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Conference paper

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Phosphonium grafted styrene–divinylbenzene resins impregnated with iron(III) and crown ethers for arsenic removal

Abstract: In the present work a polymer with phosphonium pendant groups impregnated with crown ether (dibenzo-18-crown-6) and loaded with iron ions was investigated for arsenic removal through adsorption from aqueous solutions. The impregnated polymer was loaded with iron ions due to the high affinity of arsenic to it. The characterization of the surface modification of the obtained new adsorbent material was performed on the basis of energy dispersive X-ray analysis; scanning electron microscopy and Fourier transform infrared spectroscopy. The arsenic adsorption was investigated, including effect of pH, arsenic initial concentration, the shaking time and temperature. The effect of the pH was examined over the range 2–11. The adsorption of As(V) increases with pH increasing reaching a maximum at pH higher than 8. Equilibrium, kinetic and thermodynamic studies were carried out to study the adsorption performance of the obtained material in the removal process of arsenic from aqueous solutions. For the studied materials the equilibrium data closely fitted Langmuir model and was achieved a maximum adsorption capacity of 32.6 μg As(V)/g of material. The pseudo-second order kinetic model is suitable for describing the adsorption system. The obtained results show that the studied adsorbent can be used with efficiency in the arsenic removal from underground water even from low influent arsenic concentration solutions.

Keywords: arsenic removal; crown ether; POC-2014; polymer with phosphonium pendant group.

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Introduction

Arsenic is a highly toxic element even at low concentration thus creating potentially serious environmental concerns worldwide [1–5]. Therefore the development of new technologies to remove traces of arsenic from drinking water, wastewaters and industrial effluents in order to reach acceptable levels is still a challenging for the scientific community. Several methods are used to remove arsenic from aqueous solutions like

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oxidation-reduction, precipitation, coagulation and co precipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, etc. Each of the above processes has its own advantages and disadvantages which make the difficulty to select a suitable process. The disadvantages of traditional methods are high cost (coagulation–flocculation–filtration, oxidation and nanofiltration), high sludge production (coagulation–flocculation, electrochemical treatment), membrane fouling (nanofiltration), and constant monitoring of the ions concentration (ion exchange) [6]. From all these technologies sorption technique proved to be the most effective method, especially to remove traces of arsenic from drinking water [1, 2, 7–19]. Various adsorbents have been developed for arsenic removal [2, 3, 5–8, 18–25]. Some of the studied adsorbents developed very high adsorption capacities in the removal process of arsenic from drinking water, of the order of hundreds mg/g, but unfortunately these adsorbents could not remove arsenic from aqueous solutions containing a concentration under 100 μg/L, in such a way to give residual concentrations bellow the maximum admitted value by the World Health Organization (10 μg/L). More expensive technologies are required to achieve arsenic contaminant levels <10 ppb. Therefore the purpose of our research is to obtain an adsorbent which could be efficiently used in the removal process of arsenic from aqueous solutions having concentration under 100 μg/L. These concentrations were the most common found in the underground waters from the west area of Romania and east area of Hungary [26, 27]. Crown ether compounds have a considerable potential to be used as metal-selective reagents in the separation science due to their ability to form stable complexes with metal ions [28–30]. Therefore we focused on the use of dibenzo-18-crown-6-crown ether, in the removal process of arsenic from aqueous solutions, which is the simplest and the cheapest crown ether. The selective separation of elements by crown ether is managed either by the accommodation of ions within their circular cavity or in the three dimensional cavity like structures formed between the macroring and the sidearms [31, 32]. In order that, the use of dibenzo-18-crown-6-crown ether, in the removal process of arsenic from aqueous solutions, to be considered a cost effective option, we thought to attach this compounds to a solid support. The efficiency of such system leads to the development of new separation systems, with the use of solid supported crown ethers, which are capable of high selectivity or recognition towards a particular species of metal or metalloid [32]. Styrene-7%divinylbenzene copolymer with quaternary phosphonium pendant group was used as the macromolecular support. The modification of the polymeric matrix through functionalization of their surface with different phosphorus pendant groups lead to an increase of the adsorption efficiency of the polymers in the removal process of metals ions from various aqueous solutions [33, 34]. Also, in order to enhance the adsorption properties and the selectivity of the studied materials for arsenic removal, the polymer with phosphonium pendant group and impregnated with dibenzo-18-crown-6-crown ether was loaded with iron ions due to the high affinity of arsenic to it [1, 4, 7, 8, 10, 13]. Comparing with the simple ion exchange the metal loaded ligand exchanger develops rapid, selective and great efficiency in the removal process of trace arsenic from aqueous solutions [35–37]. In this way is combined the advantages of the resin such as: excellent hydraulic properties and mechanic strength with the excellent selectivity offered by the loaded metal [38]. Even if the metal ion content (weight %) of the loaded resin is much less than the metal oxide, the resulted adsorbent present a higher efficiency due to its mechanical integrity and its possibility to be used for several cycles [39]. The purpose of this paper is to develop an adsorbent material which presents higher efficiency in the removal process of arsenic from aqueous solutions containing low concentrations. In this way the study was conducting investigating the effect of pH, arsenic initial concentration, shaking time and temperature upon the adsorption capacity of the obtained material.

