

## Review

# Adsorption of As (V) by poly (*N*-octyl-4-vinylpyridinium) bromide: Determination of As (V) by direct measurement of fluorescence on the solid phase



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## ARTICLE INFO

## Article history:

Received 8 June 2016

Received in revised form 28 October 2016

Accepted 31 October 2016

Available online 2 November 2016

## Keywords:

Adsorption

Arsenic

Solid phase

Fluorescence

## ABSTRACT

Adsorption of As (V) by poly (*N*-octyl-4-vinylpyridinium) bromide (P4VPyC8), used as solid phase, was studied. Determination of As (V) was carried out by direct measurement of the fluorescence intensity on the solid phase. Adsorption variables were optimized for obtaining optimum values of pH and agitation time, where pH 9.0 and 60 min were established as optimum values. The adsorption of arsenic (V) was characterized by infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy. It was found that the fluorescence of the solid phase increases as the concentration of arsenic increases. Linearity was observed in the concentration range 6.80 to 90.0  $\mu\text{g L}^{-1}$ . The detection limit for determination of As (V) by this method was 2.24  $\mu\text{g L}^{-1}$  and the relative standard deviation (RSD) was 1.72%. The amount of retained As (V) was 0.154 mg/g of solid phase. The determination of As (V) in a sample of tap water by this method was well compared with the value reported by an external certified laboratory. Therefore, the method of analysis proposed here could be used as a screening methodology for monitoring the fulfillment of the norm for arsenic concentration in tap water.

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## 1. Introduction

Nowadays water pollution by heavy metals is a major issue because they are highly toxic to humans [1–4]. The damages that they cause are mainly skin lesions, lung, bladder, kidney, skin and uterus cancer [5]. Therefore, the identification, quantification and removal of heavy metals in water are of great importance. Arsenic belongs to the group of heavy metals and has two oxidation states; trivalent (As III) and pentavalent (As V), being both very toxic species [6,7]. As (III) is present as  $\text{H}_3\text{AsO}_3$  and depending on the solution pH it dissociates giving rise to negatively charged species such as  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HASO}_3^{2-}$  and  $\text{AsO}_3^{3-}$ . On the other hand, As (V) is present as  $\text{H}_3\text{AsO}_4$  and dissociates in solution producing  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  [8]. The equilibrium and acidity constants for these species are [6]:



Arsenic in water can have either a natural origin or anthropogenic sources. Natural sources are thermal and volcanic activity [9,10] and anthropogenic sources include the burning of fossil fuels, smelting, liquid wastes from mining industry, landfills, wood preservatives, pesticides and herbicides [8,11].

Due to adverse effects on human health, the World Health Organization recommends  $10 \mu\text{g L}^{-1}$  as maximum concentration of arsenic in drinking water. Thus, the Environmental Protection Agency of the United States has established  $10 \mu\text{g L}^{-1}$  as standard concentration of arsenic in drinking water [12]. For this reason and due to compliance with the aforementioned legislation, there is a growing interest in removing arsenic from water. In Chile the copper mining activity has an important impact on environmental issue. The high arsenic concentration in Chilean copper ore has caused serious environmental problems, forcing the government to impose arsenic emission limits for mining [13].

There are several methods for removing heavy metals from water, including adsorption, chemical precipitation, co-precipitation, reverse osmosis, ion exchange and oxidative filtration [14,15]. Many of these methods have disadvantages such as high cost and exhibit an average removal efficiency or incomplete removal of metal. Moreover, these methods are performed in sequential steps [16,17]. Adsorption and ion exchange methods are the preferred methods since some metal species have either positive or negative charges [18]. Ion exchange is an attractive method for removing metals from water due to its ability for quantitative removal and also for the long effective life of anionic exchange resins [19]. Ion exchange resins based on polymers and modified polymers are used to perform the ion exchange process for the retention of metallic ions. Lewatit MonoPlus M 500, a copolymer based on styrene-divinylbenzene, can be used as a resin to adsorb metallic ions.

This resin allows the separation of As (V) from As (III) in water at pH lower than 8, retaining As (V) and releasing As (III) through the copolymer in a column [6]. The poly(4-vinylpyridine) *N*-alkyl quaternized is an amphipathic cationic polyelectrolyte with antimicrobial capacity and some other interesting properties [20,21]. In fact, this polymer shows formal positive charge in all the pH range, therefore, it may interact electrostatically with heavy metals anions such as Cr (VI) [22]. Polymeric adsorbents such as quaternized P4VPy hydrogels and/or nanoparticles have been also reported [23–27]. On the other hand, their hydrophilic-hydrophobic character can be modulated by using different alkyl halides for the quaternization reaction of the pyridine group. This amphipathic character would allow this polymer matrix to interact efficiently with organic anions such as phenoxides, carboxylates, etc., by both electrostatic and/or hydrophobic interactions.

