Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22676

133 (2018) 257–261
November

Removal of arsenic(V) from aqueous wastes by ion exchange with Lewatit MP64 resin

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Received 9 March 2018; Accepted 18 June 2018

ABSTRACT

The use of ion exchange technology was studied to remove arsenic(V) from waters by Lewatit MP64 (anion exchanger) resin. Batch and column experimental tests were conducted to provide data for theoretical models and verify the system performance of the exchange process. Results of batch equilibrium tests indicated that Langmuir isotherm describes well the exchange process, whereas experimental data also provide evidence that, under the present experimental conditions, arsenic(V) adsorption onto Lewatit MP64 resin is film-diffusion controlled and obeys the pseudo-first-order kinetics law (pH 4–9). Adsorption results were compared with that obtained with multiwalled carbon nanotubes and other resins. On the other hand, the theoretical model used in the present investigation was found to predict reasonably well the ion exchange breakthrough performance. Arsenic can be eluted with sodium chloride solutions to afford the ultimate arsenic recuperation via precipitation to as arsenate salts or even crystalline scorodite.

Keywords: Arsenic(V); Adsorption; Lewatit MP64 resin; Batch and column operations; Multiwalled carbon nanotubes

1. Introduction

Mostly heavy metals and metalloids are considered as non-biodegradable toxic pollutants which may be released in the environment by various activities, thus, their removal represents a necessary environmental challenge. In the case of solids (and as a part of their hydrometallurgical treatment) and liquid effluents, there are a number of technologies available for the removal of these elements: chemical precipitation, coagulation, ion exchange, solvent extraction, membrane processes, etc. [1–6].

Ion exchange and adsorption processes are one of the most popular methods and somewhat economically feasible alternatives for the removal of these hazardous ions, and particularly arsenic, from aqueous solutions [7–10].

Arsenic is widely distributed in the environment, being both natural and anthropogenic activities the cause in the significant input of the element to the environment. Arsenic is known to be essential for life in small amounts, but sufficient high exposures to inorganic arsenic in natural environments, such as waters, sediment and soil have proved to be toxic for plants, animals and humans.

The objective of this study is to address the performance of Lewatit MP64 ion exchange resin in the removal of As(V) from waters. Various parameters were studied, in both batch and continuous operational modes, to optimize conditions for effective removal of this metal ion from water containing it.

2. Experimental

Lewatit MP64 (Fluka, Spain) is a macroporous anion exchange resin, whose main characteristics are given in Table 1. The phosphine oxide Cyanex 923 (CYTEC Ind., Canada) is a solvation extractant whose characteristics are described elsewhere [11]. All other chemicals used in this work were of AR grade. The characteristics of the multiwalled carbon nanotubes (MWCN) used in this work were given

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Presented at the 6th International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE-2017), 25–30 June 2017, Thessaloniki, Greece.

Table 1
Characteristics of Lewatit MP64 ion exchange resin

Polymer matrix	Styrene-DVB
Functional group	Tertiary amine (bears also quaternary ammonium groups)
Ionic form	Free amine/Cl$^-$
Exchange capacity	>1.4 meq/g
Operating temperature	100°C (maximum)
Effective size	0.32–1.25 mm
Swelling	35%

elsewhere [12], whereas the impregnation of these nanotubes by the phosphine oxide Cyanex 923 (MWCN-C923) was done by a procedure similar to that described in Ref. [13], though in this investigation the nanotubes were impregnated by a 50% v/v Cyanex 923 in Solvesso 100 (aromatic diluent, see also Ref. [11]) solution.

Aqueous solutions were analysed for arsenic by inductively coupled plasma (ICP) spectrometry.

2.1. Batch operation

Equilibrium adsorption experiments were carried out by the use of a preweighed amount of resin which were contacted (400 rpm, unless otherwise stated) in a glass reactor with the aqueous solution containing arsenic(V) at 20°C and for various times. The residual As(V) concentrations in the aqueous solution after the desired treatment and time were measured by ICP. The arsenic uptake by the resin was calculated from the residual concentration of the element in the aqueous phase. The fractional approach to equilibrium (*F*) was calculated by the following equation:

$$F = \frac{[\mathrm{As}]_0 - [\mathrm{As}]_t}{[\mathrm{As}]_0 - [\mathrm{As}]_e} \qquad (1)$$

where $[\mathrm{As}]_0$ is the initial solution concentration, $[\mathrm{As}]_t$ is the concentration at an elapsed time and $[\mathrm{As}]_e$ is the arsenic concentration in the aqueous solution at equilibrium.

