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ARSENIC SORPTION USING MIXTURES OF ION EXCHANGE RESINS CONTAINING N-METHYL-D-GLUCAMINE AND QUATERNARY AMMONIUM GROUPS

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ABSTRACT

The method of synthesis and the arsenic removal properties of ion-exchange resins based on *N*-methyl-D-glucamine and trimethylammonium groups are presented. The N-methyl-D-glucamine based monomer was synthesized by the reaction of 4-vinyl benzyl chloride with N-methyl-D-glucamine, along with the use of *N,N*-methylene-*bis*-acrylamide as a crosslinker reagent for polymerization. In addition, poly(4-vinylbenzyl)trimethylammonium was synthesized. Arsenate sorption studies were conducted and the pH effect, kinetics, sorption capacity, and elution performance were studied. The experimental data were fitted to kinetic models, such as the pseudo-first order and pseudo-second order models. The pseudo-second order model exhibited the best correlation with the experimental data. The Langmuir and Freundlich isotherms were fitted to the experimental data, and the Freundlich isotherm exhibited the best fit.

Keywords: Arsenic, N-methyl-D-glucamine, ion exchange, ion exchange resin mixture.

INTRODUCTION

The removal of metal ions and oxyanions from dilute or concentrated solutions has received a great deal of attention in the last 40 years, to recover high-cost metals or to decontaminate effluents[1].

A number of these studies have developed sorption processes including adsorption and ion-exchange mechanisms, precipitation, solvent extraction, conjunction of membranes and polymers using simple materials such as activated carbon or more sophisticated materials such as especially tailored polymers as well as biosorbents, such as fungal or bacterial biomass, and materials of biological origin, including alginate and chitosan[2-14].

One of the more harder pollutant is arsenic which is found in various forms in all segments of the environment, and its compounds are considered as highly toxic substances; these arsenic compounds are generated from natural occurrence and antropogenic such as: pesticides, dyes and drugs, *etc*[15]. The presence of arsenic in natural waters is a worldwide problem. The major natural source of arsenic in groundwater is leaching from geological formations. Drinking arsenic-contaminated water for long periods of time causes cancers in the skin, lung, urinary bladder, and kidney[16, 17]. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan, and India[18]. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have strictly reduced the maximum contaminant level recommended for arsenic from 50 μg L^{-1} to 10 μg L^{-1} to minimize the risk to humans[19].

Arsenic can exist in many oxidation states in the natural environment, including the -3, 0, +1, +3, and +5 valences. Two forms of arsenic are common in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as arsenic (III) and arsenic (V), respectively[17, 20, 21].

Several methods, such as oxidation, precipitation, coagulation, adsorption, ion-exchange, and the use of membranes filtration, have been developed for arsenic removal from water[22-24]. The adsorption process, which can reduce the arsenic concentration to the minimum level, appears to be the most promising approach amongst the available methods and has been widely used for arsenic removal because of its low cost and high efficiency[25,26]. Strong base anion-exchange resins that contain quaternary ammonium groups attached to a polymeric matrix have been extensively studied for their ability to remove arsenic and have been found to exhibit a higher affinity for divalent species ($HAsO_4^{2-}$)[24]. Therefore, for these resins, the optimum pH for sorption is between 7 and 9, where the concentration of $HAsO_4^{2-}$ species is high[27].

Immobilization of N-methyl-D-glucamine (NMDG) on poly(vinyl benzyl chloride) beads yields an effective and highly selective sorbent for arsenate ions. Only a few studies on arsenic removal have used NMDG as the ligand (attached to new supports)[28, 29]. It has been demonstrated that ion exchange resins containing NMDG ligands improve the retention of arsenate as $H_2AsO_4^-$ and that the sorption is efficient in acidic conditions (in the pH range of 3 to 6)[28].

In this way, it is expected to achieve a high arsenic sorption in a wide range of pH by means of ion exchange resins mixture (ammonium and glucamine-based polymers) in the same batch.

In this study, the resins were characterized with FT IR spectroscopy and batch studies were performed to evaluate the efficiency of arsenic removal using mixtures of synthetic ion exchange resins that contain *N*-methyl-D-glucamine and quaternary ammonium groups. The sorption performances of these resins were investigated by changing the polymer:polymer ratio in mol. Moreover, the kinetic and equilibrium data were also evaluated by means of kinetic and isotherms models.

