Adsorption of Arsenate Anions from Aqueous Medium by Using Fe(III) Loaded XAD7-DEHPA Impregnated Resin

ADINA NEGREA[1], **MIHAELA CIOPEC**[1], **LAVINIA LUPA**[1]*, **CORNELIU MIRCEA DAVIDESCU**[1], **ADRIANA POPA**[2], **PETRU NEGREA**[1], **MARILENA MOTOC**[3]

[1] University „Politehnica” Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Piata Victoriei, 300006 Timisoara, Romania,

[2] Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

[3] “Victor Babes” University of Medicine and Pharmacy, 2 Piata Eftimie Murgu, 300041, Timisoara, Romania

This study is aimed to remove arsenate anions from aqueous solution by adsorption. As adsorbent a polymeric resin was used. The resin was prepared by impregnation of the Amberlite XAD7 resin with di(2-ethylhexyl) phosphoric acid (DEHPA) trough the dynamic column method of impregnation. Because of the high affinity of iron towards arsenic the XAD7-DEHPA resin was loaded with Fe(III) ions. The adsorption experiments were conducted at different parameters such as, contact time and initial concentration of As(V) from solution. The Langmuir and Freundlich isotherm models by non-linear regression analysis, were used to represent the experimental data and these could be relatively well interpreted by the Langmuir isotherm. The maximum As(V) adsorption capacity calculated from Langmuir model was 21.7 μg/g. By applying the kinetic models to the experimental data it was found that the removal of As(V) ions by adsorption onto Fe-XAD7-DEHPA follows the pseudo-second-order rate kinetics.

Key words: Fe-XAD7-DEHPA, dynamic column method of impregnation, arsenate anions removal, isotherm, kinetic

Contamination of groundwater resources by arsenic is a well-known environmental problem that can have severe human health implications [1, 2]. Arsenic is released from soil environments into groundwater through natural processes and as a consequence of anthropogenic activities [3-5].

So far numerous technologies have been developed for arsenic removal from the aqueous environment among which adsorption is becoming an attractive and promising technology because of its simplicity, ease of operation and handling, sludge free operation, and regeneration capacity [5-8]. Sorbents of different types like biomaterials [2, 7, 9], metal oxide/hydroxide [3, 6, 10-14], zeolite [5], activated carbon [5, 16], laterite [17] etc. have been used by workers to achieve the goal.

In the recent papers strong cation exchange resins, macroporous polymers, chelating resins and polymeric ligand exchangers have been used for metal ions removal from aqueous solutions [18-26]. In this study, very low-cost amberlite resin chemically modified by impregnation with di(2-ethylhexyl) phosphoric acid (DEHPA) and by Fe(III) ions including was chosen as adsorbent for arsenate anions removal from aqueous solution. The impregnation of the resin with di(2-ethylhexyl) phosphoric acid (DEHPA) was realised trough the dynamic column method of impregnation. Most of the research papers use the dry method of impregnation and none of these use the dynamic column of impregnation. The dynamic column method has the advantages of short impregnation time and high efficiency, which can be obtained not only in laboratory test but also on industrial scale [27]. Many researchers have shown that Fe(III) exhibits high affinity to both arsenate and arsenite [10-14, 16, 17, 28]. Therefore, the Fe(III) ions were immobilized to the functional group of the hosting resin. The optimum conditions for removing arsenate from a synthetic solution, by using Fe-XAD7-DEHPA resin as adsorbent, was investigate.

Theoretical background

Adsorption isotherm models

The sorption process considered here involves trivalent metal loaded impregnated resin as the solid phase and an aqueous phase containing dissolved species to be sorbed. Due to the higher affinity of the arsenate anions for the Fe(III) ions, they are attracted and bound to the solid by different mechanisms. This process take place until equilibrium between the amount of solid-bound ions and their concentration in solution is reached.