2.2. Continuous operation

Column trials were carried out with 1 g resin, which was loaded into the column with a nominal capacity of 5 mL and fitted with 20 μm polyethylene frit as bed support. Aqueous phases containing arsenic(V) or sodium chloride were passed through the bed using a peristaltic pump. The effluent from the column was either directed to the fraction collector or to the waste. Samples were collected regularly and analysed by ICP to monitor the arsenic concentration leaving the column.

3. Results and discussion

Arsenic(V) can be found in aqueous solutions in the form of four species, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}, with pK_a values of 2.2, 6.9 and 11.5. The repartition of these species as a function of pH is necessary to understand the ion exchange process. In the typical pH range of natural waters, that is, 6–9, arsenic(V) is present as $H_2AsO_4^-$ and $HAsO_4^{2-}$.

3.1. Arsenic adsorption, batch experiments

The stirring speed required to eliminate the effect of bulk aqueous phase convection and to minimize the thickness of the aqueous diffusion film, was determined by measuring the rate of removal of an aqueous solution containing 0.01 g/L As(V) by 5 g/L Lewatit MP64 from pH 7.5 ± 0.1 at different speeds. The As(V)/pH 7.5 system has been used in this work as a reference system to comparative purposes. Experimental data showed that there is neither an increase of the rate of arsenic removal from the solution nor an increase in the maximum metal uptake onto the resin in the range between 300 and 1,000 rpm. Thus, a maximum in metal uptake and a minimum in the thickness of the aqueous boundary layer were achieved in this stirring speed range. Consequently, all other batch experiments have been run at 400 rpm.

The removal of arsenic(V) by Lewatit MP64 (5 g/L) from aqueous phases at different pH values are reported in Fig. 1. It can be seen that in the 4–9 pH range there is practically no difference among this removal, while arsenic removal decreases at the lower and higher pH values range. For the present ion exchange system, it seems that $H_2AsO_4^-$ and $HAsO_4^{2-}$ species are adsorbed preferably over AsO_4^{3-} and these over H_3AsO_4. The metal uptake concentrations at the various pH values are summarized as: 0.11 mg As/g resin at pH 2, 1.99 mg As/g resin at pH 4–9 and 1.72 mg As/g resin at pH 10. Furthermore, the experimental data of arsenic(V) adsorption kinetics, at the 4–9 pH range, fit well (r^2 = 0.998)

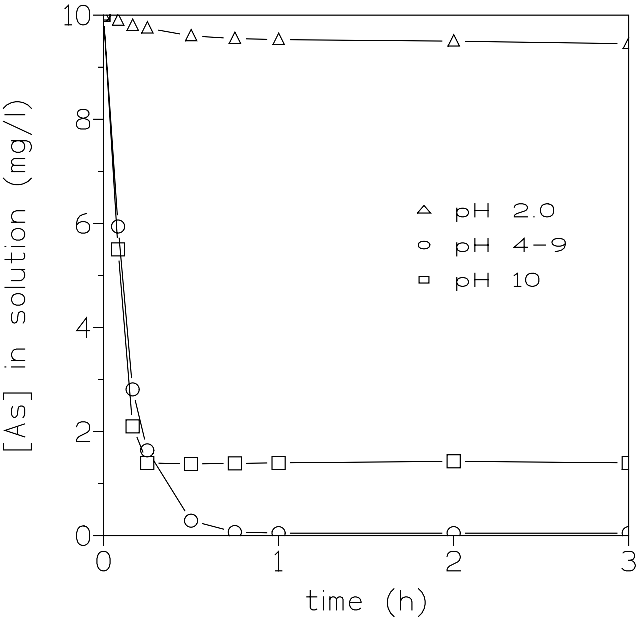

Fig. 1. Effect of pH on the removal of As(V) by Lewatit MP64. Aqueous phase: 0.01 g/L As(V), temperature: 20°C. Circle points represented averaged values obtained at pH 4.0, 6.0, 7.0, 8.0 and 9.0 ± 0.1.

with the pseudo-first-order kinetic equation [14], with the rate constant calculated as 0.125 min^{-1} and metal uptake of 2.05 mg/g (experimental 1.99 mg/g).