Experimental

Chemical reagents

Chloromethylated styrene–7%divinylbenzene copolymer (Victoria Chemical Plant, Romania), triphenylphosphine (Merck, p.a.), were used for the preparation of copolymer grafted with phosphonium groups.

The crown ether (dibenzo-18-crown-6) used for the impregnation was purchased from Sigma-Aldrich and $Fe(NO_3)_3$ in 0.5 mol/L HNO_3 solution (Merck Standard Solution) was used for the polymers loading with Fe(III).

The stock solution of arsenic was prepared by diluting an appropriate amount of H_3AsO_4 in 0.5 M HNO_3 solution (Merck Standard Solutions). Other solutions of As(V) ions were prepared from the stock solution by appropriate dilution.

All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

Preparation of phosphonium salts grafted on styrene-7%divinylbenzene copolymer impregnated with crown ether and with loaded Fe(III) ions

Quaternary phosphonium pendant groups grafted on St–DVB copolymer was obtained by the method previously described [40] (Scheme 1).

The impregnation of crown ether (dibenzo-18-crown-6) onto the copolymer functionalized with phosphonium pendant groups was realized through a dry method of impregnation [34].

One gram of polymer with pendant groups was impregnated with 0.01 g of crown ether which was previously dissolved in acetone.

After impregnation the samples were treated with 25 mL of Fe(III) solution having a concentration of 100 mg/L.

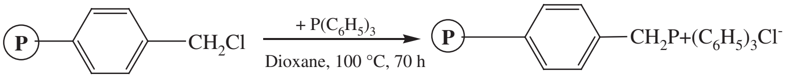
Instruments

The characterization of the surface modification of the new obtained adsorbent material was performed on the basis of energy dispersive X-ray analysis; scanning electron microscopy and Fourier transform infrared spectroscopy. The FTIR spectra (KBr pellets) of the obtained impregnated solid supports with Cyphos IL-101 were recorded on a Shimadzu Prestige-21 FTIR spectrophotometer in the range 4000–400 cm^{-1}. The surface morphology of the impregnated material was investigated by scanning electron microscopy (SEM) using a Quanta FEG 250 Microscope, equipped with EDAX ZAF quantifier. The residual concentration of As(V) ions was determined by means of atomic absorption spectrometry using a Varian SpectrAA 110 atomic absorption spectrometer with a Varian VGA 77 hydride generation system.

Sorption experiments

In order to determine the efficiency of the obtained adsorbent material in the removal process of arsenic from aqueous solutions the effect of the pH, stirring time, arsenic initial concentration and temperature, was investigated. We focused on the removal of As(V) from aqueous solutions because in the most of the water treatment systems in the first step the arsenite is oxidized to arsenate, due to the fact that arsenic in the pentavalent arsenate form is more readily removed than the trivalent arsenite form [2, 3, 12]. The adsorption performance of the studied material was expressed as arsenic metal uptake (µg/g) eq. 1. [1–5]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$



Scheme 1 Synthesis of quaternary phosphonium pendant groups grafted on St-7%DVB copolymer.

where: C_0 and C_e are the concentrations of arsenate (μg/L) in the solution, initially ($t = 0$) and at equilibrium, respectively, V is the volume of the solution and m is the mass of adsorbent.

In all the adsorption experiments the solid-liquid ratio used was 0.1 g of adsorbent in 25 mL of arsenic containing aqueous solutions. The effect of the pH was examined over the range 2–11. The effect of the arsenic initial concentration was examined over the range [25–175 μg/L As(V)]. The effect of stirring time (2, 4, 6, 8 h) was determined at three temperature (298, 308, 318 K). For the samples stirring a Julabo shaker was used.