The Langmuir isotherm assumes that all adsorbed species interact only with a site, adsorption is limited to a monolayer, and adsorption energy of all sites is identical and independent of the presence of adsorbed species on neighboring sites. It is presented by the following equation [5, 13-15, 23, 26, 28]:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \qquad (1)$$

where: q_m is the maximum adsorption capacity (μg/g), q_e is the amount of the metal ions adsorbed at equilibrium (μg/g); C_e is the equilibrium concentration of metal ions (μg/L); b is the equilibrium constant. A curve with an abrupt initial slope indicates a resin with a high affinity for the ionic species at low concentration. The affinity is measured by the coefficient b in the Langmuir equation, the higher value of b, the higher the affinity.

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly presented as [5, 13-15, 23, 26, 28]:

$$q_e = K_f C_e^{1/n} \qquad (2)$$

where, K_f and n are Freundlich constants which feature the system.

Kinetic models

Kinetic studies provide information relating to time required for the establishment of sorption equilibrium. They

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* *email address: lavinia.lupa@chim.upt.ro*

also give information about the reactant species that govern the rate of the reaction and up to what order. Various models can describe the transient behaviour of an adsorption process. Most of these have been reported as pseudo-first-order and some as pseudo-second order kinetic process.

The pseudo-first-order kinetic model is known as the Lagergren equation [5, 7, 13, 22-24]:

$$\ln(q_e - q_t) = \ln q_t - k_1 t \qquad (3)$$

where, q_t and q_e are the metal concentration in the adsorbent phase at time t and at equilibrium, respectively and k_1 is the rate constant of first-order sorption.

The pseudo-second-order kinetic model is written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where, k_2 is the rate constant of pseudo-second-order sorption.

Experimental part

Materials and methods

Adsorbent preparation and characterization

The Amberlite XAD7 resin (supplied by Rohm and Hass Co.) was impregnated with di(2-ethylhexyl)phosphoric acid (DEHPA) and ethylic alcohol as solvent by dynamic column method [29, 30]. The DEHPA ~ 98.5% used as extractant, was supplied by England and used as received. A certain amount of polymer fully swollen by the solvent was packed in a glass column of 4 cm diameter and 15 cm height. Then the extractant solution was fed into the column with a 0.1 L/h flow rate until the extractant concentration in the outlet was equal to the feed one. The polymeric beads were separated through a porous filter using a vacuum pump, washed with water and dried at 50°C for 24 h [28]. The resulting SIRs were finally washed with distilled water. For the immobilization of the Fe(III) ions onto the XAD7-DEHPA hosting resin 5 g of the hosting resin was equilibrated with 200 mL of 50 mg/L Fe^{3+} solution for 24 h. Fe-XAD7-DEHPA resin were separated through a porous filter using a vacuum pump, washed with distilled water until pH was neutral and dried at 50°C for 24 h. The obtained product after impregnation and Fe(III) loaded was submitted to physico-chemical methods of analysis (FTIR spectroscopy and energy dispersive Xray analyse) in order to establish if the impregnation with DEHPA and the iron loading occurred. The FTIR spectra was recorded using a Shimadzu FTIR spectrophotometer in the range 4000-400 cm^{-1} with 2 cm^{-1} resolution and 40 scans using KBr discs. SEM micrographs and EDX studies were performed using a FEI Inspect S scanning electron microscope.

Adsorption experiments

Adsorption experiments were conducted in 100 mL Erlenmeyer glasses. A measured amount (0.1 g) of Fe-XAD7-DEHPA resin was placed in the glases, which contained 25 mL of various concentrations of As(V) at *p*H=9. The samples were kept in contact for a prescribed length of time to attain equilibrium at 25±1°C. The effect of As(V) initial concentration (30-300μg/L) and contact time (1-24 h), were studied. After filtration the concentration of As(V) was analyzed using a Varian SpectrAA 110 atomic absorption spectrometer with a Varian VGA 77 hydride generation system.

