

Linda ANSONE¹, Linda EGLITE¹ and Maris KLAVINS^{1*}

REMOVAL OF ARSENIC COMPOUNDS WITH PEAT, PEAT-BASED AND SYNTHETIC SORBENTS

USUWANIA ZWIĄZKÓW ARSENU ZA POMOCĄ TORFU, SORBENTÓW NA BAZIE TORFU I SORBENTÓW SYNTETYCZNYCH

Abstract: Arsenic contamination of waters is a global problem; therefore, new approaches for its removal are needed. Peat, peat modified with iron compounds, iron humates and polymeric cation exchangers modified with iron were prepared and tested for sorption of arsenic compounds in comparison with weakly basic anionites. The highest sorption capacity was observed when peat sorbents modified with iron compounds were used. 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 sorption process and its endothermic nature.

Keywords: peat, synthetic sorbents, arsenic, sorption, sorption model

Environmental pollution with arsenic is a significant environmental problem. Polluted drinking water can cause important threats to the human health; therefore, it is important to study chemical processes taking place in the elements when they reach the environment, environmental pollution and solutions for environmental remediation, for example, development of new, environmentally friendly sorbents.

Arsenic contamination of waters is an extremely serious problem in Bangladesh, Vietnam, Taiwan, and India. Moreover, Chile, Mexico and Western United States indicated that many of their natural water resources have been contaminated with arsenic [1-4]. Furthermore, drinking water supplies in polluted areas contain dissolved arsenic in excess of 10 µg/dm³, which is the maximum level recommended by the World Health Organization [1, 4].

Arsenic enters waters through a combination of natural processes, such as rock and mineral weathering reactions, biological activity, and volcanic emission, as well as through a range of anthropogenic activities. Anthropogenic arsenic sources include discharges from various industries, such as smelting, petroleum refinery, fertilizer production, use of insecticides, herbicides as well as glass manufacturing [1, 5].

¹ Department of Environmental Science, University of Latvia, Raina blvd. 19, Riga, LV 1586, Latvia

*Corresponding author: maris.klavins@lu.lv, phone +371 67334096, fax +371 7332704

Arsenic is predominantly present as inorganic species - trivalent arsenite As(III) and the pentavalent arsenate As(V) - in natural waters. As(V) is a thermodynamically stable form and generally predominates in surface waters, but reducing conditions, such as in anaerobic ground waters are favourable for arsenite.

It has been established that the toxicity of arsenic depends on its speciation form and As(III) is more toxic, soluble and mobile for biological systems in comparison with As(V) compounds [5, 6]. In the pH range of most natural waters ($6.5 \div 7.5$), As(III) predominantly exists as uncharged (H_3AsO_3^0) specie due to the fact that it is very difficult to remove this form of arsenic by the conventionally applied physicochemical treatment methods [1, 6].

Although the removal of arsenic from groundwater is based on various principles - such as oxidation, coagulation, precipitation, ion exchange, adsorption and reverse osmosis - adsorption and ion exchange are considered to be the best methods [7-9]. Adsorption technique is one of the most popular methods because of its simplicity and potential of regeneration. It is also economical and easy to set up [4, 6, 7]. A wide range of adsorbents have been used for the removal of arsenic from water and wastewater. There are numerous methods which use iron oxides, hydroxides, oxyhydroxides and other iron compounds as promising adsorbents for removing arsenic from water [6, 5]. According to previous studies, amorphous hydrous ferric oxide (FeOOH), goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are also promising effective adsorptive materials for removing arsenate and arsenite from aqueous systems. Among chemically modified adsorbents, the solid phases loaded with iron species, due to formation of stable inner and outer sphere surface complexes that result from interaction of As_2O_3 or AsO_4 with FeO_6 polyhedra, are particularly efficient in removing the As(III) and As(V) ions from contaminated waters [6].

Peat is one of important natural resources with a wide application potential. Chemically and thermally treated peat can be used for the production of humic substances, activated carbon and other materials [1]. Owing to a considerable number of functional groups in peat, it can also be used as a sorbent for metal ions, keeping in mind that 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 [2].

Sorption as an approach and sorbents as materials have found widespread application in different areas of production and everyday life; and new areas of sorbent application are still emerging, thus calling for new types of sorbents. One of the directions on the way of developing new sorbents is aimed at the sorbents based on natural materials, since they often are cheap, their use is environmentally friendly and they are recyclable or can be utilized in environmentally friendly way, while their efficiency is similar to synthetic sorbents. In this respect, peat is a prospective matrix for sorbent development. Search for peat-based sorbents is also topical considering the available significant peat resources in Northern countries.

The aim of this study was to investigate and compare peat, modified peat and synthetic sorbent application possibilities for arsenic sorption.

Materials and methods

For the preparation of solutions, high purity water Millipore Elix 3 (Millipore Co.) $10 \div 15 \text{ M}\Omega/\text{cm}$ was used throughout. Analytical quality reagents (usually "suprapure" grade,

unless otherwise stated) (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification.

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 Dizais Veikenieks peat bog (Latvia). We also used in two ways with iron-modified peat sorbents, synthetic sorbent (AN-221) (Reachim) and with iron modified commercially produced sorbent - Amberlite 200C Na (Rohm and Haas).

Modification methods were developed using methods similar to those published in literature [4, 10, 11].

Furthermore, we investigated arsenic sorption on iron humates. For preparation of iron humates, commercially produced potassium humate was used. It was produced by Intelecco SIA, using peat from Ploce peat bog (Latvia). Chloromethylated polystyrene divinylbenzene modification with polyethylene imine was done to use it as a sorbent. Chloromethylated polystyrene divinylbenzene (Cl - 15.05%) was produced by Reachim (Russia).

Modified peat I. Method was based on peat impregnation with iron hydroxide. 0.25 mol (67.55 g) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 250 cm³ distilled water, adding 250 cm³ 3M NaOH and leaving for 2-4 hours. Then reaction mixture was rinsed and decanted in 1 dm³ vessel. A dispersion of $\text{Fe}(\text{OH})_3$ was mixed in 100 g of homogenized peat. After filtration, the reaction product was rinsed with approximately 0.5 dm³ deionized water and heated for 4 hours at 60°C temperature. After that, the iron content was determined.

Modified peat II. Method was based on peat impregnation with iron salts. 0.25 mol iron chloride hexahydrate was dissolved in 540 cm³ water. 100 g homogenized peat was mixed with 540 cm³ iron chloride hexahydrate and left overnight. Then the mixture was filtered, the wet peat was poured with 500 cm³ 1.5 M NaOH and left for one hour. Reaction mixture was filtered and rinsed with deionized water up to pH ~7. The product was heated for 4 hours at 60°C temperature.

Fe humate I. Commercially produced solution of potassium humate was used for preparation of iron humate I. Potassium humate was obtained from peat of Ploce bog (Latvia). 500 cm³ 10% $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was added to the solution of potassium humate, suspension was mixed and left for 24 h. After that, the iron humate that has formed was filtered off and heated for 4 hours at 60°C temperature. Then the product was rinsed with 200 cm³ 1 M NaCl and distilled water and dried.