In order to evaluate the efficiency of the obtained adsorbent it was used for the treatment of real underground water having the next composition: NO^{3-}: 18 mg/L; NO^{2-}: 0.5 mg/L; P_2O_5: 5 mg/L; SO_4^{2-}:11 mg/L; NH_4^+: 6.4 mg/L; Fe^{n+}: 1.8 mg/L; Mn^{2+}: 0.6 mg/L; Na^+: 120 mg/L; K^+: 1.75 mg/L; Ca^{2+}: 30 mg/L; Mg^{2+}: 18 mg/L; As^{n+}: 60 μg/L.

In order to recover and reuse of the adsorbent 0.2 g of exhausted adsorbent was treated with 25 mL of HCl solution having various concentrations (5, 10 and 15 %) under stirring for 4 h at the room temperatures. After the contact time elapsed the filtrate was collected for arsenic analysis.

Results and discussion

Adsorbent characterization

The obtained St-DVB copolymer after grafting with phosphonium pendant groups and impregnating with crown ether and Fe(III) ions was subjected to the FTIR analysis in order to prove that the impregnation occurred. The FTIR spectrum is provided in Fig. 1.

In the IR spectrum of this material the absorption band can be observed of the dibenzo-18-crown-6-crown ether unit [the intense bands about 1000 cm^{-1} and 1100 cm^{-1} are attributed to the $\nu_{sym}(C_{alphatic}\text{-}O\text{-}C_{aromatic})$ respectively $\nu_{asym}(C_{alphatic}\text{-}O\text{-}C_{alphatic})$] [36, 37]. The formation of the PPh_3Cl^- was confirmed by the appearance of the absorption bonds at 1130–1110 and 1440–1390 cm^{-1} associated with the stretching vibrations of the C_{phenyl}-H bonds and with the planar P-C_{phenyl} bonds, respectively [41, 42]. The band at 498 cm^{-1} is attributed to the group of vibrations $\nu_{Fe\text{-}O} + \nu_{C\text{-}C}$. The IR spectrum confirms the fact that the studied solid support was impregnated with the crown ether and loaded with the iron ions.

The SEM image and the EDAX quantification of the obtained material is presented in Fig. 2. From the SEM image can be observed that the smooth surface of the polymer with phosphonium pendant group is covered with a thin film of crown ether on which is bound the iron ions (the white particles). The EDAX quantification

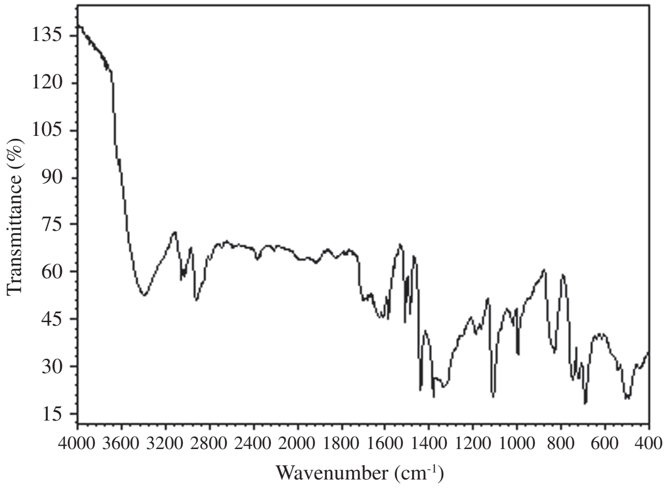
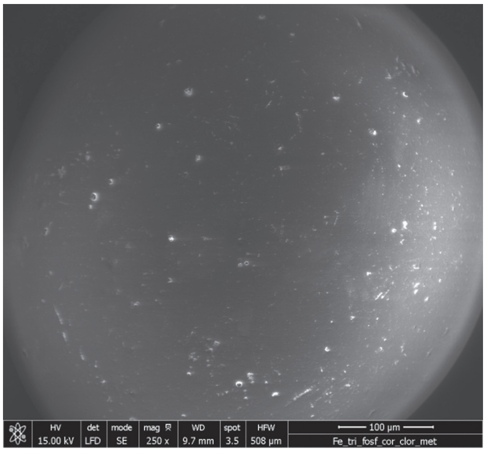


Fig. 1 IR vibrational spectrum of the obtained material.



Element	Wt %
C	86.77
O	7.55
P	3.8
Cl	1.56
Fe	0.22
Total	100.00

Fig. 2 SEM image and the EDX quantification of the obtained material.

also proved that the polymer with phosphonium pendant group was impregnated with the crown ether and loaded with iron ions.

The pH influence onto As(V) adsorption process

The influence of pH on the amount of As(V) uptake can be explained by the results given in Fig. 3.