EXPERIMENTAL

Materials

The monomer *N*-(4-vinylbenzyl)-*N*-methyl-D-glucamine (VBNMDG) was synthesized using the precursors 4-vinylbenzyl chloride (VBC, Aldrich) and *N*-methyl-D-glucamine (NMDG, Aldrich) as received. The reagent *N,N*-methylene-*bis*-acrylamide (MBA, 98% Aldrich) and ammonium persulphate (Aldrich) were used as crosslinker and initiator reagents, respectively. For the synthesis of poly[(4-vinylbenzyl)trimethylammonium chloride] resin (PClVBTA), (4-vinylbenzyl) trimethylammonium chloride (Aldrich) was employed. Hydrochloric acid, nitric acid, and perchloric acid were used as stripping agents.

Synthesis

Synthesis of poly[N-(4-vinyl benzyl)-N-methyl-D-glucamine] resin

The reaction of *N*-methyl-D-glucamine and 4-vinyl benzyl chloride was performed in a three-neck round-bottom flask using a mole ratio of 1:1. Reagent grade *N*-methyl-D-glucamine (44 mmol) was dissolved in 150 mL of a 2:1 volume solvent mixture of dioxane and deionized water. The solution was added to the reactor and heated for 20 min until the NMDG was completely dissolved. Subsequently, 44 mmol of 4-vinyl benzyl chloride was dissolved in 20 mL of dioxane, and then was added slowly to the reactor. The reaction was maintained under reflux with constant stirring for 5 h, and a yellowish solution was obtained. To remove unreacted VBC, the final solution was washed with ethyl ether twice. The VBNMDG monomer, which was dissolved in a dioxane/water solvent, was transferred to the reactor, and then *N,N*-methylene-*bis*-acrylamide (15 mol-% based on monomer) was added. After the crosslinking reagent was dissolved, ammonium persulfate (1 mol-%) was added. The mixture was degassed with a nitrogen gas for 10 min, and then the reaction was stirred overnight under nitrogen atmosphere at 70ºC. The resin was extracted and washed with dioxane and distilled water and subsequently dried in an oven at 50 ºC. Finally, dry resin was sieved, and a particle-size fraction in the range of 180 to 250 μm was chosen for all of the sorption experiments (see Fig. 1).

Synthesis of poly[(4-vinylbenzyl)trimethylammonium chloride] resin

The reaction was performed using 37.7 mmol of (4-vinylbenzyl) trimethylammonium chloride and *N,N*-methylene-*bis*-acrylamide (15 mol-% based to monomer) dissolved in water. After the crosslinking reagent was dissolved, potassium persulfate (1 mol-%) was added. The mixture was

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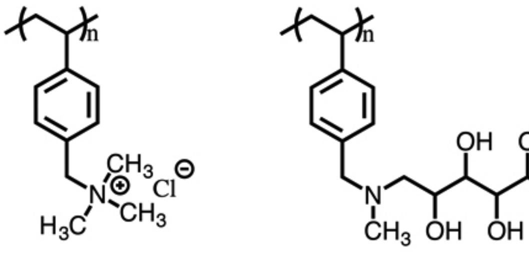
degassed using nitrogen gas for 10 min. The reaction was stirred overnight under nitrogen atmosphere at 70 ºC. The resin was washed with distilled water and subsequently dried in an oven at 50ºC. Finally, dry resin was sieved, and a particle-size fraction in the range of 180 to 250 µm was chosen for all of the sorption experiments (see Fig. 1).



P(ClVBTA) P(VBNMDG)

Fig. 1. Synthetic resin structures

Physicochemical characterization

The morphology and structure of the resin was evaluated by infrared spectroscopy (Perkin Elmer 1760-X spectrometer using a range of 4000 to 400 cm^{-1} and KBr pellets). The arsenic concentrations were determined by atomic absorption spectroscopy (FIAS-100 flow injection atomic spectrometry); for these measurements, As(V) was reduced to As(III) using HCl (50%), KI (20%) and ascorbic acid (10%).

