

As(III) Removal by Dynamic Adsorption onto Amberlite XAD7 Functionalized with Crown Ether and Doped with Fe(III) Ions

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Arsenic content in groundwater's present a wide range of concentration, ranging from hundreds of micrograms to thousands of micrograms of arsenic per liter, while the maximum permitted arsenic concentration established by World Health Organization (WHO) is 10 $\mu\text{g L}^{-1}$. According to the WHO all people, regardless of their stage of development and their social economic condition, have the right to have access to adequate drinking water. The most efficient and economic technique used for arsenic removal is represented by adsorption. In order to make this remediation technique more affordable and environmentally friendly is important to new materials with advance adsorbent properties. Novelty of present paper is represented by the usage of a new adsorbent material obtained by physical - chemical modification of Amberlite XAD polymers using crown ethers followed by iron doping, due to well-known affinity of arsenic for iron ions. Present paper aims to test the obtained modified Amberlite polymer for arsenic removal from real groundwater by using adsorption in a fixed bed column, establishing in this way a mechanism for the adsorption process. During experimental work was studied the influence of competing ions from real water into the arsenic adsorption process.

Keywords: arsenic, groundwater, adsorption, crown ether, fixed bed column, breakthrough curves modelling

Arsenic is 20th element present in the Earth's crust, in form of 245 mineral species, considering its distribution, predominantly ores containing sulphides, nickel, copper, cobalt, lead etc. [1].

Arsenic it is a toxic metalloid that is known to be a contaminant into groundwater's from many parts of world, like South-East Asia area [2, 3], but also in the West of Romania [4, 5]. Consumption of arsenic contaminated water leads to a series of health problems.

Acute toxicity of arsenic occurs due to accidental ingestion, consumption of contaminated waters or inhalation of arsenic compounds with suicidal intent. First symptoms of poisoning appear when a dose less than 5 mg of arsenic compounds is ingested [6], even if the arsenic forms are of different toxicity. Thus, for inorganic arsenic the highest toxicity form is the *methylate* (MMA and DMA) [7, 8] and the lethal dose for an adult being considered between 1 and 3 mg·Kg⁻¹ body weight [9]. Also, arsenic ingested in the inorganic form is adsorbed in gastrointestinal tract and turns into MMA and DMA forms [9-12].

Studies have demonstrated that arsenic removal can be realized through various technologies [13] such as: coagulation with salts [14], ion exchange, which is becoming more popular due to the simplicity and ease of operation and due to the fact that not result sludge. A particular technique used for arsenic removal is represented by the adsorption onto the iron oxide particles, knowing the As (III) affinity for iron ions [15, 16].

The fact that, in general, the classical methods used for arsenic removal from aqueous solutions are expensive methods, but also lead to production of some secondary products, we aim to implement an environmentally friendly technology for arsenic removal from water. It is possible to

obtain that by using adsorption as removal technology, but in order to get higher efficiencies it is necessarily to use materials with advanced adsorbent properties. Such materials can be obtained by chemical synthesis [17, 18], or by functionalization of organic solid supports (natural or synthetic polymer) or inorganic solid support (silica or florasil) with pendant groups (N, P or S) in order to improve the adsorption properties [19-23].

Based on the operation mode, adsorption can be generally classified into static adsorption and dynamic adsorption. Static adsorption, also called batch adsorption, occurs in a closed system containing a desired amount of adsorbent kept in contact with a certain volume of contaminated solution, while dynamic adsorption usually occurs in an open system where contaminated solution continuously passes through a column packed with adsorbent.

A variety of adsorbent materials used for arsenic removal from water such as metal iron, iron oxides, zirconium oxides, but also wastes from various technologies with high iron content have been developed [24-36].

In some studies, materials with highly efficient adsorbent properties, specific to arsenic removal are presented. These materials point out significant adsorption capacities (> 100 mg As·g⁻¹ of material), but such materials cannot be used to remove trace arsenic from underground waters (below 100 $\mu\text{g}\cdot\text{L}^{-1}$) and also the residual concentration in these cases is higher than 10 $\mu\text{g}\cdot\text{L}^{-1}$, which does not agree with WHO requirements for arsenic content, especially in drinking water (maximum 10 $\mu\text{g}\cdot\text{L}^{-1}$) [18].

