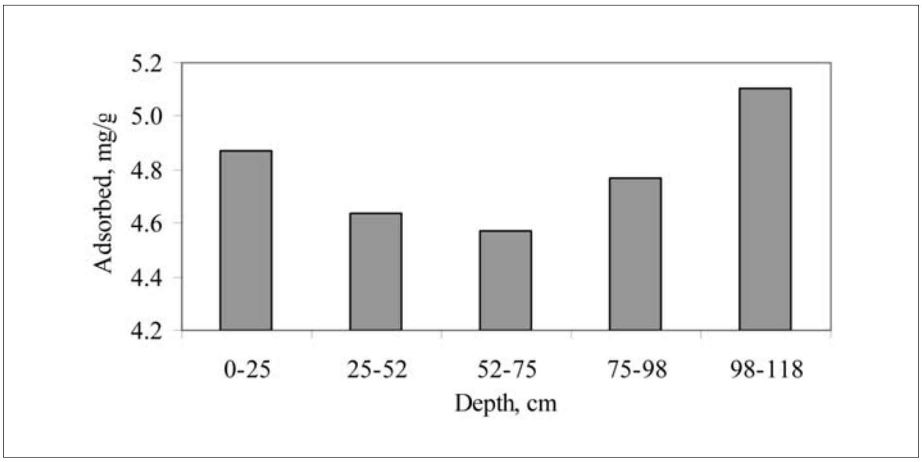

Figure 6. **Adsorption of Cr^{+3} onto peat depending on the depth of the peat column**

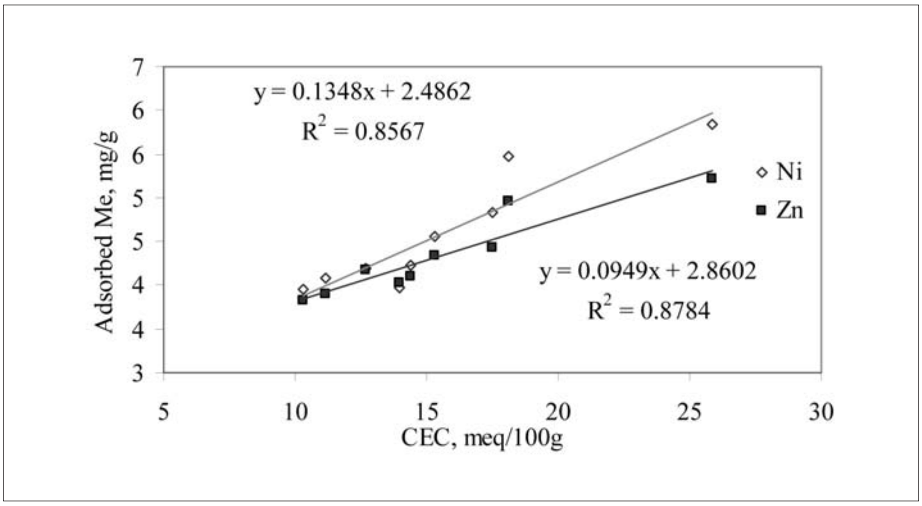

Figure 7. **Correlation between the amount of adsorbed Ni^{+2} and Zn^{+2} and the cation exchange capacity of the studied peat samples**

From the perspective of practical application possibilities, of importance are the possibilities to use sorbent in a dynamical regime. To test this possibility, we have done test runs (Fig. 8). As we can see, peat as a sorbent does have good quality breakthrough curves confirming reasonably high sorption capacities of peat in respect to the studied metal ions and the possibilities to use peat as a sorbent.

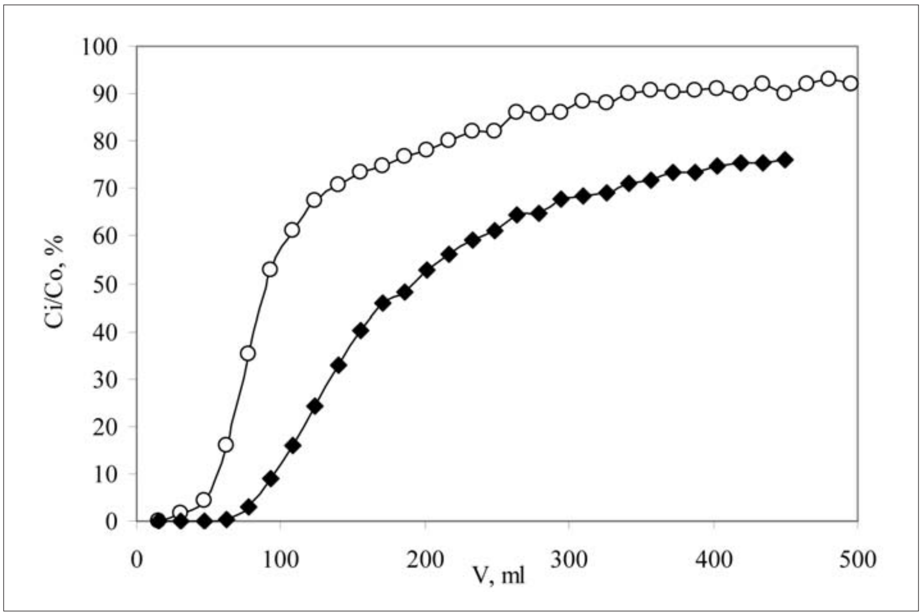

Figure 8. **Breakthrough curves of Cu^{+2} (◆) and Cr^{+3} (○) from a column packed with peat (inlet metal concentration – 100 mg/l, flow rate – 2ml/min)**

CONCLUSIONS

The common methods used for removal of toxic metals and trace elements from municipal and industrial wastewater are based on their adsorption onto insoluble compounds – sorbents. Synthetic sorbents usually are quite expensive; therefore, as a prospective approach to metal removal, the use of a natural sorbent – peat or its modification products – was tested. Peat from an ombrotrophic bog in Latvia was tested considering the possibilities to use it as a sorbent for removal of trace elements. Peat as sorbent was proved to have a relatively high sorption capacity in respect to trace elements, it can be used batchwise and in a dynamic regime and is a relatively robust and reliable sorbent regarding pH, the ionic strength, and the amounts of sorbed metal.

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