Sorption studies

Batch sorption experiments were performed to evaluate the arsenate retention by PVBNMDG and PClVBTA resins. The effect of pH on retention was studied to obtain a correlation between arsenic speciation and the sorption performance of the resins PVBNMDG and PClVBTA at a particle size range of 180 to 250 µm. The arsenic aqueous solutions were adjusted to a pH of 3-9 using dilute HNO_3 and NaOH solutions. In these studies, various amounts of PVBNMDG (10, 20, 30, 40, and 50 mg) and PClVBTA (1, 2, 3, 4, 5, and 10 mg) were contacted with 10 mL As(V) solution (10 mg/L) in a shaker at 30 ºC under a stirring rate of 140 rpm for 24 hours. The sorption performances of these resins were investigated by changing the polymer:polymer ratio in mol. The different PVBNMDG:PClVBTA molar ratios, such as 1:3, 1:1, and 3:1, were prepared, resulting in a total amount of 50 mg of resin per ratio. These experiments were performed by contacting 50 mg resin with 10 mL As(V) solution (10 mg L^{-1}) at 30 ºC under a stirring rate of 140 rpm for 24 hours. To evaluate the effect of time on sorption, kinetic experiments were performed using 10 mL of As(V) solution (10 mg L^{-1}) at 3-9 pH and with the sorbents of molar ratio of PVBNMDG: PClVBTA as 25:75 (50 mg). The experiments were performed at 30 ºC and under a stirring rate of 140 rpm. The samples were withdrawn from the shaker at different time intervals (0, 1, 3, 5, 10, 15, 30, 60, 120, and 1440 min). The experimental data were evaluated using conventional and diffusion-reaction kinetic models. The equilibrium experiments (isotherms) were performed using a range of arsenic concentrations (5-650 mg L^{-1}) and a 1:3 molar ratio of PVBNMDG:PClVBTA. These experiments were performed at 30 ºC for 24 hours at pH 3.0, 6.0, and 9.0. The experimental data were evaluated using Langmuir and Freundlich isotherm models to evaluate the sorption process. To study the arsenate elution process, different acid solutions were used. In the sorption step, a 1:3 molar ratio of PVBNMDG:PClVBTA was contacted with 10 mL of As(V) solution 10 mg L^{-1} in a shaker at 30 ºC under a stirring rate of 140 rpm for 24 hours. After the sorption step, the resin was contacted with 4 M HCl, HNO_3 and $HClO_4$ in a shaker for 4 hours at 30 ºC to evaluate the elution performance.

RESULTS AND DISCUSSION

Infrared spectroscopy

Figure 2 shows the infrared spectra of the synthetic resins. The PVBNMDG resin exhibited the characteristic absorption bands at 1080 cm^{-1} ν(C-O), 1455 cm^{-1} ν(CH_2), 1653 cm^{-1} ν(C=C), and 2956 ν(C-H). The signals in the region of 1000 cm^{-1} and 1150 cm^{-1} are characteristic of the glucamine group attributed to the C-O and C-N vibrational bands, respectively. Meanwhile, the PClVBTA resin exhibited the characteristic absorption bands at 1120 cm^{-1} ν(C-N), 1482 cm^{-1} ν (N^+-$(CH_3)_3$), and 1644 cm^{-1} ν (C=C). The presence of these bands confirms the structure of the resins.[30]

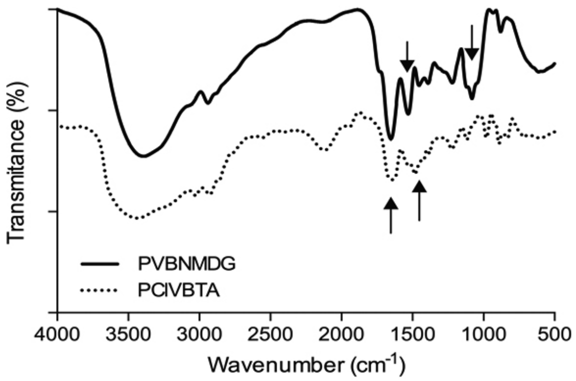


Fig. 2. Infrared spectra of the PVBNMDG and PClVBTA resins.