Crown ethers present a considerable potential for use as high selectivity reagents for metals due to their ability to form stable complexes with their ions [37-39], but also

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metal ions are able to penetrate the circular cavity of the crown ether forming rings with three-dimensional structure [40, 41].

Aim of present study it is to test a new material obtained by functionalization of a commercial polymer-Amberlite XAD7 with Di-benzo 18-crown- 6 (DB18C6) ether, doped with Fe (III) ions for arsenic removal from real water samples obtained from Western area of Romania. All adsorption experiments were carried out using adsorption in a fixed bed column.

Also, the influence of competing ions (nitrite, nitrate, ammonium, phosphate sulphates and bicarbonates) present in water sample onto the As(III) adsorption process was studied.

Experimental part

Materials and methods

In order to establish the adsorption mechanism of As(III) ions presents in natural ground water using a dynamic regime through fixed bed column, filled with an adsorbent material obtained by functionalization of Amberlite XAD7 with DB18C6 and doped with Fe (III), the content of residual arsenic was determined as function of the volume of water passed over the material and the time required for breakthrough column, as well as a number of parameters specific to the drinking water quality (pH, nitrite, nitrate, ammonium, phosphate and bicarbonate content).

Adsorbent material was obtained by functionalization of Amberlite XAD 7 commercial polymer (Sigma-Aldrich, Merck) with Di-benzo 18 -crown- 6 (DB18C6) (purity 98%, Sigma-Aldrich, Merck) in 1:0.01 ratio (%w/w). Support functionalization was obtained by using SIR dry method [19].

The extractant and the support remain in contact for 24 hours, after which the modified support was filtered and dried in oven (Nitech oven) at 50°C for 24 h. In order to include iron ions into the modified material, his was mixed with 25 mL of FeCl₃ (Sigma -Aldrich, Merck) solution (100 mg·L⁻¹) and kept in contact for 24 h, then filtered and dried in the oven for 24 h.

All adsorption experiments using real water were performed in dynamic mode using a glass column with diameter of 2.5 cm and length of 30 cm, loaded with 20 g of prepared adsorbent material. The height of the material layer inside of the column was 10 cm.

Real water containing 80 µg·L⁻¹ As(III) with pH 7.3 was introduced into the column using a HEIDOLF peristaltic pump with a flow-rate of 10 mL·min⁻¹. Analysis of As (III) content in water were determined by using inductively coupled plasma mass spectrometry ICP-MS BRUKER AuroraM90.

To study the influence of competing ions from real water upon arsenic adsorption process the content of nitrites, nitrates, ammonium, phosphate and bicarbonates was determined by atomic absorption spectrometry in UV-Vis using the VARIAN Cary 50 spectrometer.

Results and discussions

Column adsorption experiments

In order to characterize the As(III) adsorption process in dynamic regime on column, the maximum adsorption capacity and the time need it to breakdown column were determined.

Evolution of residual concentration as function to volume sequence and implicitly time needed for analysis are presented in figure 1.

From figure 1 can observe that by increasing the volume of water passed over the adsorbent material, and implicit

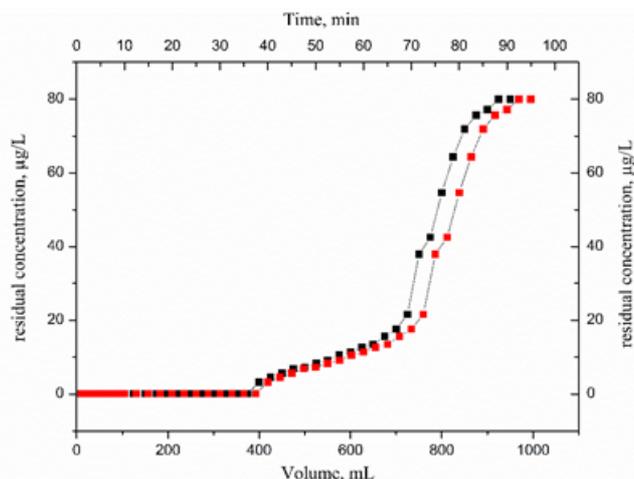


Fig. 1. Evolution of residual concentration function to volume and time

the time, the residual concentration of As (III) decreases below the detection limit of the device (<0.01 µg·L⁻¹) until the column is breakdown (after ~ 400 mL of water and ~ 40 min). The adsorption capacity of the material begins to decrease after a volume of 700 mL water, respectively after a period of 70 min.