The influence of temperature (10°C–40°C) on 0.01 g/L arsenic(V) adsorption at pH 7.5 ± 0.1 by 5 g/L of the resin was also investigated, and the results obtained shown that the arsenic adsorption is favoured by a decrease of temperature, though nearly 80% of the initial arsenic content of the solution were adsorbed in 15 min for every temperature. The arsenic uptake process can be related to an exothermic reaction.

The Langmuir and Freundlich models are two general isotherms commonly used to describe the equilibrium ion exchange and/or adsorption relation between the solid and liquid phases [15,16], these isotherms relate metal, or a given solute, uptake per unit weight of adsorbent to the equilibrium adsorbate concentration in the bulk liquid phase. The observed data of the equilibrium ion exchange tests are shown in Fig. 2. This figure also shows the model fit using the two isotherms. The model fit (Table 2) reveals that the Langmuir isotherm represents Lewatit MP64 adsorption of As(V) better the Freundlich isotherm. It is worth to note here that the Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface.

The rate law governing the adsorption of arsenic(V) by Lewatit MP64 had been determined by using various experimental conditions. Three possible adsorption mechanisms had been evaluated if the adsorption of arsenic(V) into the resin must be considered as a liquid–solid phase reaction which includes diffusion of arsenic species from the aqueous phase to the resin surface, the diffusion of these species within the resin and the chemical reaction between them and resin functional groups. The rate equations for the above three cases are described elsewhere [17]. Results from this investigation are shown in Table 3, and shows that the arsenic(V) uptake by Lewatit MP64 resin is best fitted by the film-diffusion controlled mechanism.

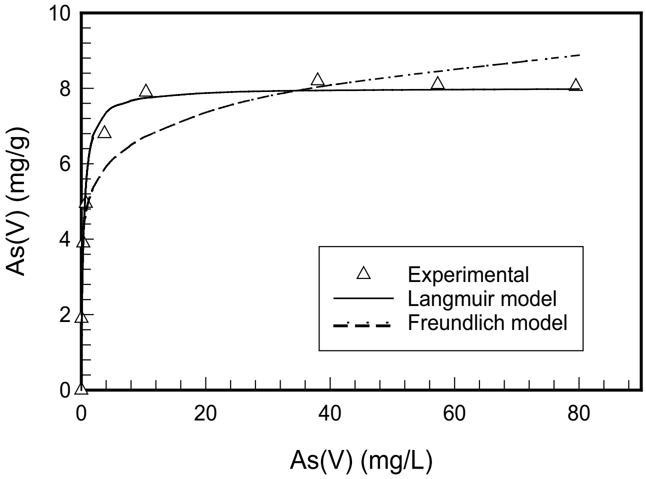

Fig. 2. Isotherm model fits of experimental equilibrium ion exchange data of Lewatit MP64 at 20°C.

Table 2
Parameters of the Freundlich and Langmuir isotherms

	r^2	k (mg/g)	n	$[\text{As}]_m$ (mg/g)	b (L/mg)
Freundlich	0.934	4.9	0.14		
Langmuir	0.975			8.0	2.8

k relates to sorption capacity, n to sorption intensity, $[\text{As}]_m$ to maximum uptake capacity and b to binding constant.

The performance of this system was compared against other potential exchangers or adsorbents for arsenic(V). The results from these series of experiments were shown in Table 4. It can be seen that resins, having a quaternary ammonium salt as exchanger group, present the best results, whereas adsorbents with no active groups such as MWCN, Lewatit EP63 and even MWCN-C923 did not remove arsenic(V) from these solutions under the present experimental conditions. In the case of the resins containing quaternary ammonium salts as active group, the uptake of arsenic(V) onto the resin can be explained by an anion exchange reaction between the anionic arsenic(V) specimens in the solution and the chloride ions from the resin, that is:

$$\left.\right]-\text{N}^+\text{Cl}^-_r + \text{H}_2\text{AsO}^-_{4_{aq}} \Leftrightarrow \left.\right]-\text{N}^+\text{HAsO}^-_{4_r} + \text{Cl}^-_{aq} \qquad (2)$$

where]– represented the inert matrix of the resin, and r and aq subscripts, the resin and aqueous phases, respectively. In the case of the Cyanex 923-impregnated carbon nanotubes, the result can be explained in terms of

Table 3
The regression coefficients and rate constants for the tested adsorption mechanisms of arsenic onto Lewatit MP64 resin

$[\text{As}]_0$ (mg/L)[a]	Temperature	Equation	r^2	k (min^{-1})
10	10°C	$\ln(1 - F)$	0.997	0.10
		$\ln(1 - F^2)$	0.986	1.5×10^{-3}
		$3 - 3(1 - F)^{2/3} - 2F$	0.976	3.5×10^{-4}
10	20°C	$\ln(1 - F)$	0.998	0.13
		$\ln(1 - F^2)$	0.977	1.9×10^{-3}
		$3 - 3(1 - F)^{2/3} - 2F$	0.991	4.7×10^{-4}

[a] At pH 7.5 ± 0.1.