Arsenic sorption

For all adsorbents, pH is a key factor determining the performance of the sorption processes. Hydronium in water can change the structural properties of the ligands of the resins and also the speciation of the metal ions in aqueous solution, thereby affecting the sorption. Figure 3 shows the effect of pH and the adsorbent amount on the arsenate sorption determined by the batch equilibrium procedure. The curves indicate that removal of arsenic for both resins increases as the amount of resin increases due the higher of number of exchange sites. However, the pH significantly affects the sorption. For PClVBTA resin, maximum retention was observed at pH 9, where arsenic is found primarily as $HAsO_4^{2-}$. This result is consistent with strong basic anion exchange resins with ammonium groups, which interact better with the divalent species of arsenic in the pH range of 8 to 10.[27] The arsenic removal decreased at pH 6 because $HAsO_4^{2-}$ and $H_2AsO_4^-$ ions exist in equilibrium, and at pH 3.0, the removal exhibits its lowest value. By contrast, PVBNMDG resin exhibits maximum retention at pH 6.0, where arsenic is found primarily as $H_2AsO_4^-$. The main characteristic of *N*-methyl-D-glucamine as a ligand was the interaction of monovalent arsenate species with the protonated tertiary amine.[28, 29, 31] However, the efficiency of the PVBNMDG resin was lower than that of the PClVBTA resin.

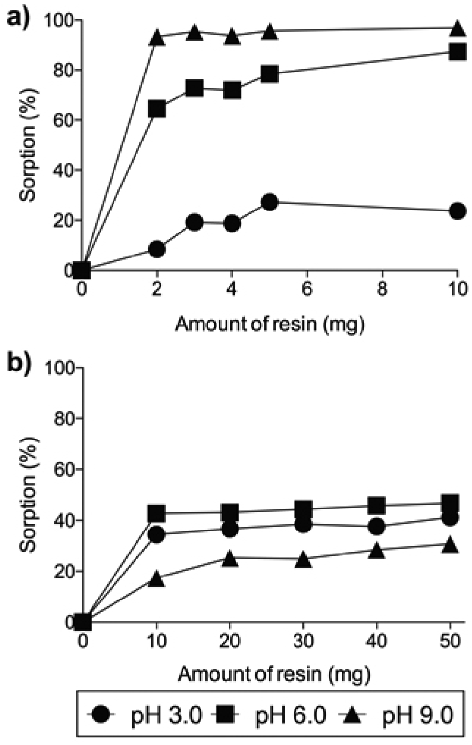


Fig 3. Curves of As(V) removal using a) PClVBTA, b) PVBNMDG for different pH.

Figure 4 shows the effect of pH on arsenate sorption using different resin molar ratios. At pH 3.0, the mixtures of resins exhibited the lowest sorption, reaching only a removal of 33% (1.0 mg g^{-1}), whereas at pH 6.0 and pH 9.0, the uptake efficiency increases; the 1:3 molar ratio presented the best sorption (70.3 % (2.2 mg g^{-1}) and 75.0 % (2.4 mg g^{-1}) for pH 6.0 and 9.0, respectively). The decrease in sorption as the mole content of PVBNMDG decreases reveals the contribution of glucamine-based resin on arsenic sorption.

Because the 1:3 mixture exhibited the best sorption, this mole ratio was selected for further experiments.

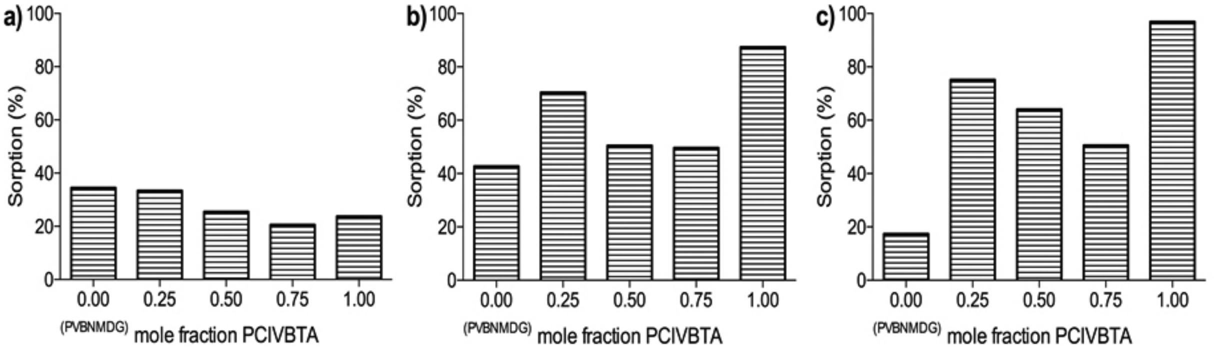


Fig 4. Removal of arsenic for different PClVBTA:PVbNMDG molar ratios at a) pH 3.0, b) pH 6.0, and c) pH 9.0.