Modelling of fixed bed adsorption

In order to determine the arsenic adsorption mechanism, it is necessarily to make the kinetic study of the adsorption process in a dynamic regime by using several simplified mathematical models. Thus can be achieved by fitting the experimental data with Bohart-Adams, Yoon-Nelson and Thomas simplified models [42].

Bohart-Adams model is used for description of the initial part of the breakdown curve of the column, by using the following mathematical expression:

$$\ln\left(\frac{C_t}{C_0}\right) = k_{BA}C_0t - k_{BAN_0}\frac{Z}{F} \quad (1)$$

where:

C_0 is the influent concentration, µg·L⁻¹

C_t is the effluent concentration, µg·L⁻¹

t is time, min

k_{BA} is the kinetic constant of the Bohart-Adam model, L µg⁻¹·min⁻¹

F is the linear velocity calculated by dividing the flow rate by the column section area,

Z is the bed depth of column, cm

N_0 is the saturation concentration, µg·L⁻¹

Curve associated with Bohart-Adam model, consisting in linear dependence of $\ln(C_t/C_0)$ versus time is depicted in figure 2. Analyzing data presented in figure 2 can evaluate

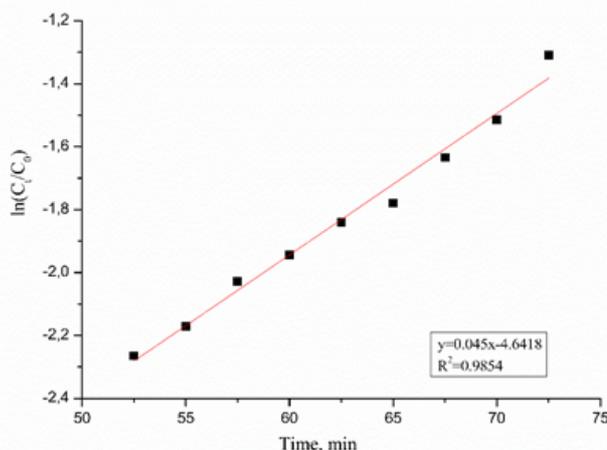


Fig. 2. Bohart-Adams model

the values of N_0 and k_{BA} from the intercept and slope the linear plot of $\ln(C_t/C_0)$ against time (t).

From obtained results can evaluate if the column adsorption process is due to an external mass transfer during the first part of the process. The k_{BA} and N_0 constants are presented in table 1 and the obtained regression coefficient is 0.9854.

In order to model the column breakdown time, two models can be used, namely Yoon-Nelson and Thomas.

Yoon-Nelson model is used to model a monocomponent system and does not require data on the characteristic of adsorbate, the type of adsorbent and the adsorbent physical properties of the adsorption bed.

The equation regarding a single component system is expressed in its linearized form as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (2)$$

where:

C_t is the solution concentration at time t, $\mu\text{g}\cdot\text{L}^{-1}$

C_0 is initial solution concentration, $\mu\text{g}\cdot\text{L}^{-1}$

k_{YN} is the rate constant, min^{-1}

τ is the time required for 50% adsorbate breakthrough, min.

The parameters τ and k_{YN} can be obtained from the intercept and slope of the plot linear dependence graph $\ln[C_t/(C_0 - C_t)]$ function time (fig. 3).