Fe humate II. We used humic acids (HA) from Ploce bog (Latvia) for preparing iron humate II. 100 g HA was dissolved in 2 dm³ 0.5 M NaOH. 500 cm³ 10% $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was added to the humic acid solution, left for 24 h and filtered. The obtained precipitate was dried, and 1 dm³ 10% $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was added to 2 dm³ of filtrate and left for 4 h, then filtered. After that, the product was heated at 150°C temperature for 3 h and washed with 250 cm³ distilled water, 50 cm³ ethanol and dried.

Amberlite-Fe. 709 cm³ 4% (0.105 mol) $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ was added to 50 g (0.105 mol) commercially produced Amberlite 200C Na at pH~2, left overnight, then adding NaOH and NaCl solutions, each 252 cm³ 5% (0.315 mol). Reaction mixture was left for 24 h and then filtered, rinsed and washed with 50/50 ethanol/water solution, followed by a mild thermal treatment at 60°C temperature for 1 h [11].

CCD-PEI. 50.07 g chloromethylated polystyrene divinylbenzene (Cl - 15.05%) was added to 200 cm³ *N,N*-dimethylformamide and 25 g of polyethyleneimine. Reaction mixture

was stirred for 24 h at 75°C. The obtained product was filtered, rinsed with *N,N*-dimethylformamide, acetone and water. The reaction product was treated with 0.5 M Na₂CO₃ for 24 h, after that washed with methanol and dried.

Immobilized humic substances. Synthesis was based on immobilization of humic substances on chloromethylated polymer. 50 g chloromethylated polymer was added to 34.5 g K₂CO₃, 10 g humic substances (soil humic substances) and 500 cm³ 50% *N,N*-dimethylformamide solution. Reaction mixture was heated in water bath for 20 h at 80°C temperature with continuous stirring. The obtained precipitate was filtered and washed with 20 cm³ *N,N*-dimethylformamide, 500 cm³ 0.1 M Na₂CO₃, 1000 cm³ deionized water, 100 cm³ 0.1 M HCl, 1000 cm³ deionized water and 500 cm³ acetone.

Characterization of sorbents

Iron concentration in the studied sorbents was determined, using *atomic absorption spectrometry* (AAS).

Fourier transformation infrared spectra (FT-IR) were obtained for all sorbents, using Perkin Elmer Spectrum BX FT-IR spectrometer, and data processing was made by Spectrum v 5.3.1 program. Sample was pressed in KBr pellets and the spectra were usually recorded in the range of 4000÷400 cm⁻¹ with 4 cm⁻¹ resolution. *Scanning electron microscopy* (SEM) data were obtained by Scanning electron microscope JOEL ISM T-200. Samples were measured in secondary electron regime, with SEM operating voltage 25000 V. The surface area was measured by Surface area and pore size analyzer NOVA 1200e, and data processing was made by NovaWin2 program. BET method was used for the specific surface area measurements.

Sorption experiments

Arsenic solutions were made by dissolving the necessary amount of arsenic compound (Na₂HAsO₄·7H₂O, AsNaO₂ and C₂H₇AsO₂) 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. 0.5 g of sorbent was poured in 100 mL glass vessels with 40 mL of necessary arsenic solution. Vessels were shaken for 24 h at room temperature. After that, suspension was filtered, and arsenic analyses of samples were carried out using a Perkin-Elmer AAnalyst 200 atomic absorption spectrophotometer (AAS) with flame atomization.

Influence of pH. To determine the pH influence of sorption process, we used citrate buffer solution on a pH interval 3÷6 and borax buffer solution on a pH interval 7÷9. In glass vessels, 0.5 g of peat was poured with buffer solution, left for 24 h, then measured for pH and poured with the necessary amount of arsenic stock solution; the reaction mixture was shaken for 24 h at room temperature, filtered, and measured for pH. The arsenic concentration used for the final solution was 100 mg/L. The filtrate was analyzed with AAS.

Influence of temperature. Sorption experiments were made as previously described: sorbate/sorbent relations were not changed, and the experiments were made at 275, 283, 298 and 313 K.

Results and discussion

Due to widespread groundwater pollution with arsenic and good perspectives of possible application of sorbents for arsenic removal, we studied sorbents based on natural and synthetic materials, using different modification methods. Two of them were based on peat impregnation with iron compounds (modified peat I and modified peat II); according to another approach, iron humates were obtained. Selected reaction conditions were used, because the results of preliminary experiments were satisfactory and comparable with those reflected in literature [11]. Synthetic sorbent modification with iron compounds was done according to DeMarco et al study [11]. Because polymers are often used as sorbents with effective results, we also studied chloromethylated styrene-divinylbenzene (CCD-PEI) copolymer and immobilized humic substances for the removal of arsenic.

Scanning electron microscope (SEM) figures, data of specific surface area analysis, Fourier transformation infrared spectra (FT-IR) and iron content were estimated to characterize the obtained sorbents. The type, age, element content, cation exchange capacity (CEC) and content of carboxylic groups (COOH, meq/g) were determined for the raw peat material and humic substances used in this study. Characterization of the raw peat material is shown in Table 1, and characterization of humic substances used in this study is shown in Table 2, respectively.

Characterization of peat used in this study

Table 1

Parameters		Peat from Dizais Veikenijs peat bog (Latvia), depth 25÷52 cm
Peat type		Raised bog <i>fuscum</i> peat
Peat age, ^{14}C years		730 ± 50
Element content	C [%]	48.19
	H [%]	5.53
	N [%]	0.66
CEC [cmol/kg]		6.6

Characterization of humic substances used in this study

Table 2

Parameters		Ploce bog peat HA	Soil HA
Element content	C [%]	53.38	39.13
	H [%]	4.87	4.27
	N [%]	2.03	3.41
COOH [meq/g]		5.59	4.4

Specific surface area is one of the parameters that were used to characterize sorbents. The specific surface area (according to BET) was $3.196 \text{ m}^2/\text{g}$ for raw peat and 3.055 and $5.757 \text{ m}^2/\text{g}$ for modified peat I and modified peat II, respectively. Considerably lower surface area was for iron humate - $0.288 \text{ m}^2/\text{g}$ and for synthetic sorbent AN-221 - $0.589 \text{ m}^2/\text{g}$. The highest specific surface area was for macroreticular Amberlite-Fe, CCD-PEI and immobilized humic substance sorbents - 22.25, 25.53 and $26.05 \text{ m}^2/\text{g}$ accordingly. The obtained results show that peat modification has affected the specific surface area. It is assumed that sorbent with larger specific surface area could have higher sorption capacity.