The data obtained indicate that the relative amount of As(V) taken up by the studied adsorbent increases with increasing pH of the medium, reaching a maximum at pH higher than 8. This behavior confirm the fact that As(V) is present in the aqueous solution as anionic species [$H_2AsO_4^-$ or $HAsO_4^{2-}$] [3, 7, 8] and is more easily removed due to the fact that the surface of the studied adsorbent is protonated because of the Fe(III) ions loaded [33, 43]. The further experiments were performed at an initial pH of the As(V) solution around 8.

Equilibrium studies

The equilibrium studies were conducted in order to determine the maximum adsorption capacities of the studied material in the removal process of As(V) from aqueous solutions as a function of its surface prop-

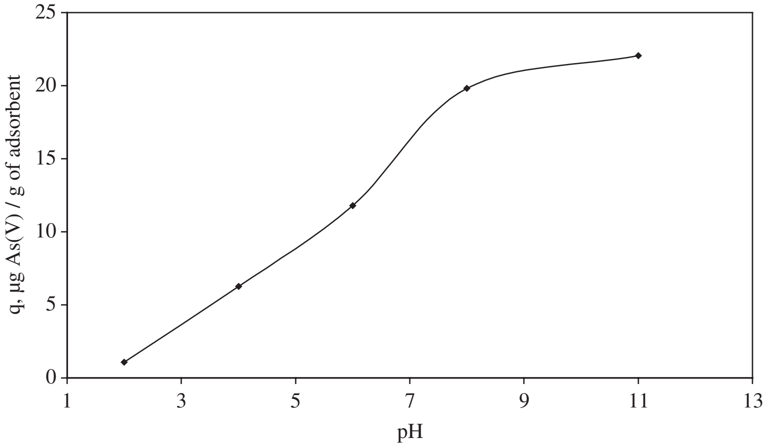


Fig. 3 The dependence of the As(V) uptake versus the pH of the solution.
C_i = 100 µg/L, V = 25 mL, t = 1 h, m = 0.1 g.

erties. The adsorption isotherm of As(V) removal by the studied material is presented in Fig. 4. It can be observed that the initial removal of As(V) is fast and at higher equilibrium concentration the adsorption capacity achieve a constant value.

The profile obtained from the study of As(V) initial concentration was used to obtain Langmuir and Freundlich adsorption isotherms by using well-known adsorption isotherm equation [1–4, 8]. In both cases linear plots were obtained, that reveal the applicability of these isotherms in the outgoing adsorption process. Figures 5 and 6 exhibit Freundlich and Langmuir plots, respectively, for As(V) adsorption onto the studied materials. The regression coefficients together with different Freundlich and Langmuir parameters derived from Freundlich and Langmuir plots are presented in Table 1.

From the experimental data can be observed that the correlation coefficient (R^2) obtained for the Freundlich isotherm is less than that obtained with Langmuir isotherm, where it is closed to unity. This indicate that the Langmuir isotherm describe better the adsorption process of As(V) onto the studied material. Moreover the maximum adsorption capacity of the studied material obtained from the Langmuir plot is very close to that obtained experimentally. The Langmuir mode assumes that the surface of the adsorbent is homogenous and the sorption energy to be equivalent for each sorption site. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

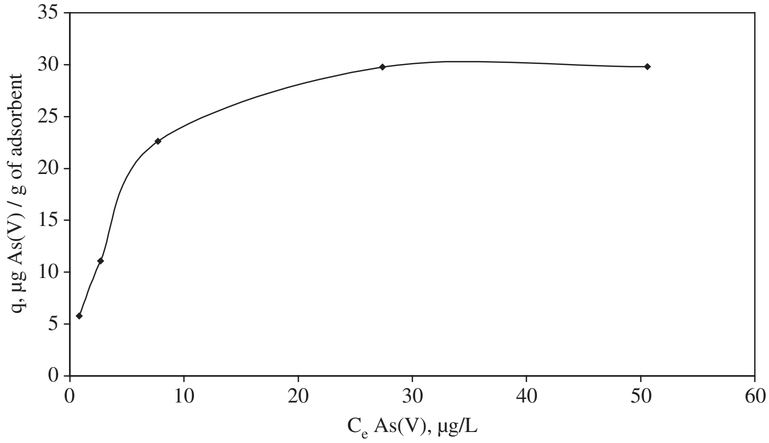


Fig. 4 As(V) adsorption isotherm onto the studied material.
pH = 8, V = 25 mL, t = 4 h, m = 0.1 g.