Kinetic studies

The kinetic behavior of the resin mixture at the 1:3 molar ratio (PClVBTA:PVbNMDG) was examined for an arsenic concentration of 10 mg L^{-1} at pH 3.0, 6.0 and 9.0. Figure 5 shows the change of arsenic concentrations as a function of time. The curves reveal a rapid uptake of arsenic oxyanions, with the maximum sorption achieved after only 2 h of contact, whereas the pH effect exhibits the same trend observed in the previous experiments (highest sorption at pH 6.0 and pH 9.0).

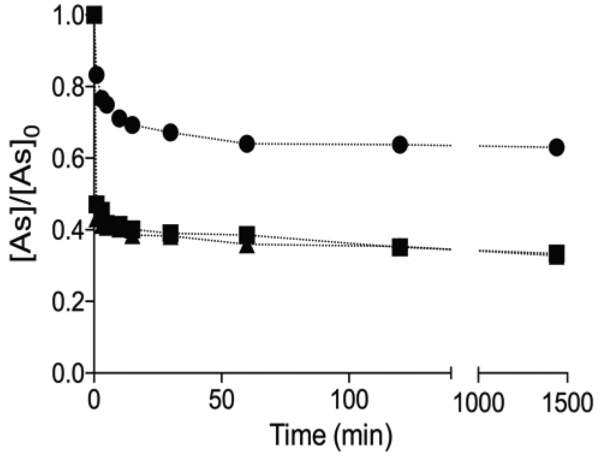


Fig 5. Change of arsenic concentrations as a function of time using a 1:3 molar ratio of PClVBTA:PVbNMDG polymer. ([As]= 14.3 mg L^{-1}; resin dosage: 5 mg L^{-1}]

The kinetic data were evaluated using the conventional kinetic models of the pseudo-first-order and pseudo-second-order kinetics models, [32,33] and the diffusional/reaction models of the infinite solution model and the unreacted core model.[34]

Lagergren proposed the pseudo-first order model for describing the adsorption process of solid-liquid systems, and its linear form is formulated below[35]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

where q_e (mg g^{-1} resin) and q_t are the amount of arsenic adsorbed at equilibrium and at time t, respectively. The slope from a plot of $\log(q_e - q_t)$ vs. t allows the determination of the rate constant k_1 (min^{-1}).

The pseudo-second order equation has been widely used due the excellent fit of the experimental data for the entire sorption period of many systems.[36] The kinetic model can be expressed as below:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

Integrating and assuming boundary conditions, the rearranged linear form of the pseudo-second order model is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_e and q_t are the arsenic amount adsorbed (mg g^{-1}) at equilibrium and at time t, respectively, $h=kq_e^2$ is the initial sorption of arsenic (mg g^{-1} min^{-1}), and k_2 is the rate constant of sorption (g mg^{-1} min^{-1}). The sorption kinetic data were adjusted to the models described above, and the parameters obtained are presented in table 1. Clearly, the pseudo-second order model exhibited the best fit, with a correlation coefficient above 0.999. The rate constant increases with the pH, which can be explained by the speciation of arsenic. As stated before ammonium-based resin exhibits greater affinity towards divalent arsenic oxyanions, which its maximum concentration occurs at the pH 9.0. In this way, the mixture contains a major proportion of ammonium-based resin favoring the sorption at pH 9.0.

Table 1. Kinetic parameters for the pseudo-first order and pseudo-second order models.

	pH 3.0	pH 6.0	pH 9.0
Pseudo-first order			
$q_{e,cal}$ (mg g^{-1})	0.41	0.23	0.17
k_1 (min^{-1})	0.058	0.018	0.037
r^2	0.9111	0.7055	0.8365
Pseudo-second order			
$q_{e,cal}$ (mg g^{-1})	0.93	1.69	1.70
k_2 (g mg^{-1} min^{-1})	0.70	1.60	2.81
h (mg g^{-1} min^{-1})	0.61	4.57	8.12
r^2	0.9990	0.9999	0.9998

The models for process dynamics include both the diffusional steps (bulk solution, a film layer at the external surface of the particle, pores) and the exchange reaction on the active sites. Because the resistance in the bulk solution is easily controlled and negligible, three resistances, i.e., film diffusion, particle diffusion, and chemical reaction, usually determine the overall rate of the ion-exchange process.[37] The kinetic study data were evaluated by using two approaches. The first approach is based on Fick's first law of integration of material balance for infinite solution volume (ISV). The second method uses the unreacted core model (UCM), in which ion exchange is treated as a heterogeneous reaction. According to the UCM, the metal ions are exchanged on the outermost layer of the particle, and as time passed, the reaction sites are gradually moved toward the core of the particle. The diffusional and reaction models summary is shown in table 2.