Iron content was determined for all sorbents modified with iron compounds. The iron content for the sorbent that was synthesized using the method based on peat impregnation with $\text{Fe}(\text{OH})_3$ was 47.0 ± 1.0 mg/g (modified peat I); using peat impregnation with iron salts, the iron content was 47.3 ± 0.9 mg/g (modified peat II); for iron humate I - 26.2 ± 0.3 mg/g; iron humate III - 22.8 ± 0.4 ; and the iron content for Amberlite-Fe was 22.5 ± 0.4 mg/g. The iron content in raw peat material was 0.095 mg/g [12]; therefore, it can be suggested that modification with iron has been successful. Differences of iron content in Fe humates result from different original materials as well as from differences in humate synthesis, for instance, added iron amount, heating temperature and heating time.

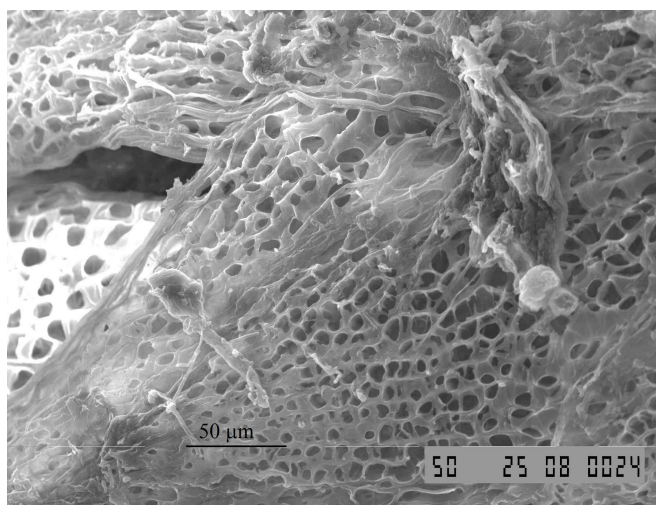


Fig. 1. SEM figure of raw peat material

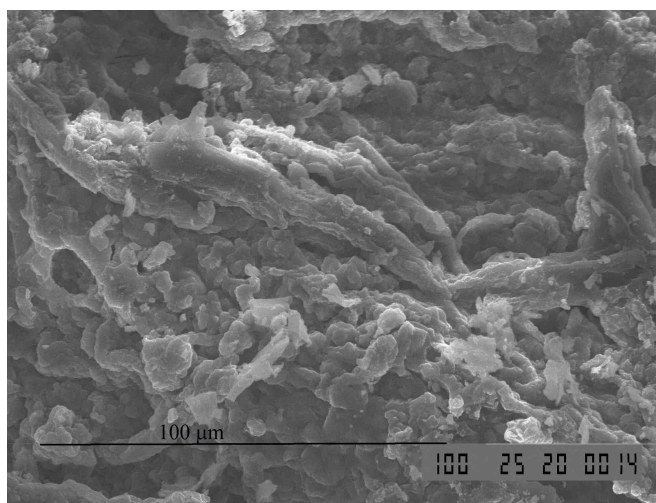


Fig. 2. SEM figure of modified peat I

It can also be seen from scanning electron microscope figures (Figs. 1 and 2) that the used sorbents have different surface morphologies. Decomposed plant residues are characteristic of raw peat material (Fig. 1).

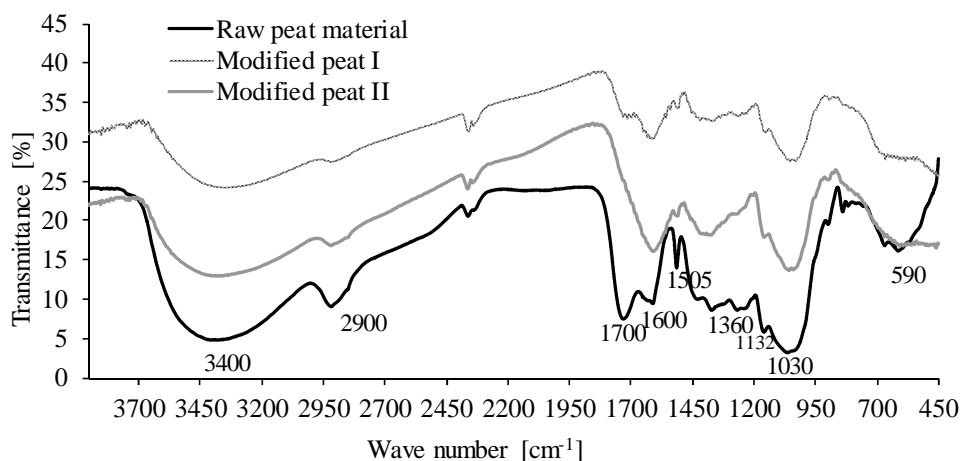


Fig. 3. FT-IR spectra of raw peat and modified peat sorbents

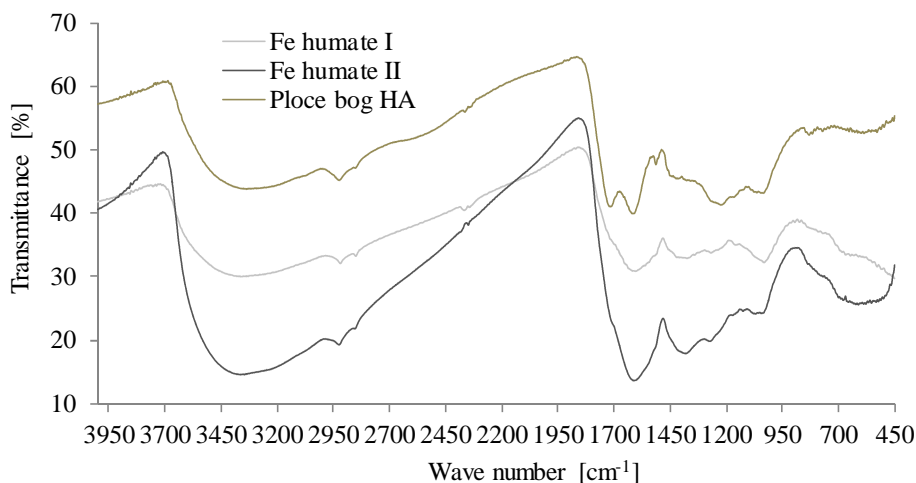


Fig. 4. FT-IR spectra of peat humic acid and Fe humates I and II

Comparing raw and modified peat materials, FT-IR spectra show structural changes as a result of modification (Fig. 3). Major changes can be observed at $1700\div500\text{ cm}^{-1}$. Carbonyl group signal ($1700\div1725\text{ cm}^{-1}$) has disappeared for modified peat sorbents, thus indicating salt formation. Conjugated C=C double bond signal (1600 cm^{-1}) is characteristic for all peat sorbents. Aromatic nitrocompound N-O bond asymmetric valence vibrations

(1505 cm^{-1}) signal for modified peat samples is less intensive. Alcohol -OH group deformation vibration can be observed at 720÷590 cm^{-1} , and this signal is more intensive for raw peat material [13]; it also indicates structural changes after modification, which could be explained with salt formation.