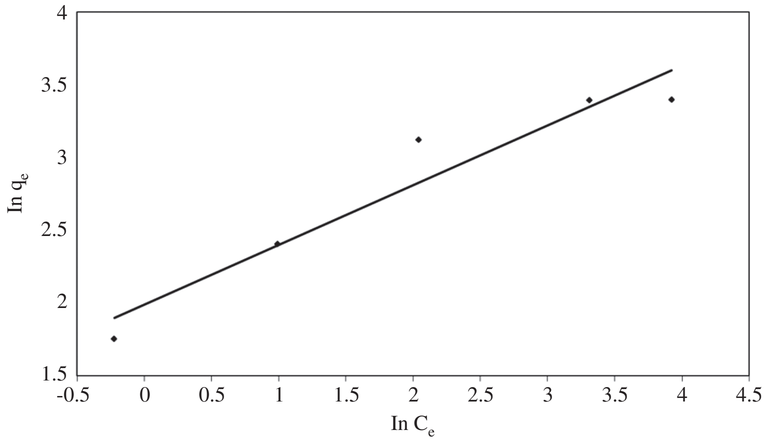


Fig. 5 Freundlich isotherm of As(V) adsorption onto the studied material.

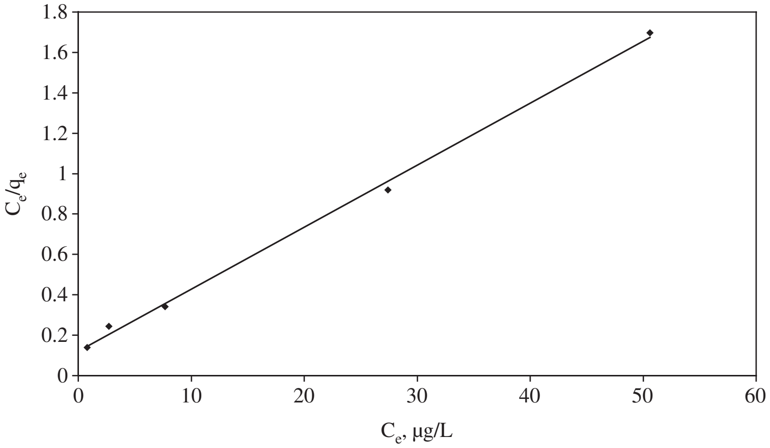


Fig. 6 Langmuir isotherm of As(V) adsorption onto the studied material.

Table 1 Parameters of Langmuir and Freundlich isotherms for As(V) adsorption onto the studied material.

$q_{m,\text{exp}}$ µg/g	Langmuir isotherm			Freundlich isotherm		
	K_L L/µg	$q_{m,\text{calc}}$ µg/g	R^2	K_F µg/g	$1/n$	R^2
30	0.2556	32.6	0.9975	7.31	0.4048	0.9271

$$R_L = \frac{1}{1+K_L C_0} \tag{2}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of As(V) ions. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L was found to be between 0 and 1 for the entire concentration range, which indicates the favorable adsorption of As(V) onto the studied material. Due to the fact that the Langmuir isotherm fit the experimental data better than the Freundlich isotherm, it can be mentioned that the arsenic ions are adsorbed uniform onto the surface of the studied adsorbent, because of the homogenous distribution of active site onto the surface. In this case there is no migration of the arsenic ions onto the surface of the studied adsorbent, these suggesting that there is a possible chemisorption between the adsorbent and adsorbate.

Kinetic studies

In the batch experiments, kinetic studies are used to determine the contact time of the adsorbent with adsorbate and to evaluate the reaction coefficients. Adsorption kinetics were evaluated at pH = 8 at an initial As(V) solution concentration of 100 µg/L at three different temperatures (298 K, 308 K, 318 K). Arsenate adsorption onto the studied material was rapid and essentially complete within 4 h for all the studied temperatures (Fig. 7). At higher stirring times the adsorption capacity becomes linearly constant. This may be due the overlapping of active sites with arsenic species and also due to decrease in the effective surface area resulting in the conglomeration of exchange particle [8]. Adsorption capacity increase with the temperature, this indicates that the adsorption is endothermic in nature.