Table 3 presents the correlation coefficients (r^2) resulting from the fit of kinetic data to diffusional and reaction models. The maximum correlation coefficients for the linear models indicate that the rate is particle-diffusion controlled according to the ISV models, and the reacted layer is controlled according to the UCM models for all pH.

Table 2. Diffusional and reaction models [34].

Model	Equation	Rate-determining step
ISV[a]	$F(X) = -\ln(1-X) = K_{li}t$ where $K_{li}=3DC/r_0\delta C_r$	Film diffusion
ISV[a]	$F(X) = -\ln(1-X^2) = kt$ where $k=D_r\pi^2/r_0^2$	Particle diffusion
UCM[a]	$F(X) = X = (3C_{Ao}K_{mA}/a_{ro}C_{so})t$	Liquid film
UCM[a]	$F(X) = 3-3(1-X)^{2/3}-2X = (6D_{eR}C_{Ao}/a_{ro}^2C_{so})t$	Reacted layer
UCM[a]	$F(X) = 1-(1-X)^{1/3} = (k_sC_{Ao}/a_{ro}C_{so})t$	Chemical reaction

[a] $X = q_e/q_t$ and q_e and q_t are the amounts of As(V) adsorbed at equilibrium and at time *t*, respectively.

Table 3. The correlation coefficients (r^2) according to diffusion and reaction models.

	ISV		UCM		
	Film diffusion	Particle diffusion	Liquid film	Reacted layer	Chemical reaction
pH=3	0.9112	0.9366	0.7135	0.7896	0.7135
pH=6	0.7056	0.7140	0.5566	0.5728	0.5566
pH=9	0.8365	0.8385	0.7597	0.7670	0.7597

Adsorption isotherms

Equilibrium sorption isotherms are one of the most important tools used to design adsorption processes. Moreover, isotherms provide useful information about the interaction between the adsorbate and the adsorbent. The experimental data were fitted to the isotherm models of Langmuir and Freundlich. The curves indicates that for a concentration as high as 600 mg L^{-1} of As(V), the resins do not saturate (Fig. 6a). Unusual for this type of experiment is the shape of the curve for experiments at pH 3.0, which exhibits a concave shape, indicating an initial stage of low sorption and then increasing from *Ce* = 110 mg L^{-1}. The explanation of these results can be ascribed to the low affinity of monovalent arsenic species with the mixture, whereas the increase of sorption can be attributed to the increment of the gradient concentration. The isotherms at pH 6.0 and pH 9.0 were adjusted to isotherm models (Langmuir and Freundlich) by means of a non-linear regression fit (see Figure 6b). Both of the isotherm models describe well the experimental data, with correlation coefficients above 0.98. The maximum uptakes of resins from the Langmuir fit were 237 mg g^{-1} and 392 mg g^{-1} for pH 6.0 and pH 9.0, respectively. Different studies have investigated the efficiency of arsenic sorption using commercial ion exchange resins, such as Amberlite IRA-400, Purolite A-505, Relite A-490, and Diaion WA20/30 [38-40]. Anion exchange resins have a higher affinity towards divalent anions than towards monovalent anions, and the maximum sorption is reached between pH 6.0 and 9.0, where the concentration of divalent anions is maximal. For instance, Awual et al.[40] studied the arsenic sorption using commercial weak-base anion exchange resins and found that as the pH increases the arsenic sorption decreases, which was attributed to the diminishing of protonated amine form. On the other hand, Donia et al.[41] prepared a synthetic ion exchanger starting from a glycidyl methacrylate/methylene-bis-acrylamide resin with immobilized tetraethylenepentamine, and subsequently modified with glycidyl trimethylammonium chloride. The sorbent displayed the highest sorption at pH 6.0 and a equilibrium capacity (Langmuir) of 1.8 mmol g^{-1}.