From the concentration measured before and after adsorption (C_0 and C_e, respectively) and dry weight of adsorbent (m), as well as volume of aqueous solution (v), the adsorption capacity was calculated according to eq. (5):

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (5)$$

All experiments were performed at a initial *p*H of As(V) solution of 9, because the predominant anionic species of As(V) [$H_2AsO_4^-$ or $HAsO_4^{2-}$] are found in the environment samples at this *p*H value [5, 13, 14]. The *p*H of the solutions was adjusted to this value using a 1 M NaOH solution, thereby keeping the volume variation of the solution to a value as low as possible. The *p*H of the solutions was measured via a CRISON MultiMeter MM41 fitted with a glass electrode which had been calibrated using various buffer solutions. 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.

Results and discussion

Adsorbent characterization

A FT-IR spectrum of the Fe-XAD7-DEHPA impregnated resin was recorded and is presented in figure 1.

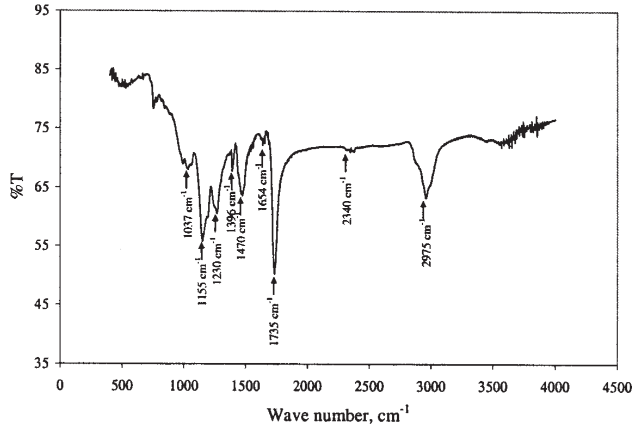

Fig. 1. FTIR spectra of Fe-XAD7-DEHPA resin

IR peak assignments for the matrix are listed in table 1. Amberlite XAD7 is an acrylic ester that contains ester groups O-C=O. All esters give rise to three strong infrared bands that appear at approximately 1700, 1200 and 110 cm^{-1}. The spectrum for our sample exhibits a strong band at 1735 cm^{-1} which represent the C=O stretch of the ester group. The IR spectrum exhibit a band at 2975 (strong sharp) which is attributed to the stretching modes (asymmetric and symmetric) of aliphatic C-H groups. The absorption band 1390 cm^{-1} is due to C-H deformation of $-CH_3$. From the analysis of the FTIR spectra can be observed that the characteristic vibrations originated from DEHPA in which the sorbent was impregnated are: P-OH, P=O and P-O-C which are observed in the spectrum at the wavelengths: 2340 cm^{-1}/1654 cm^{-1}, 1230 cm^{-1} and 1155 cm^{-1} (figure 1). The loading of Fe(III) ions onto the XAD7-DEHPA impregnated resin is put in evidence by the specific band of Fe-OH stretching attributed at the 1037 cm^{-1} wave length.

The energy dispersive XRay spectrum for the Fe-XAD7-DEHPA impregnated resin is presented in figure 2. One may notice the presence of the characteristic peak of phosphorous and iron ions.

All these proves the adsorption of DEHPA and the loading of the Fe(III) ions, respectively onto the XAD7 support.

Adsorption isotherm

The adsorption isotherm of As(V) onto Fe-XAD7-DEHPA resin was conducted using various initial As(V)

Table 1

FUNDAMENTAL FREQUENCY OF THE Fe-XAD7-DEHPA IMPREGNATED RESIN

Frequency, cm^{-1}	Assignments
2975	C-H stretching of CH_3
2340	P-OH stretching
1735	C=O stretching
1654	P-OH stretching
1470	P-CH_2 and C-H bending
1394	C-H deformation of the $-CH_3$ group
1230	P=O stretching (-O-P=O)
1155	P-O-C stretching
1037	Fe-OH stretching