Table 4
Arsenic removal from aqueous solution using various resins and multiwalled carbon nanotubes

Resin-adsorbent	Active group	% As(V) removal
Lewatit EP63	Nil	10
MWCN-C923	Phosphine oxide	<1
Dowex 1 × 8	QAS	64
Ionac SR7	QAS	35
MWCN	Nil	4
Amberlite 958	QAS	87
Lewatit MP64	see Table 1	>98

Aqueous solution: 0.01 g/L As(V) at pH 7.5 ± 0.1, resin-adsorbent dosage: 5 g/L, temperature: 20°C, time: 3 h, QAS: quaternary ammonium salt.

the chemistry associated with the metal uptake process, Cyanex 923 is a solvation reagent with formula R_3PO, being R alkyl chains, thus its extraction (metal uptake) abilities are due to the donation of the free electron pair of the oxygen atom to a neutral molecule which are extracted (uptake) to the organic phase. Due to that in this work, the arsenic(V) specimens in the aqueous solution are in the form of anionic species, the previous reaction is not possible, and the arsenic uptake onto the impregnated carbon nanotubes is nil, the above probably will reverse if the pH of the solution reached acidic pH values, with arsenic(V) present in the aqueous solution as the neutral H_3AsO_4 specimen. With respect to the adsorbents having no active groups, very probably the adsorption results will increase in experimental conditions different to that employed in this work (which are the best for Lewatit MP64, which is the goal of our investigation), but that at present are out of the scope of our investigation.

3.2. Arsenic adsorption, continuous experiments

Ion exchange is a process whose performance is affected by a number of operational variables which included the equilibrium resin adsorption capacity and the mass transfer rate. Often, the behaviour of an ion exchange/adsorption column can be expressed by the following equation:

$$\ln\frac{[\mathrm{As}]_t}{[\mathrm{As}]_0-[\mathrm{As}]_t}=K[\mathrm{As}]_0\left(t-\frac{[\mathrm{As}]_e\,m}{[\mathrm{As}]_0\,f}\right) \tag{3}$$

where $[\mathrm{As}]_t$ is the solute concentration in the outlet solution at time t, $[\mathrm{As}]_0$ is the inlet solute concentration, K is the rate constant of adsorption, $[\mathrm{As}]_e$ is the equilibrium solid-phase (i.e. resin) concentration of sorbed solute, m is the mass of adsorbent, f is the flow rate and t is the time [18]. Moreover, the above equation is related to the following equation:

$$\ln\frac{[\mathrm{As}]_t}{[\mathrm{As}]_0-[\mathrm{As}]_t}=k(t-\tau) \tag{4}$$

where the two parameters k and τ can be estimated from the slope and the intercept when plotting ln $[\mathrm{As}]_t/[\mathrm{As}]_0 - [\mathrm{As}]_t$ versus time, respectively. These two parameters for Lewatit MP64 adsorption of As(V) for the different flow rates are listed in Table 5. Using the estimated parameters, the breakthrough curves for various flow rates could be predicted for As(V) adsorption. Fig. 3 compares the predicted and experimental data for various flow rates. It can be observed that the model predictions compare reasonably well with the experimental data, thus, Eq. (3) can be used for convenient representation of the column process under the present experimental conditions.

Table 5
Parameters of Eq. (4)

Flow rate (cm^3/min)	Inlet concentration[a] (mg/L)	k (min^{-1})	τ (min)
3	20	0.037	310
6	20	0.070	129
12	20	0.062	74

[a] At pH 7.5 ± 0.1.