Elution studies

Metal ion elution and sorbent regeneration is a critical consideration in the analysis of the process costs and the metal recovery in a concentrated form or further disposal. For effective reuse, a successful desorption process must restore the sorbent such that it exhibits properties that are close to its initial properties. This process must be performed when the sorbent is exhausted by the use of a suitable eluent. Arsenic acid (H_3AsO_4) is a weak acid with three pKa values: 2.2, 6.9, and 11.5. Therefore, when acid reagents are used as eluents, the arsenic monovalent and divalent anions attached to the resin ($H_2AsO_4^-$ and $HAsO_4^{2-}$) are transformed into the acid H_3AsO_4, which is a non-charged molecule and later leached.[38] The elution study was performed with different 4 M acid solutions (HCl, HNO_3 and $HClO_4$). Figure 6 shows the elution efficiency of HCl, HNO_3 and $HClO_4$ solutions reaching 96.0%, 96.1% and 92.3% elution, respectively. These results demonstrate that acid solutions are good stripping reagents for arsenic.

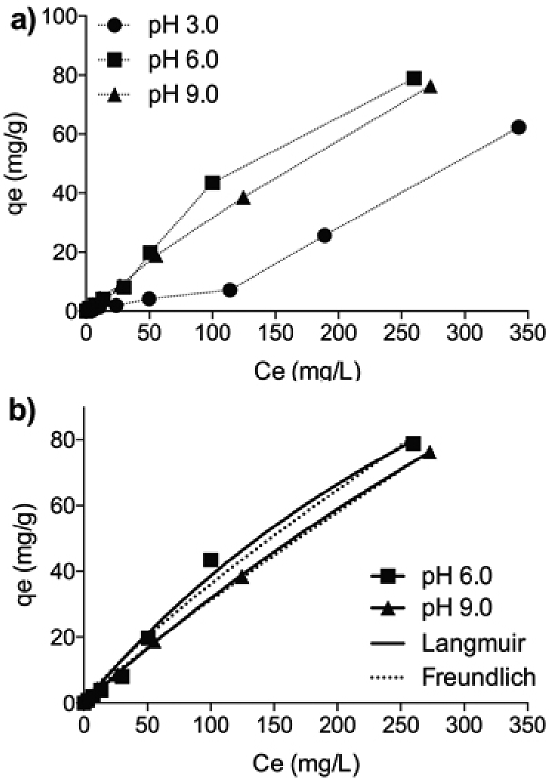


Fig 6. Arsenic sorption isotherms for mixture 1:3 at different pH values.

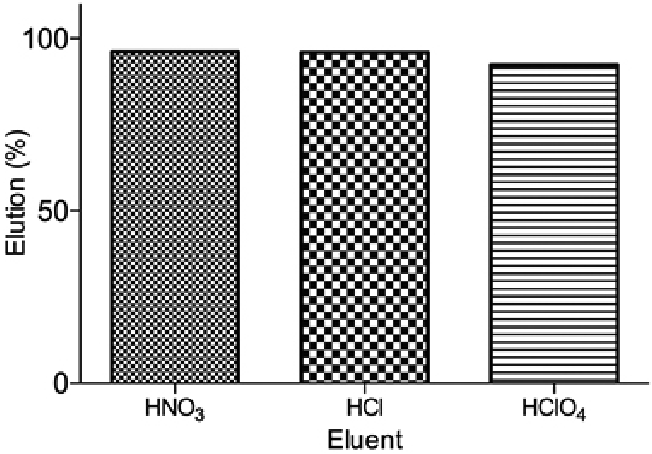


Fig 7. Elution profile of arsenic using HCl, HNO_3 and $HClO_4$.

CONCLUSIONS

Ion exchange resins poly[(4-vinylbenzyl)trimethylammonium chloride] and poly[*N*-(4-vinyl benzyl)-*N*-methyl-D-glucamine] were successfully synthesized. The evaluation of the arsenic uptake revealed that ammonium-based resins possess the highest sorption. Ion exchange resins mixtures of 0.25 mole fraction of PClVBTA exhibited the best performance reaching approximately 80% of removal. Kinetic and equilibrium studies showed that the sorption process is well described by the pseudo-second order model and the Langmuir isotherm. Regarding the elution performance, the acidic conditions by means of HCl and HNO_3 exhibited the best results.

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