

PEAT SORBENTS FOR ARSENIC REMOVAL

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SUMMARY

Arsenic contamination of waters is a global problem; therefore, new types of sorbents are needed. A way forward lies in developing new sorbents by working with sorbents based on natural materials because they often are cheap and their use is environmentally friendly. Peat, peat modified with iron compounds, and iron humates were prepared and tested for sorption of arsenic 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 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 the sorption process. It is of endothermic nature.

KEY WORDS: peat sorbents, arsenic, adsorption, adsorption model

INTRODUCTION

Peat is an important natural resource with a wide application potential. Chemically and thermally treated peat can be used in production of humic substances, alcohols, activated carbon and other materials (Spedding, 1988). Owing to a considerable number of functional groups in peat, it can be used as a sorbent. Peat can be used as a sorbent for different metals, but the effect is dependent on its origin. Interaction between peat and pollutants may occur via formation of hydrogen bonds, cation exchange and chelate complex formation (Twardowska et al., 1999).

Arsenic contamination of waters is a severe problem (Zhang and Itoh, 2005; Nemade et al., 2009; Dupont et al., 2007). Drinking water supplies in polluted areas contain dissolved arsenic in excess of 10 µg/L which is the maximum level recommended by the World Health Organization. More than 40 million people are suffering from arsenic contamination worldwide. (Dupont et al., 2007). Arsenic enters waters through a combination of natural processes as well as through a range of anthropogenic activities.

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 (Dupont et al., 2007). 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 Northern countries. The aim of this study was the investigation of peat, modified peat and iron humates application possibilities for arsenic sorption.

MATERIALS AND METHODS

For the preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) 10-15 MΩ/cm was used throughout. Analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification. All chemicals used in this study were of high purity (usually “suprapure” grade unless otherwise stated).

The studied arsenic compounds were obtained from Sigma-Aldrich ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{C}_2\text{H}_7\text{AsO}_2$) and AsNaO_2 was obtained from Fluka.

To investigate arsenic sorption on peat, we used peat from the Dizais Veikenijs peat bog (Latvia) and also in two ways with iron modified peat sorbents. Modification methods were developed using similar research methods as published in literature (Gu, 2005; Zhang and Itoh, 2005; DeMarco et al., 2003). Two different peat modification methods were selected. One of the methods was based on peat impregnation with iron hydroxide (modified peat I), and the other method was based on peat impregnation with iron salts (modified peat II). Moreover, we investigated arsenic sorption on iron humates. For preparation of iron humates commercially produced potassium humate was used. It was produced by SIA Intelecco using peat from the Ploce peat bog (Latvia).

In this study, a scanning electron microscope (SEM), a specific surface area, Fourier transformation infrared spectra (FT-IR), and iron content were used to characterize the sorbents. The obtained results indicate the success of modification methods.

Sorption experiments were carried out using arsenic solutions that were made dissolving the necessary amount of arsenic compound ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, AsNaO_2 and $\text{C}_2\text{H}_7\text{AsO}_2$) in distilled water so that concentrations of arsenic were 300, 200, 100, 50, 25, 10 and 5 mg/L; in several cases it was also 1000, 800, 600 and 400 mg/L. In 100 mL glass vessels 0.5 g of sorbent was poured with 40 mL of necessary arsenic solution. Vessels were shaken for 24 h at room temperature. After that the suspension was filtered, and total dissolved arsenic analyses of samples were carried out using a Perkin-Elmer AAnalyst 200 atomic absorption spectrophotometer (AAS) with flame atomization.

RESULTS

Sorption experiments were carried out using peat, modified peat sorbents as well as iron humate. We used two inorganic forms of arsenic As (V) and As (III) and organic form – cacodylic acid ($\text{C}_2\text{H}_7\text{AsO}_2$).