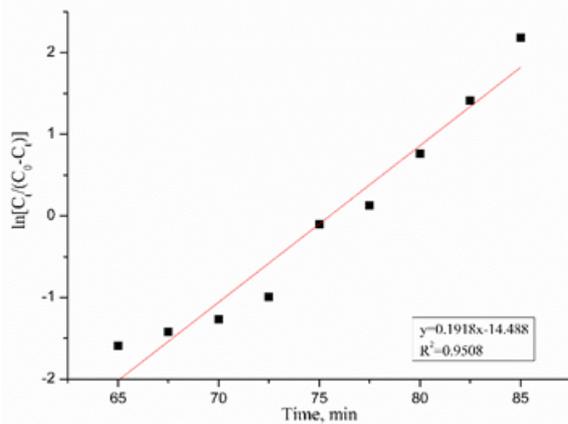


Fig. 3. Yoon-Nelson model

Based on the experimental data modelling, it was found that the process folds relatively well, the correlation coefficient R^2 being 0.9508, slightly lower than in the Bohart-Adams model. Also, the parameters τ and k_{YN} are calculated and are found in table 1.

If the adsorption process is a process follows a second-order reversible reaction kinetics, then obtained experimental data can be modelled using Thomas model. The Thomas model is frequently applied to estimate the adsorptive capacity of an adsorbent and predict breakthrough curves [43, 44].

The Thomas model in its linearized form is given by:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_{Th}m}{Q} - k_{Th}C_0t \quad (3)$$

where:

C_0 is the solution concentration in the influent, $\mu\text{g}\cdot\text{L}^{-1}$

C_t is the solution concentration at time t in the effluent, $\mu\text{g}\cdot\text{L}^{-1}$

k_{Th} is the Thomas rate constant, $\text{L}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$

q_{Th} is the equilibrium compounds uptake per g of the resin, $\mu\text{g}\cdot\text{g}^{-1}$

m is the mass of adsorbent resin, g

Q is he flow rate, $\text{mL}\cdot\text{min}^{-1}$.

A linear plot of $\ln[(C_0/C_t - 1)]$ against time (t) was employed to determine values of k_{Th} and Q_{Th} from the intercept and slope of the plot (fig. 4).

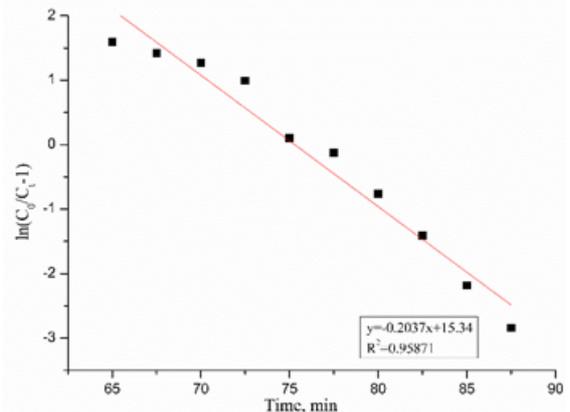


Fig. 4. Thomas model

It can be estimated that the adsorption process is due to an external and internal diffusion and the resistance forces being extremely small [45]. Based on this model,

Table 1
As (III) ADSORPTION PROCESS PARAMETERS ON FIXED BED COLUMN

Column parameters							
Material amount (g)	Material layer height in the column (cm)	Models			Saturation concentration, N_0 ($\mu\text{g}\cdot\text{L}^{-1}$)	Theoretical time, τ (min)	Theoretical adsorption capacity, q_{Th} ($\mu\text{g}\cdot\text{g}^{-1}$)
		k_{B-H} ($\text{L}\cdot\mu\text{g}^{-1}\cdot\text{min}^{-1}$)	k_{Y-N} (min^{-1})	k_{Th} ($\text{L}\cdot\mu\text{g}^{-1}\cdot\text{s}^{-1}$)			
20	10	0.0005625	0.1918	0.00254625	16809.5	75.53	3.01200
Regression coefficient, R^2		0.9854	0.9508	0.9587	Experimental time, min		72.5
				Experimental adsorption capacity, $\mu\text{g}\cdot\text{g}^{-1}$		2.18	