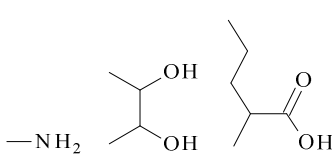
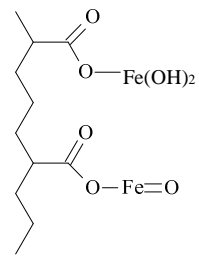
FT-IR spectra of iron humates and Ploce bog HA (Fig. 4) show differences from 1600 to 450 cm^{-1} , thus indicating that structural differences have arisen during modification process. Hydrogen bond valence vibrations of hydroxyl groups can be observed at 3570÷3200 cm^{-1} . Methyl group valence vibrations can be observed at 2900 cm^{-1} . This signal as well as the hydroxyl group signal is characteristic of iron humates and humic acids, thereby indicating the presence of these functional groups. Carbonyl group signal (1700÷1725 cm^{-1}) can be observed only for humic acids. Obviously, it has disappeared for iron humates as a result of modification. Carbonyl group could be involved in salt formation. Aromatic ring valence vibrations (1615÷1580 cm^{-1}) are characteristic of iron humates and humic acids [13].

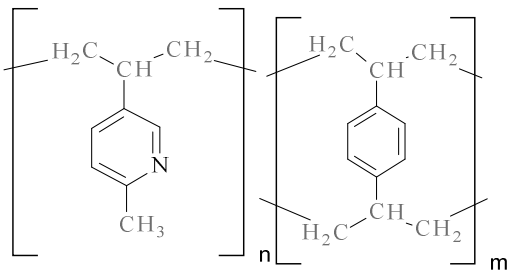
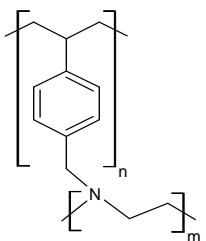
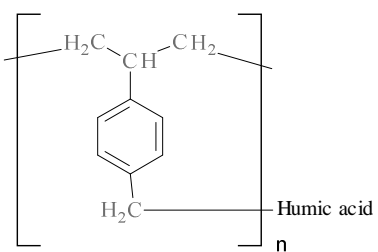
It is obvious that the FT-IR spectra of all sorbents are different, although differences can be seen only for separate functional group signals. Therefore, it is not possible to have a complete conception about the modification results with using FT-IR spectra.

For raw peat, the main functionalities that can bind arsenic are carboxylic and amino groups, while the formation of As-O-Fe bond could support interaction between arsenic and iron-modified sorbents. Possible functional groups of used sorbents that can bind arsenic are shown in Table 3.

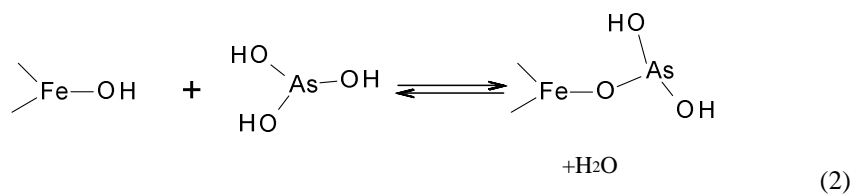
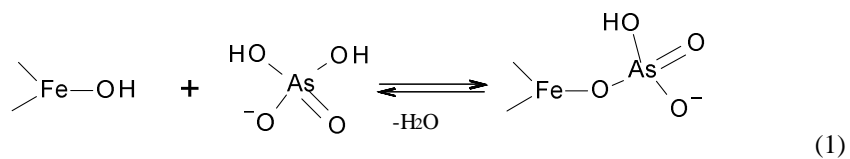
Table 3

Functional groups of studied sorbents

Sorbent	Functionality
Raw peat	
Modified peat	

AN-221	
CCD-PEI	
Immobilized humic substances	
Amberlite-Fe	FeOOH microparticles onto sorbent surface and inside the polymer beads

Possible interaction between iron compounds and arsenates or arsenites may occur as shown in Eqs (1) and (2) [14]:



Sorption isotherms

Sorption experiments were carried out using peat, modified peat sorbents, iron humates as well as commercially produced and synthetic sorbents. We used two inorganic forms of arsenic, *ie* As(V) and As(III), and an organic form - cacodylic acid ($C_2H_7AsO_2$).

In order to investigate the obtained sorption isotherms, Langmuir, Freundlich as well as Dubinin-Radushkevich sorption models were analysed [9, 15]. Our data best fitted to the Langmuir isotherm:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

The constants q_m and K_a are characteristics of the Langmuir equation and can be determined from its linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \quad (4)$$

where C_e is the equilibrium concentration [mg/dm^3], q_e - amount of arsenic sorbed [mg/g], q_m is q_e for a complete monolayer [mg/g], K_a is the sorption equilibrium constant [dm^3/mg] [15].

Sorption results indicate that when modified peat and also synthetic sorbents are used, sorption is much higher in comparison with peat. It can be seen from Figure 5 that high sorption capacity for arsenate sorption is observed when Amberlite-Fe sorbent is used, although the sorption capacity of Amberlite-Fe is lower in comparison with modified peat I and commercially produced sorbent AN-221 (Fig. 6). Modification of sorbent indicates that it has enhanced the sorption capacity. The reason could be the As-O-Fe bond forming for Fe-modified sorbents and ionogenic interaction for weak basic anion exchangers.

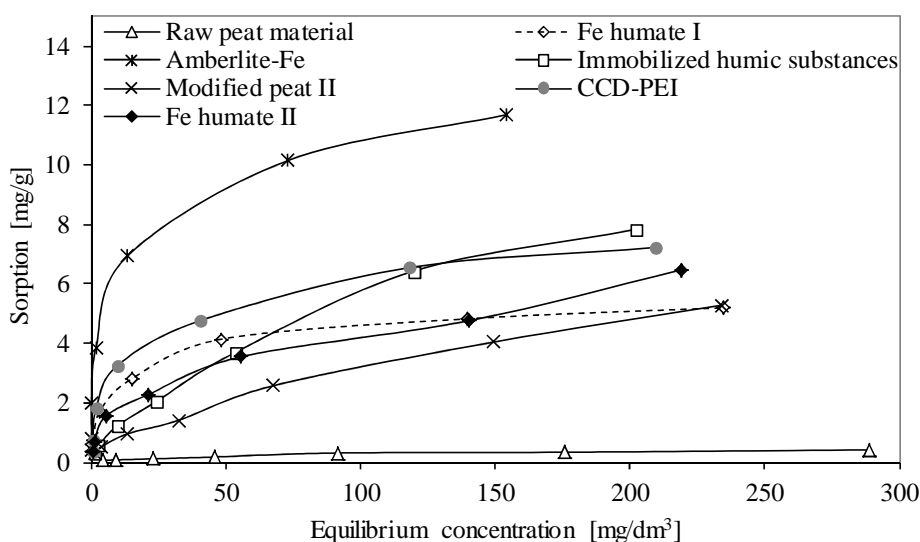


Fig. 5. As(V) sorption isotherms when raw peat material, iron-modified and polymeric sorbents are used