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

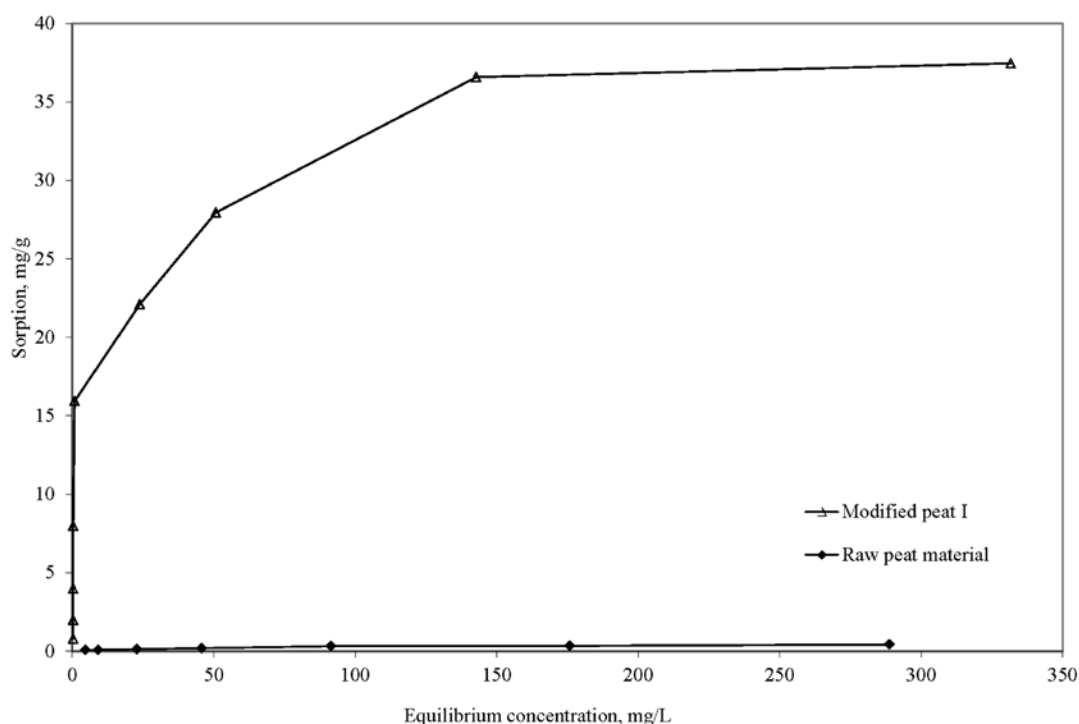


Figure 1. As (V) sorption isotherm using modified peat I and raw peat material

Sorption experiments of arsenic indicated that sorption onto modified peat is much higher in comparison with non-modified peat (Fig. 1). Modification of peat managed to enhance the sorption capacity. The reason could be the 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 the sorbent, wherewith a different binding ability of iron containing sorbent to arsenic is present.

To compare sorption isotherms of As (V), As (III) and cacodylic acid (As(org.)), it can be suggested that arsenites have a larger sorption capacity on iron modified peat sorbents (Figs 1-2). Therefore, such modified peat samples could be very useful for removing arsenites from polluted areas.

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 results indicate that the optimal arsenate uptake occurs between pH 6 and pH 8, when HAsO_4^{2-} and H_2AsO_4^- are the predominant species in solution. Our results were in good agreement with the results found in previous studies (Buschmann et al., 2006; An et al., 2005; Dambies et al., 2004; Anirudhan and Unnitha, 2007), where different kinds of sorbents to remove As (V) from aqueous solutions were used.

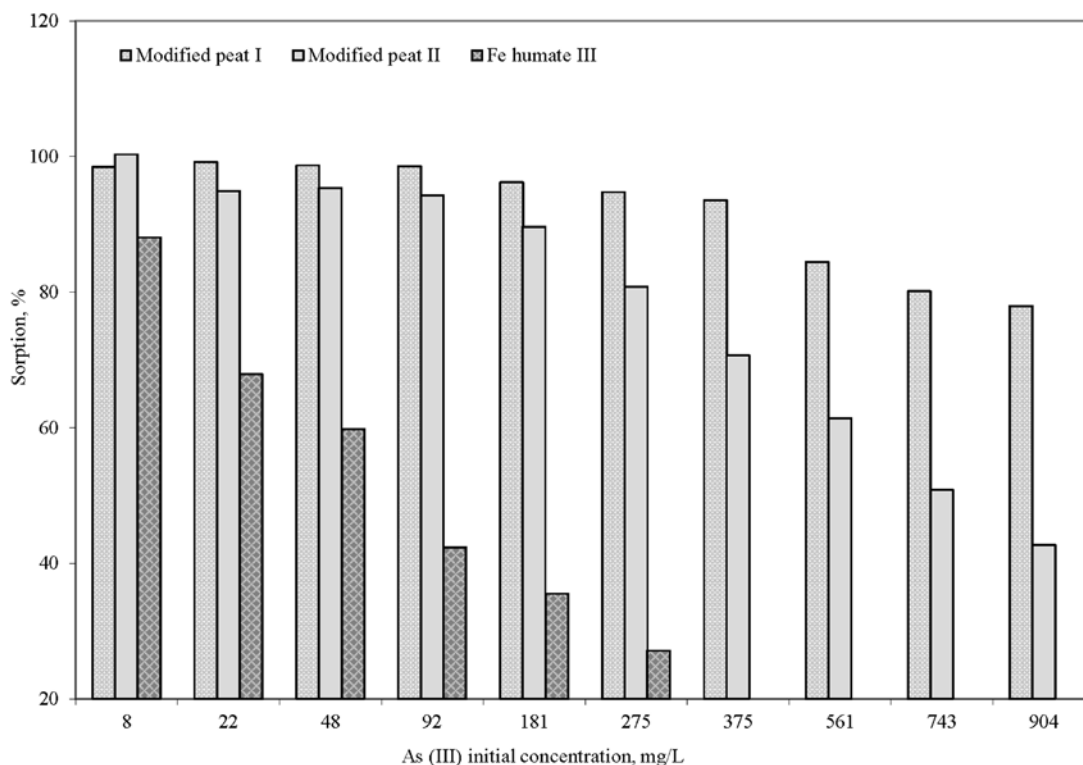


Figure 2. Sorption of arsenites using iron modified sorbents

The results of arsenate sorption onto modified peat at 2, 10, 25 and 40 ° C showed that sorption capacity increases with temperature (Fig. 3.). According to Partey the reason for this could be a diffusion rate increase of adsorbate molecules as the temperature rises, as well as changes of sorbent pore size. An increase of temperature may also affect an increase in proportion and activity of arsenic ions in solution, the affinity of the ions for the surface, or the charge and therefore the potential of the surface of sorbent (Partey et al., 2008).