Table 2
COMPETING IONS INFLUENCE ONTO As(III) ADSORPTION PROCESS

Parameter	Initial water	Water after As (III) adsorption	Maximum admissible concentration	Legislation
pH	7.3	6.9	6.5-9.5	STAS 6325/75 SR ISO 10523/97
Nitrite (NO_2^-), $\text{mg}\cdot\text{L}^{-1}$	0.4	0.1	0.5	STAS 3048/2-96 SR ISO 6777/96
Nitrate (NO_3^-), $\text{mg}\cdot\text{L}^{-1}$	32,6	30.9	50	STAS 3048/1-77 SR ISO 7890/1-98
Ammonium (NH_4^+), $\text{mg}\cdot\text{L}^{-1}$	0.7	0.2	0.5	STAS 6328/85
Phosphate (PO_4^{3-}), $\text{mg}\cdot\text{L}^{-1}$	12.5	3.6	5	OMS
Bicarbonate (CO_3^{2-}), $\text{mg}\cdot\text{L}^{-1}$	424	225	-	-

the regression coefficient R^2 have value of 0.9587 and constant k_{th} and the material adsorption capacity q_m , are presented in table 1.

From the data presented in table 1 it can be observed that the value of the theoretical time is 75.53 min being close to the experimental time value (fig. 1), namely 72.5 min. Also, theoretically adsorption capacity value is $3.012 \mu\text{g}\cdot\text{g}^{-1}$ value that is approaching the experimental value from adsorption capacity $2.18 \mu\text{g}\cdot\text{g}^{-1}$.

Influence of competing ions present in water onto As(III) adsorption process

Present study investigates the effect of the presence of some competing ions (NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , SO_4^{2-} and CO_3^{2-}) in real water, but also the pH of water onto As(III) adsorption process on produced material obtained by functionalization of Amberlite XAD7 with DB18C6 and doped with Fe (III) ions (experimental data are depicted in table 2).

From experimental data presented in table 2 can observe that in addition to the adsorption of the As (III), the use of such adsorbent material exhibit adsorption capabilities for other ions present in real water. It was also noted that the adsorbent material present affinity for the phosphate anions, reducing them from $12.5 \text{ mg}\cdot\text{L}^{-1}$ to $3.6 \text{ mg}\cdot\text{L}^{-1}$ and from bicarbonate ions reducing them from $424 \text{ mg}\cdot\text{L}^{-1}$ to $225 \text{ mg}\cdot\text{L}^{-1}$. Also, can be affirmed that presence of phosphate anions and bicarbonate ions in water have a positive effect upon As(III) adsorption process [46]. Based on experimental data can conclude that the adsorbent material present adsorbent capacities for As (III) ions and for the competing ions present into the real waters. The pH of water decreases from 7.3 to 6.9 but not significantly.

Conclusions

Present paper aimed to study As(III) removal from a real water collected from Western area of Romania by adsorption on a new material obtained by the functionalization of Amberlite XAD7 polymer with Di-benzo 18- crown-6 (DB18C6) crown ether and then doped with iron ions. The studies were performed in dynamic regime using a glass column. Also, was studied the influence of competing ions (nitrite, nitrate, ammonium, phosphate

and bicarbonates) present in water sample during the As(III) adsorption process.

To establish the adsorption mechanism, the experimental data obtained in this study were analyzed using three mathematical models: Bohart-Adams, Yoon-Nelson and Thomas models. Modelling was performed by linear regression analysis of experimental data. Regression coefficients R^2 were calculated, which are an indicator of the model, providing information about how well the process studied folds on one of the three models. Each model allows the determination of some parameters characteristic of the adsorption process.

Thus, the Thomas model allows the prediction of maximum adsorption capacity (q_{Th}) and Thomas rate constant (k_{Th}), the Yoon-Nelson model simulates breakthrough time (t) and Yoon-Nelson rate constant (k_{YN}) and the Adams-Bohart model predicts the saturation constant (N_0). In conclusion, the material can be used for treatment of water with arsenic content provided that the maximum adsorption capacity is increased and finding a solution to reduce the occurrence of preferential drainage through the column.

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