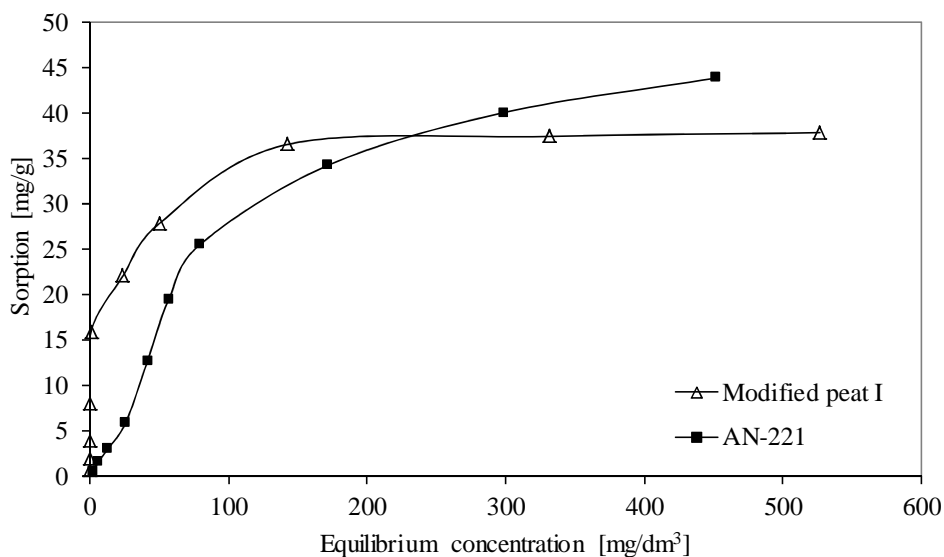


Fig. 6. As(V) sorption isotherms when modified peat I and synthetic sorbent AN-221 are used

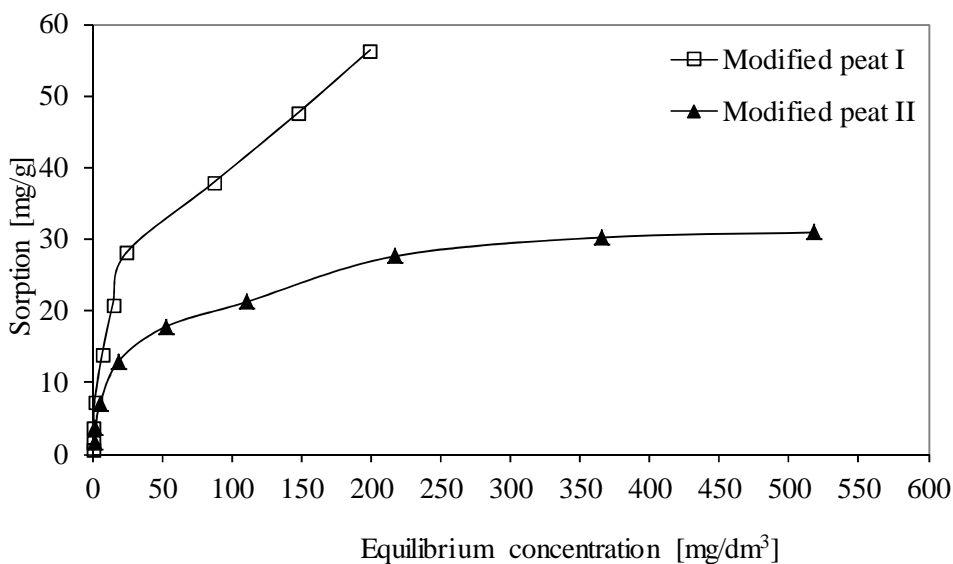


Fig. 7. As(III) sorption isotherms when modified peat sorbents are used

In comparison with the sorption isotherms of arsenates, arsenites have the highest sorption capacity when modified peat I and modified peat II are used (Fig. 7), and they can be effectively sorbed by Amberlite-Fe (Fig. 8). In addition, the synthetic sorbent AN-221 can be effectively used only for removal of arsenates.

Modified peat I is a better sorbent in comparison with modified peat II in both cases - for sorbing arsenates and arsenites. This result indicates that modification method has a great impact on the sorption capacity of sorbents. As the iron content in both above-mentioned peat sorbents is almost equal, it can be suggested that it is affected by other factors, for example, the iron speciation form present in the sorbent.

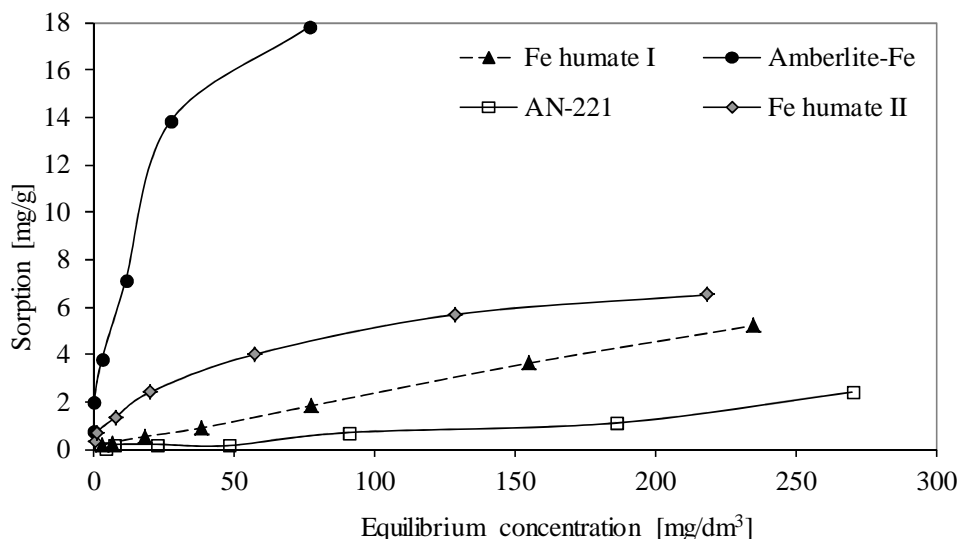


Fig. 8. As(III) sorption isotherms when iron-modified sorbents and the synthetic sorbent AN-221 are used

Comparison of the sorption isotherms of As(V), As(III) and cacodylic acid (As(org.)) demonstrates that arsenites have higher sorption capacity on iron-modified peat sorbents. Therefore, such modified peat samples could be very useful for removal of arsenites.