In order to investigate the mechanism of arsenate adsorption onto the studied material the two kinetic models were analysed: pseudo-first-order equation [1–4, 33], based on the solid capacity and pseudo-second-order reaction model [1–4, 33], based on the solid phase adsorption and implying that the chemisorption is

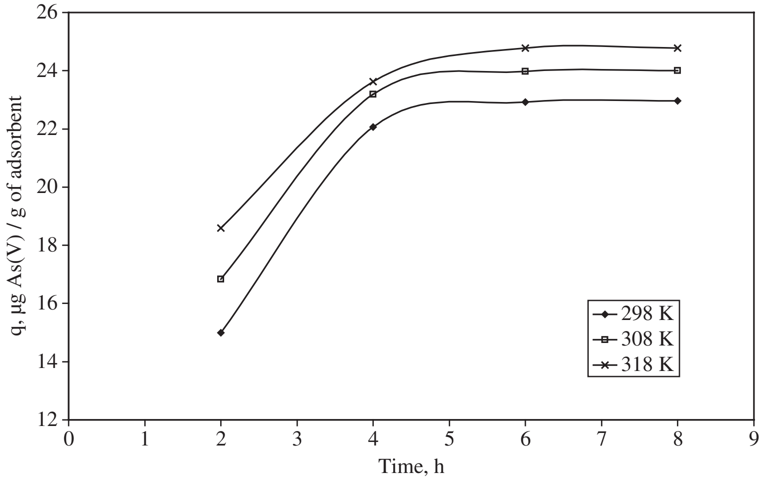


Fig. 7 Effect of contact time on the adsorption capacity of the studied materials. $C_0 = 100$ µg/L; m = 0.1 g; V = 0.025 L; pH = 8.

the rate controlling step. The pseudo-first-order and pseudo-second-order kinetic models were employed to investigate the mechanism of sorption processes such as mass transfer and chemical reactions. The plots of the both linear equation are presented in Figs. 8 and 9. The slopes and intercepts were used to calculate the adsorption rate constant and theoretical adsorption capacity which were presented in Table 3. From Table 2 it can be observed that the degree of fit R^2 for the pseudo-second-order ($R^2 > 0.99$) is higher than those of the pseudo-first-order model ($R^2 < 0.90$). Accordingly, the pseudo-second-order kinetic model is applicable the plot of t/qt versus t showing a straight line (Fig. 9). Also, the q_e calculated values are fitted the experimental data. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the As(V) adsorption process appeared to be controlled by the chemical process [5, 8].

Thermodynamic studies

Thermodynamic parameters like activation energy, Gibbs free energy (ΔG), entropy (ΔS) and heat of adsorption (enthalpy ΔH) were evaluated by the following equation [7, 8]:

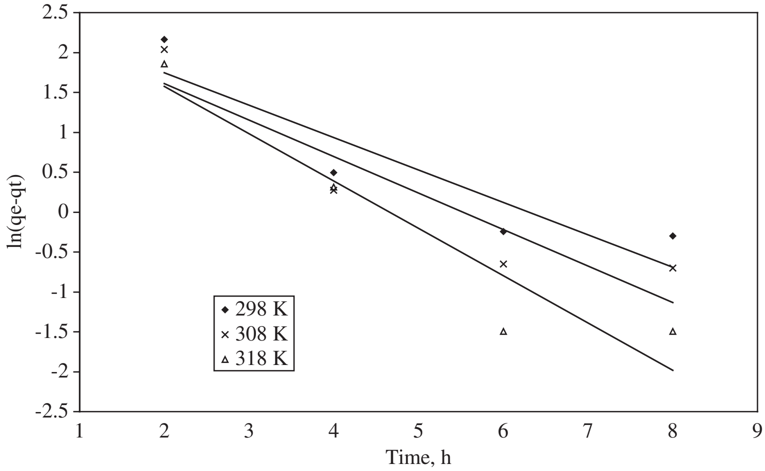


Fig. 8 Pseudo-first-order kinetic model of As(V) adsorption onto the studied material.

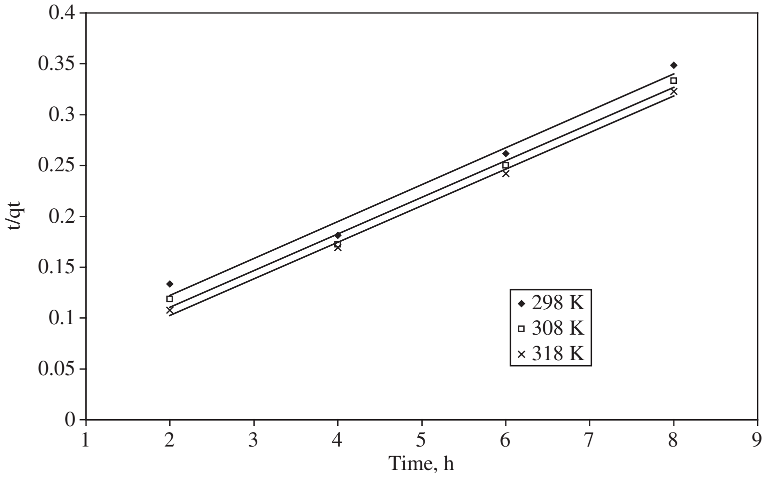


Fig. 9 Pseudo-second-order kinetic model of As(V) adsorption onto the studied material.