We used the linear Langmuir equation to determine the Langmuir isotherm constant and after that thermodynamic parameters were calculated as well. The negative ΔG° values ($\Delta G^\circ < 0$) for arsenate sorption onto modified peat or synthetic sorbent indicates that arsenic sorption process has a spontaneous nature. Decrease in ΔG° with increasing temperature implies stronger sorption at higher temperatures. The ΔH° value is positive ($\Delta H^\circ = 41.43$ kJ/mol) indicating the endothermic nature of the arsenic sorption onto modified peat or synthetic sorbent. The endothermic nature of the sorption of the arsenates can be attributed to the disruption of water molecules from the surface. This allows direct bonding of the arsenic to the surface hydroxyl groups. The positive ΔS° ($\Delta S^\circ = 214$ J/mol K) values reflect the affinity of sorbent for arsenate and suggest some structural changes (Partey et al., 2008; Ho, 2005).

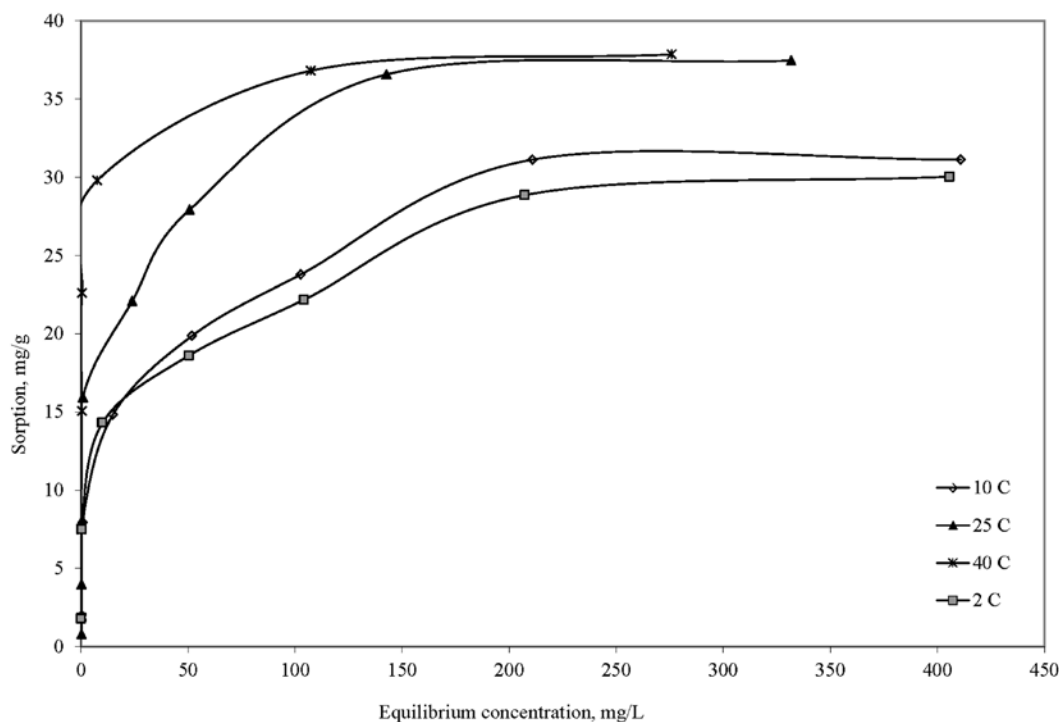


Figure 3. As (V) sorption onto modified peat – dependence in temperature

CONCLUSIONS

Arsenic sorption onto peat is much weaker than on modified peat and iron humate. Peat modification with iron compounds has managed to enhance sorption capacity. The reason probably could be the forming of As-O-Fe bond for Fe modified sorbents. The best sorbent for arsenic removal is peat modified with iron oxo(hydroxides) because it is able to adsorb arsenates, arsenites as well as the organic form of arsenic.

Sorption at different pH values mainly is influenced by the form of arsenic ion present in solution. Arsenate sorption isotherm data best fit the Langmuir isotherm model.

Arsenate sorption capacity increases with increasing temperature. Calculated thermodynamic parameters indicate that the sorption process is 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) shows increasing randomness at the solid/liquid interface during the sorption of arsenic ions onto modified peat.

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