Figure 9 shows that the sorption of As(V) onto modified peat I exceeds 90% if the initial concentration of arsenic does not exceed 300 mg/dm³. In case the initial arsenic concentration reaches 800 mg/dm³, sorption decreases to 60%. A similar tendency has been observed for the synthetic sorbent as well. However, sorption of arsenates onto iron humates and Amberlite-Fe exceeds 50% if the initial concentration of arsenic does not exceed 50 mg/dm³. It can be suggested that both iron humates can be effectively used for removal of As(V) if arsenic concentration is lower than 25 mg/dm³.

As previously mentioned, As(V) was sorbed more effectively than As(III) and cacodylic acid onto sorbents used in this study, with the exception of modified peat II and Amberlite-Fe, which are more effective in sorbing arsenites. Nevertheless, modified peat sorbents as well as Amberlite-Fe sorbents can sorb more than 80% of arsenites if the initial As(III) concentration does not exceed 200 mg/dm³, and modified peat I can sorb more than 80% of arsenites even if the initial concentration of As(III) reaches 900 mg/dm³ (Fig. 10). Most of the sorption methods available for arsenic removal have a higher efficiency for As(V) than for As(III) [14]; therefore, it is important to point out that two of the synthesized

sorbents - modified peat II and Amberlite-Fe - have greater sorption efficiency for arsenites in particular.

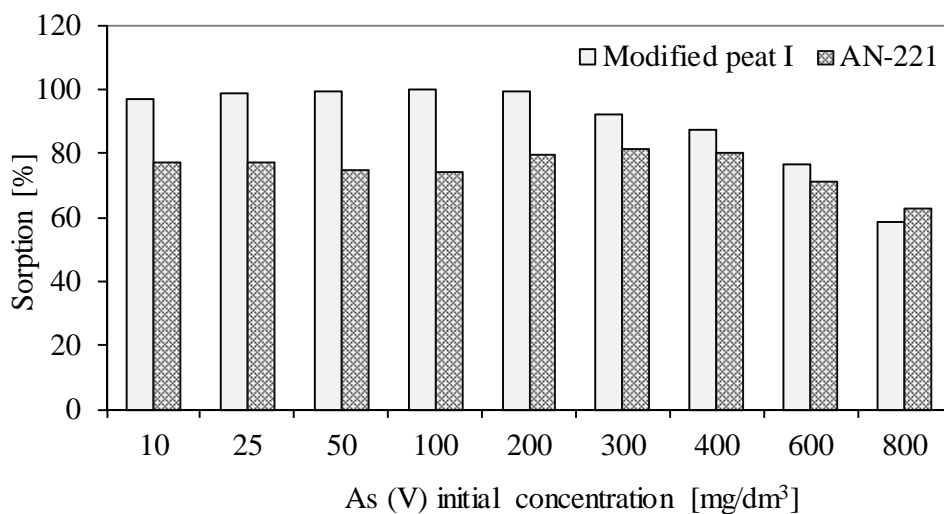


Fig. 9. Sorption [%] of arsenates on modified peat and synthetic sorbents

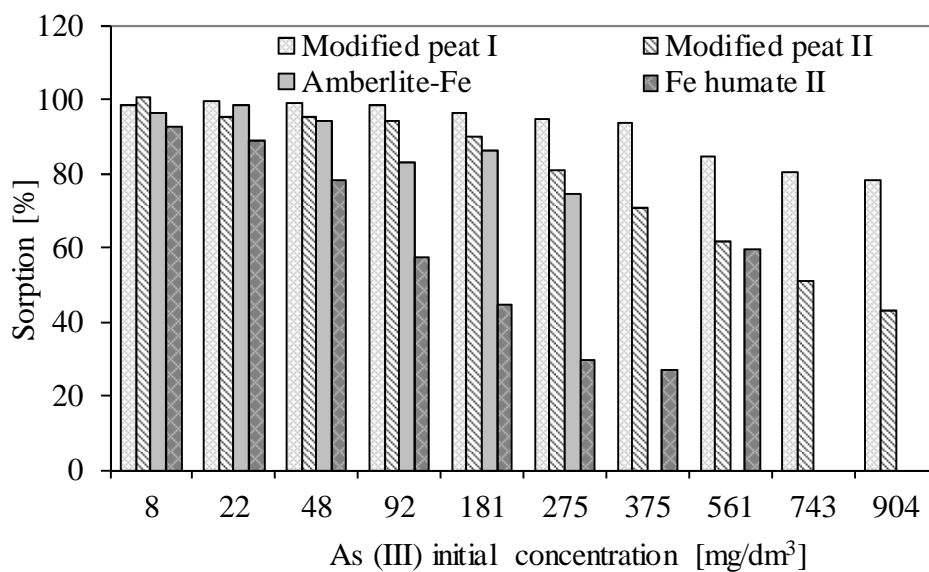


Fig. 10. Sorption [%] of arsenites on sorbents modified with iron

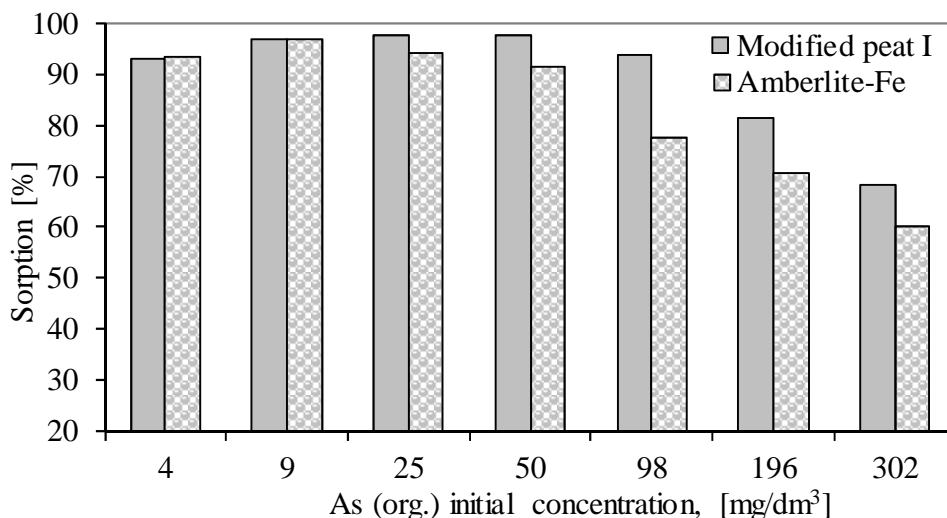


Fig. 11. Sorption of cacodylic acid (organic form of arsenic), using sorbents modified with iron

The most effective sorbents for removal of cacodylic acid is modified peat I and Amberlite-Fe (Fig. 11).

Influence of pH on the sorption of arsenic onto peat

To understand the likely fate and behaviour of arsenic in the environment, it is important to understand its interaction with natural environment components under a variety of physicochemical conditions, for example, pH, a type and concentration of natural organic macromolecules.