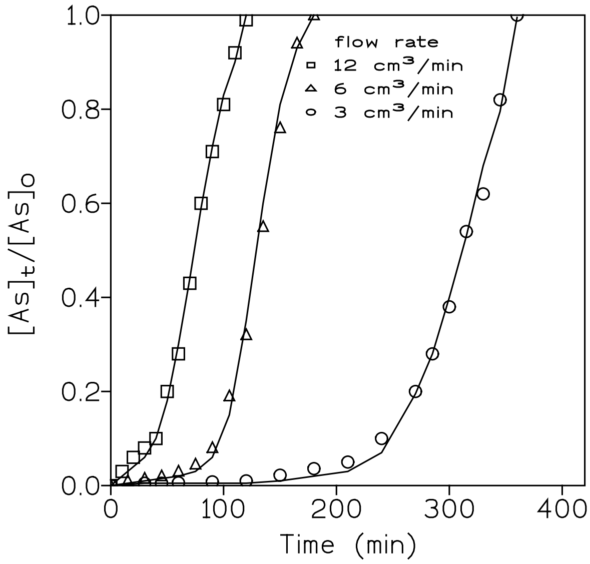

Fig. 3. Comparison of predicted (lines) and experimental (symbols) As(V) adsorption breakthrough curves of Lewatit MP64 for different flow rates. Temperature 20°C. Inlet solution 0.02 g/L As(V) at pH 7.5 ± 0.05.

3.3. Arsenic elution

Previous experiments had shown that sodium chloride solutions can be used effectively to remove arsenic from the arsenic-loaded resin phase and at the same time the resin is regenerated. Fig. 4 shows the elution results using the eluant flow rates of 6 and 12 cm^3/min. When a flow rate of

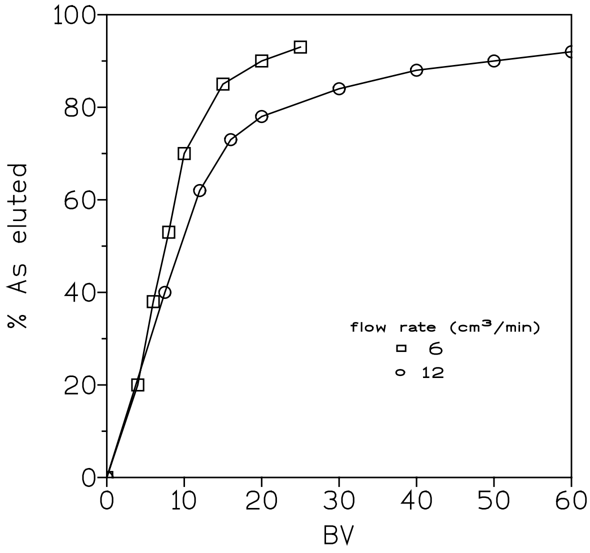

Fig. 4. Effect of flow rate on As(V) elution from resin. Stripping phase: 2 M NaCl, resin loading: 5 mg As/g resin, temperature: 20°C.

6 cm^3/ min was applied, nearly 85% of arsenic was eluted by 15 bed volume of eluant in 7.5 min. Comparing with the result of 12 cm^3/min, the elution time was reduced to an half but the amount of arsenic eluted was decreased to about 70%.

The column performance had been tested on continuous use of five consecutive loading (0.02 g/L As(V) at pH 7.5 ± 0.1)-elution (2 M NaCl) processes, and results obtained shown no appreciable loss in the column properties after these cycles.

3.4. Arsenic precipitation

Removal of arsenic from the eluate can be performed by precipitation, as a metal (most commonly iron (III) or calcium) arsenate or even crystalline scorodite, with the proper metal salt and subsequent adjustment of the pH. It should be noted here that the experimental conditions used, that is, the stoichiometric amount of the corresponding added salt, temperature, pH, etc., depends upon the final product that one want to obtain [19,20].

4. Conclusions

Lewatit MP64 resin had been used to remove arsenic(V) from aqueous solutions, with maximum metal uptake (1.99 mg As/g resin) at the 4–9 pH range. The Langmuir isotherm was found to adequately describe the equilibrium relation between the resin and liquid phases of the ion exchange process, whereas kinetics experiments showed that arsenic adsorption by Lewatit MP64 resin is film-diffusion controlled and obeys the pseudo-first-order kinetic law. Under continuous conditions, the increase in the flow rate causes a decrease of the breakthrough performance. A model was adopted for representing the column performance. Arsenic elution from loaded resin is accomplished by the use of sodium chloride solutions, resulting in eluates in which arsenic can be finally precipitated as arsenate salts.

Acknowledgement

To CSIC (Spain) for support.

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