Table 2 Kinetic parameters for As(V) sorption onto the studied material at three different temperatures.

Temperature	**298 K**	**308 K**	**318 K**
Model/parameters			
$q_{e,exp}$, μg/g	23.5	24.5	25
Pseudo-first-order model			
$q_{e,calc}$, μg/g	12.4	12.5	15.8
k_1, 1/h	0.4062	0.4571	0.5928
R^2	0.8343	0.8513	0.8967
Pseudo-second-order model			
$q_{e,calc}$, μg/g	27.5	27.7	27.9
k_2, 1/h·1/(μg/g)	0.0265	0.0340	0.0418
R^2	0.9907	0.9912	0.9961

$$\ln(k_2) = \ln(A) - \frac{E}{RT}; \tag{3}$$

$$\Delta G^{\circ} = -RT \ln K_d; \tag{4}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}; \tag{5}$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}; \tag{6}$$

$$K_d = \frac{q_e}{C_e}; \tag{7}$$

where: k_2 is the pseudo-second-order rate constant of sorption (1/h·1/(μg/g), A the Arhenius constant which is a temperature independent factor (h·g/μg), E is the activation energy of sorption (kJ/mol), T is the absolute temperature (K), R is universal gas constant (8.314 J/mol·K) and K_d is the distribution coefficient.

The activation energy (*E*) was obtained from the slope of the plot between ln(K_2) versus 1/*T* (Fig. 10).

The magnitude of activation energy can give information whether the adsorption process is physical or chemical. The activation energy of physical sorption is normally not more than 4.2 kJ·mol^{-1} [5]. In this case was obtained a value of activation energy of 17.9 kJ/mol (Table 3) suggesting that the adsorption of As(V) onto

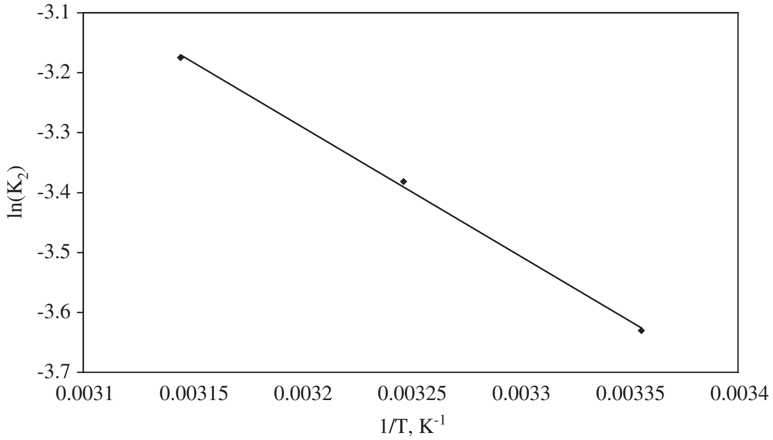


Fig. 10 Arrhenius plot of AS(V) adsorption onto the studied material.

Table 3 Thermodynamic parameters of As(V) adsorption onto the studied material.

Activation energy		Thermodynamic parameters					
E, kJ/mol	R^2	$\Delta H°$, kJ/mol	$\Delta S°$, J/mol·K	$\Delta G°$, kJ/mol			R^2
				298 K	303 K	308 K	
17.9	0.9988	86.3	299	27.5	57.9	87.3	0.9485

the studied material is a chemical adsorption. This is in accordance with the conclusions raised from the equilibrium studies.

The thermodynamic parameters of ΔH, ΔS were also calculated from the linear regression according to the eq. 6. The plot is shown in Fig. 11 and the obtained parameters are listed in Table 3.

The ΔH was observed to be 86.3 kJ/mol, which implies the endothermic nature of As(V) adsorption on the polymer with phosphonium pendant groups impregnated with crown ether and loaded with Fe(III) ions. The Gibbs free energy change (ΔG) was also calculated according to the eq. 5 which indicated the spontaneous nature of the sorption process. In addition, the positive value of ΔS suggested an increase in randomness at the solid/liquid interface during adsorption of As(V) ions onto the studied material [3, 7, 8].