The effect of modified peat samples on As(V) and As(III) removal was studied in a pH range between 3 and 9. Solution pH can affect the arsenic uptake of peat samples in two different ways. First, solution pH governs the speciation of arsenate, resulting in arsenate species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) of different ionic charges and ligand strength [16], whereas arsenite forms a neutral hydroxo complex $\text{As}(\text{OH})_3$ (or H_3AsO_3) in the pH range studied [6, 17].

There are differences in the removal of As(III) and As(V) that can be explained by their respective speciation in aqueous medium. As(III) is present as an anion only above pH 9, and, in order to interpret the experimental data between pH 3 and 8, it is reasonable to assume that the neutral form $\text{As}(\text{OH})_3$ interacts mainly with iron hydroxide surface sites. In this case, weak Van der Waals forces are predominant. Such a specific complexation mechanism is in agreement with a pH dependence observed for As(III) binding onto humic substances. The binding is influenced by H^+ competition for humic functional groups at low pH values and OH^- competition for the As(III) centres at high pH values [17].

As previously mentioned, the corresponding stable species and pH values for pentavalent arsenic are H_3AsO_4 in a pH range 0÷2, H_2AsO_4^- (pH 2÷7), HAsO_4^{2-}

(pH 7÷12) and AsO_4^{3-} (pH 12÷14) [4]. In contrast to As(III), the inorganic As(V) species HAsO_4^{2-} and H_2AsO_4^- are negatively charged in the pH range 3÷9 [17].

Interaction can be explained, mainly considering the electrostatic interactions between the ionic species in solution and the charged surface groups. According to Dupont, the Fe(III) ions loaded in the peat have nearly the same reactivity than iron oxide surface sites, and the active form is the hydrolyzed surface species of iron hydroxide, which behaves like an amphoteric site with a point of zero charge ranging between pH 7 and 9 [6]. According to other studies, it is possible that adsorption occurs by reaction between the positively charged surface groups - FeOH_2^+ and the arsenate ions - which leads to the formation of surface complexes [6]. For As(V), maximum binding at pH ~7 was observed in both types of the modified peat samples. Figure 12 indicates 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. The obtained results were in a good agreement with the results found in previous studies [7, 16-18], where different kinds of sorbents were used to remove As(V) from aqueous solutions.

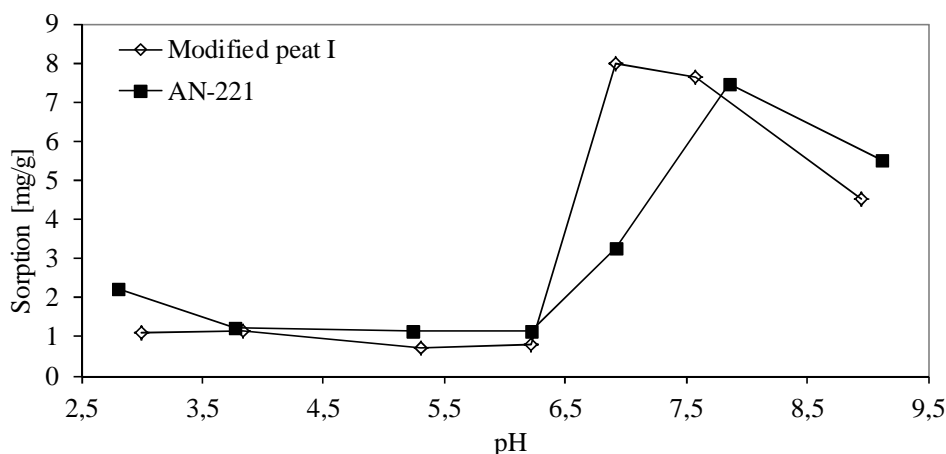


Fig. 12. As(V) (100 mg/dm^3) sorption as a function of pH

The obtained results could also be related to pH-based chemical changes, leading to electronic changes in humic acid molecules, and full deprotonation of carboxylic and other functional groups, leading to charge repulsion and change in the conformation of the humic acid as pH increases. The pH will affect dissociation of functional groups and develop differences in the amount of negative charge on the humic substances. At lower pH values, there is less dissociation; at neutral pH, humic substances reduce electrostatic forces by grouping hydrophobic structures together in a core and aligning charged functional groups in the molecule towards solvating water molecules. On higher pH, there will be more dissociation, but it will be energetically more favourable for the hydrophobic groups to align on a surface [19].

Influence of temperature on the arsenic sorption onto peat

Temperature is one of the factors that influence sorption capacity [20]. Results of arsenate sorption onto AN-221 and modified peat at 275, 283, 298 and 313 K are shown in Figures 13 and 14. The sorption capacity for both AN-221 and modified peat increases with temperature (Table 4); however, the increase in sorption capacity for modified peat I is significantly higher than that for AN-221. The reason could be the diffusion rate increase of adsorbate molecules as the temperature raises, as well as changes of sorbent pore size. An increase in temperature may also affect an increase in the 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 sorbent surface [20].

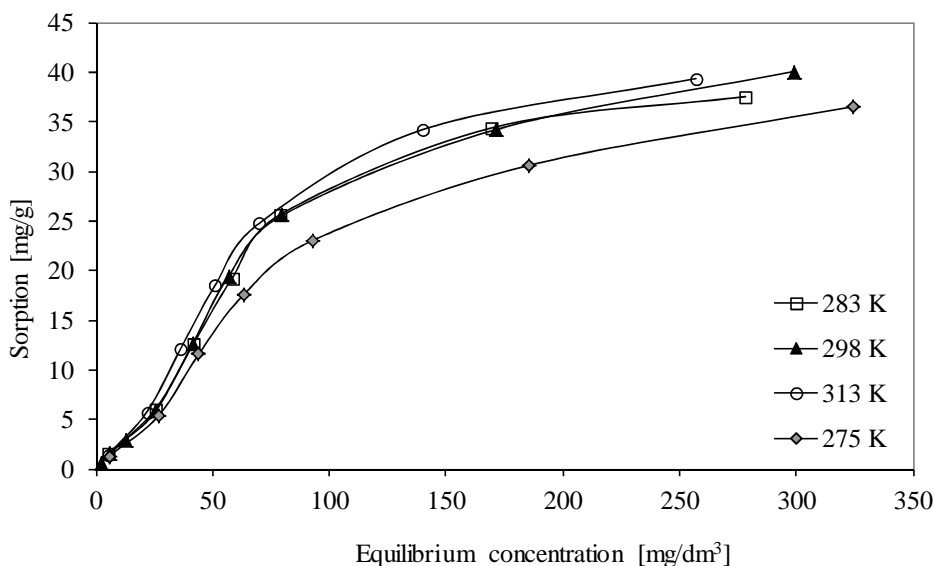


Fig. 13. As(V) sorption onto AN-221 depending on temperature

Linear Langmuir equation form (Fig. 15) was used for determination of the Langmuir isotherm constant. The Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy changes (ΔS°) are calculated for the sorption process using:

$$\Delta G^\circ = -R \cdot T \cdot \ln K_a \quad (5)$$

$$\ln \left(\frac{K_{a1}}{K_{a2}} \right) = -\frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

where K_a is the Langmuir isotherm constant [dm^3/mol] at temperature T [K] and R is the ideal gas constant (8.314 J/mol K) [20]. Calculated Langmuir constants and thermodynamic parameters are given in Table 4.