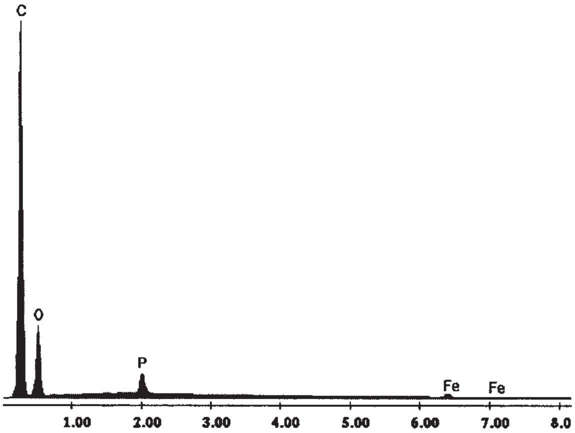

Fig. 2. EDX diagram of Fe-XAD7-DEHPA

concentrations raging from 30 to 300 µg/L at 25±1°C and at a contact time of 10 h. The experimental data were fitted with the Langmuir and Freundlich isotherms by non-linear regression analysis. The results are presented in figure 3 and the values of the correlation coefficients R^2 and the parameter q_m, b, K_f and 1/n are reported in table 2.

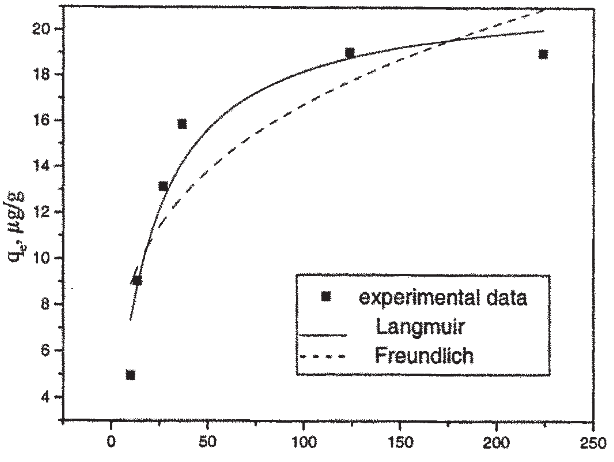

Fig. 3. Adsorption isotherms of As(V) onto Fe-XAD7-DEHPA (m=0.1 g; v=0.025 L; t=10 h; pH=9; T=298 K)

The adsorption capacity increased with increasing equilibrium concentration of arsenic. Then, they approached a constant value at the high equilibrium concentration. The maximum adsorption capacity of the studied material experimentally obtained, in the removal process of As(V) from aqueous solution, is 19µg/g.

Table 2

PARAMETERS OF DIFFERENT ISOTHERM FOR THE As(V) ADSORPTION ONTO Fe-XAD7-DEHPA

Freundlich isotherm			Langmuir isotherm		
K_F, µg/g	1/n	R^2	b, L/µg	$q_{m\,calc}$, µg/g	R^2
4,6886	0.2763	0.7562	0.051	21.7	0.9919

The Freundlich plot has a correlation coefficient very low; this suggests a restriction on the use of Freundlich isotherms. The numerical value of 1/n< 1, which provides information about surface heterogeneity and surface affinity for the solute, indicates a favourable sorption of As(V) and a very high affinity of the Fe-XAD7-DEHPA for As(V).

The Langmuir model effectively describes the sorption data with a correlation coefficient of 0.9919. Thus the isotherm follows the sorption process in the entire concentration range studied. Furthermore, the maximum adsorption capacity from the Langmuir plot is almost the same with the maximum adsorption capacity experimentally obtained. The dimensional constant, called separation factor (R_L), was used to describe the essential characteristics of Langmuir isotherm (R_L >1, unfavourable; R_L = 1, linear; 0<R_L<1, favorable; and R_L=0, irreversible),

$$R_L = \frac{1}{1+K_L \cdot C_0} \qquad (6)$$

In fact, the separation factor is a measure of the adsorbent capacity used. R_L values were calculated for the entire concentration range studied and found to be higher than 0 and less than 1, showing favourable adsorption.

Adsorption kinetic

Figure 4 shows the effect of the contact time on the As(V) adsorption onto the studied material. It is evident that the adsorption capacity increased initially as contact time increased, and then became almost stable, denoting attainment of equilibrium. To ensure enough time to reach equilibrium, 24 h of contact time was used.