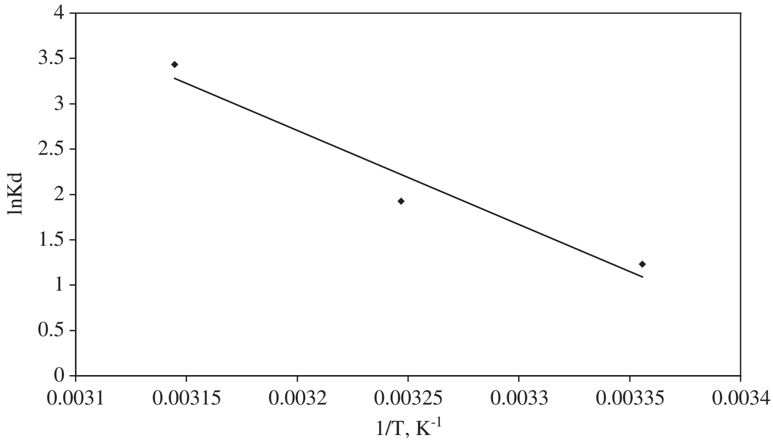


Fig. 11 Effect of temperature on the adsorption of As(V) onto the studied material.

Arsenic removal from real underground water

The efficiency of the treatment technique depends on the concentration and species of arsenic as well as on the presence of other constituents in the water. The studied adsorbent showed good efficiency in the treatment process of the real underground water. It can be notice that the presence of the other constituents in the water sample did not influence the efficiency of the studied adsorbent, the residual concentration of arsenic being under the maximum limit allowed by the World Health Organization of 10 µg/L. In the same time decreased the concentration of sulphate ions, these means that there can be a competition between the phosphate and arsenic ions present in the water samples, but at these concentrations the adsorbent has the capacity to remove the both ions.

Mechanism of arsenic adsorption

Based on the experimental data and their modeling it can be supposed that the mechanism of arsenic removal through chemisorption onto the studied adsorbent is formed from two distinguish parts: in the first step the Fe(III) ions is caught through coordinative bounds inside the macro cycle of the crown ether [44, 45]; and in the second step the arsenate ions are retained through ionic bounds by the formed crown ether-iron ions complex [23]. The proposed mechanism of arsenic adsorption onto the studied material is presented in Scheme 2.

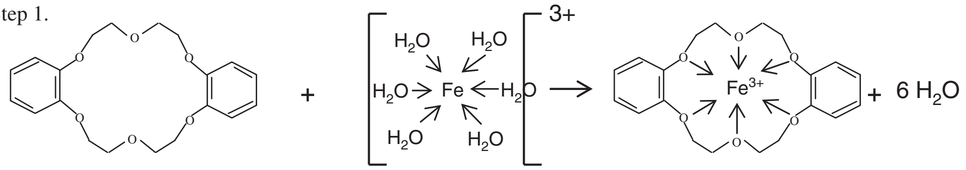
Desorption studies

From the experimental data it was observed that the desorption degree of As(V) from the exhausted adsorbent increase with the increasing of the HCl concentration. The degree of arsenic desorption is over 95 % in all the cases. From the economically point of view is not recommended to be used a solution of HCl having a concentration higher than 5 %. In this case the studied adsorbent material can be used in more cycles of adsorption-desorption.

Conclusions

Polymer with phosphonium pendant group impregnated with dibenzo-18-crown-6-crown ether and loaded with iron ions was investigated for As(V) adsorption from aqueous solutions containing arsenic concentration from 25 to 175 µg/L. The adsorption behaviors were thoroughly studied by Langmuir and Freundlich isotherms. The adsorption was observed to be a chemisorption process. The adsorption kinetics was better described by pseudo-second-order kinetic model compare to pseudo-first-order model. The endothermic

Step 1.



Dibenzo-18-crown-6 (DB-18-C6) Solvated Fe(III) ion crown ether-iron ions complex

Step 2. [dibenzo-18-crown-6 Fe]$^{3+}$ + AsO_4^{3-} → (DB-18-C6 Fe)(AsO_4)

Scheme 2 Mechanism of arsenic adsorption onto the studied material.

and spontaneous nature of adsorption was confirmed by thermodynamic study. The studied material can be effectively used in the removal process of As(V) from aqueous solutions containing trace concentration of arsenic (the most often found concentrations in the real underground waters) and obtaining a residual concentration under the maximum admitted value by the WHO.

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