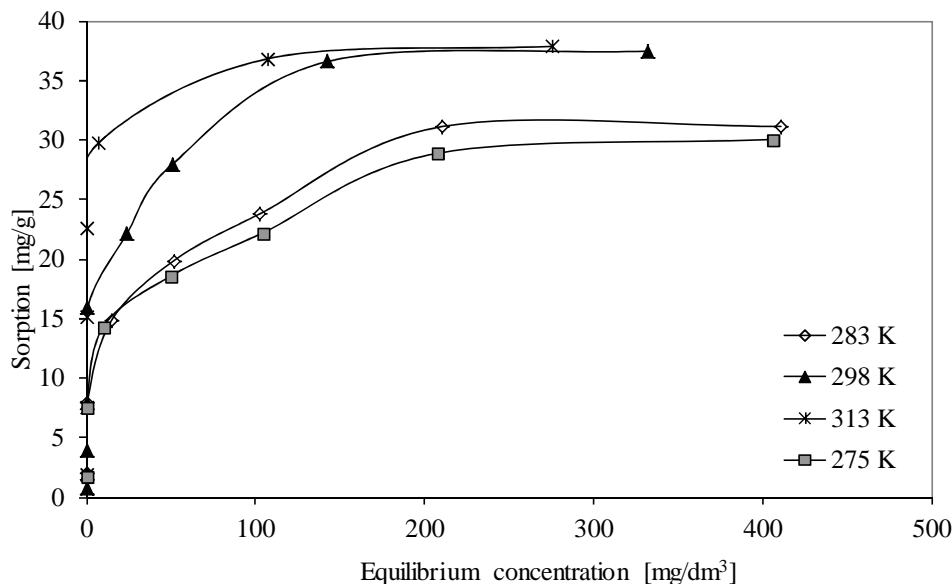


Fig. 14. As(V) sorption onto modified peat I depending on temperature

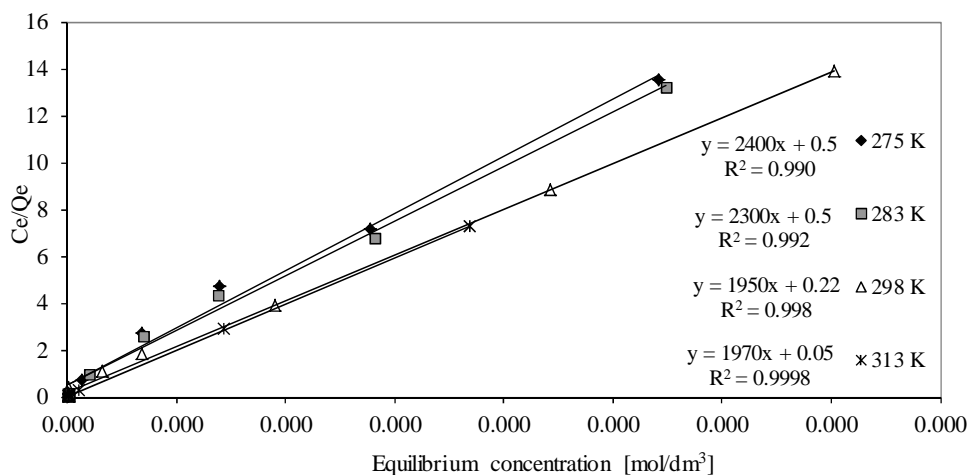


Fig. 15. Langmuir sorption isotherms of As(V) on modified peat I at different temperatures. C_e is the equilibrium concentration [mg/dm³], q_e - amount of arsenic [mg/g] sorbed onto solid phase

The negative ΔG° values for arsenate sorption onto modified peat or synthetic sorbent indicate 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, indicating the endothermic nature of the arsenic sorption onto modified peat or

synthetic sorbent. The endothermic nature of the sorption of arsenates can be attributed to the disruption of water molecules from the surface. This allows direct bonding of arsenic to the surface hydroxyl groups. The positive ΔS° values reflect the affinity of sorbent for arsenate and suggest some structural changes [13, 21].

Table 4

Calculated Langmuir constants and thermodynamic parameters

Sorbent	T [K]	Q_m [mg/g]	K [dm ³ /mol]	ΔG° [kJ/mol]	ΔH° [kJ/mol]	ΔS° [J/mol K]
Modified peat I	275	$4.0 \cdot 10^{-4}$	4802	-19.4	41.43	214
	283	$4.3 \cdot 10^{-4}$	4628	-19.9		
	298	$5.1 \cdot 10^{-4}$	8838	-22.5		
	313	$5.0 \cdot 10^{-4}$	43331	-27.8		
AN - 221	275	$8.9 \cdot 10^{-4}$	316.8	-13.2	1.92	55.1
	283	$9.2 \cdot 10^{-4}$	379.8	-14.0		
	298	$9.1 \cdot 10^{-4}$	349.6	-14.5		
	313	$1.4 \cdot 10^{-4}$	350.8	-15.3		

Conclusions

Arsenic sorption onto peat is much weaker than on modified peat and synthetic sorbents. Modification of the studied sorbents with iron oxy(hydroxides) helps to significantly enhance the sorption capacity, probably due to the formation of As-O-Fe bonds. Peat modified with iron oxy(hydroxides) is able to absorb arsenates, arsenites as well as the organic form of arsenic. Sorption at different pH values is mainly influenced by the ionic form of arsenic 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) show increasing randomness at the solid/liquid interface during the sorption of arsenic ions onto modified peat.

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USUWANIA ZWIĄZKÓW ARSENU ZA POMOCĄ TORFU, SORBENTÓW NA BAZIE TORFU I SORBENTÓW SYNTETYCZNYCH

Abstrakt: Skażenie wód arsenem jest problemem globalnym, dlatego potrzebne są nowe sposoby jego usuwania. Zbadano sorpcję związków arsenu przez torf, torf modyfikowany związkami żelaza, sole żelaza i kwasów humusowych oraz polimerowe kationity modyfikowane żelazem. Wyniki porównano z sorpcją związków arsenu przez aniony słabo zasadowe. Najwyższą wydajność sorpcji zaobserwowano dla torfowych sorbentów modyfikowanych związkami żelaza. Badano sorpcję różnych form specjacyjnych arsenu na sorbentach na bazie torfu modyfikowanych żelazem, w zależności od pH i temperatury. Stwierdzono wzrost pojemności sorpcyjnych tego materiału wraz ze wzrostem temperatury. Obliczone parametry termodynamiczne procesu sorpcji wskazują na samorzutność tego procesu i jego endotermiczność.

Słowa kluczowe: torf, sorbenty syntetyczne, arsen, sorpcja, model sorpcji