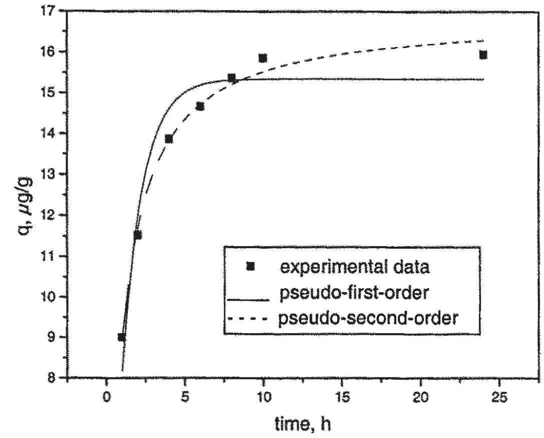

Fig. 4. Effect of adsorption time on As(V) adsorption onto Fe-XAD7-DEHPA. Fitting of the pseudo-first-order and pseudo-second-order kinetic models to the experimental data (C_0 = 100 mg/L; m=0.1 g; V=25mL; pH = 9; T=298 K)

Table 3

KINETIC MODEL PARAMETERS FOR As(V) IONS REMOVAL BY Fe-XAD7-DEHPA

q_e, exp, µg/g	Pseudo-first-order model			Pseudo-second-order model		
	q_e, kinetic plot, µg/g	k_1, h^{-1}	R^2	q_e, kinetic plot, µg/g	k_2 $min^{-1}(µg/g)^{-1}$	R^2
16	4.74	0.2143	0.8577	16.5	0.0819^4	0.9996

Kinetic data of arsenate adsorption were fitted to the pseudo-first-order and pseudo-second order kinetics models by non-linear regression analysis. Model parameters including kinetic constants, adsorption capacity and the correlation coefficients are presented in table 3.

Data presented in table 3 show that the correlation coefficient for the pseudo-first-order kinetic model is lower than that obtained for the pseudo-second-order model, where the correlation coefficient is very close to 1. Furthermore, the value of the equilibrium sorption capacity calculated ($q_{e,kinetic\ plot}$) using the first-order model, is not close to the experimental value ($q_{e\ exp}$). In the case of the pseudo-second-order model the theoretically predicted equilibrium sorption capacity is close to the value experimentally determined. This shows that the kinetics of As(V) removal by sorption on the Fe-XAD7-DEHPA is described by a pseudo-second-order expression.

Conclusion

In the present paper the performance of the Fe-XAD7-DEHPA resin, in the removal process of As(V) from aqueous solution, has been investigated. The studied materials have been obtained by impregnation of Amberlite XAD7 resin with DEHPA through dynamic column of impregnation and because of the high affinity of arsenic towards iron the Fe(III) ions were loaded onto the functionalized resin. The FTIR and the EDX analysis of the materials proved the adsorption of DEHPA and the loading of Fe(III) ions on the XAD7 support. The studied material showed good performance in the removal process of As(V) from aqueous solutions. The Langmuir and Freundlich isotherm models by non-linear regression analysis, were used to represent the experimental data and these could be relatively well interpreted by the Langmuir isotherm. R_L values between 0 and 1.0 further indicate a favourable adsorption of As(V) ions onto Fe-XAD7-DEHPA. The maximum As(V) adsorption capacity calculated from Langmuir model was 21.7 μg/g. By applying the kinetic models to the experimental data it was found that the removal of As(V) ions by Fe-XAD7-DEHPA follows the pseudo-second-order rate kinetics.

Acknowledgement: This work was supported by CNCSIS- UEFISCDI, project number PN II-IDEI 927/2008, "Integrated Concept about Depollution of Waters with Arsenic Content, through Adsorption on Oxide Materials, followed by Immobilization of the Resulted Waste in Crystalline Matrices".

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Manuscript received: 31.05.2011