Retention of metallic ions by solid phases can also be used as an enrichment or pre-concentration method to increase the concentration of an analyte for its subsequent determination [28]. Some methods of enrichment are co-precipitation, solvent extraction, solid-phase extraction and electrolysis, among others. The solid phase extraction has some advantages over other methods of enrichment. These advantages are low solvent volumes, short sample preparation time and low disposal costs. The solid phase extraction has been used in the adsorption of metallic ions in aqueous samples [29]. An example is an adsorbent material based on chitosan and carbon nanotubes. This adsorbent can be used as enrichment for determination of V(V), Cr (VI), Cu(II), As (V), and Pb(II) in aqueous and biological samples, resulting in a fast method with good sensitivity and excellent accuracy [30].

On the other hand, expensive instrumentation such as inductively coupled plasma optical emission spectroscopy (ICP-OES) [31,32], inductively coupled plasma mass spectroscopy (ICP-MS) [33,34], electrothermal atomic absorption spectroscopy (ETAAS) [35,36] and flame atomic absorption spectroscopy (FAAS) can be used for the determination of As or other metallic species in water [37–39]. However, the development of a simple method for direct determination of arsenic (V) or other metals in aqueous solution, that does not require expensive instrumentation, is necessary.

The main objective of this study is to determine the optimal parameters of adsorption of As (V) and arsenic retention capacity by using poly(4-vinylpyridine) quaternized with octylbromide as solid-phase. This new method allows the determination of As (V) by direct measurement of fluorescence on the solid phase and was applied to a tap water sample.

## 2. Material and methods

### 2.1. Materials

Poly (4-vinylpyridine) (P4VPy) with molecular weight of  $6 \times 10^4 \text{ g mol}^{-1}$  and octylbromide were obtained from Sigma-Aldrich Inc. Anhydrous chloroform and ethyl acetate was from Merck AG. All reagents used in this work were of analytical grade. The solutions were prepared using deionized water provided by Milli-Q system with a specific conductivity of  $0,055 \mu\text{S cm}^{-1}$ . All glass materials used was washed with 10%  $\text{HNO}_3$  and rinsed three times with deionized water. Stock solutions of As (V)  $1000 \text{ mg L}^{-1}$  were prepared dissolving solid  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  in deionized water. Working solutions were prepared

by dilution of the stock solution. NaOH and HCl solutions, used for pH adjustment, were prepared by dissolution of adequate amount of each reagent in deionized water.

## 2.2. Synthesis of poly (*N*-octyl-4-vinylpyridinium) bromide (P4VPyC8)

The quaternization of poly (4-vinylpyridine) with octylbromide in anhydrous chloroform was previously reported by our group [22]. The degree of quaternization of the *N*-octyl-quaternized poly(4-vinylpyridine) (P4VPyC8) was determined by infrared spectroscopy by monitoring the absorption band of the pyridine ring at  $1600\text{ cm}^{-1}$  and the characteristic absorption band of the quaternized group at  $1640\text{ cm}^{-1}$ . The total disappearing of the  $1600\text{ cm}^{-1}$  band in the IR spectra of P4VPyC8 was considered as 100% of quaternization.

## 2.3. Optimal conditions for the As (V) adsorption

Two experimental variables were considered for the As (V) retention: stirring time and solution pH. In the latter case, the pH range was chosen according to some theoretical considerations in such a way that the predominant specie was only one. For the optimization purpose a STATGRAPHICS software was used. This allowed designing an experimental  $2^2$  factorial type screening with stirring time and solution pH as variables. The screening design includes also two central points and three reproductions (Tables 1 and 2).

## 2.4. Adsorption of As (V) by batch experiment

According to the optimized results for the stirring times and solution pH in the As (V) adsorption, a uni-variant study for the influence of the stirring time was performed. The volume of solution (100 mL) and the amount of P4VPyC8 (0.2 g) were kept constant and the concentration of As (V) was  $400\text{ }\mu\text{g L}^{-1}$ . The pH of all solutions was adjusted to 9. The pH was measured using a pH meter from Hanna Instruments model HI 111. The concentration of arsenic in solution and in the polymer matrix was determined by fluorescence spectroscopy by using a Hitachi F-2700 fluorescence spectrophotometer. The amount of metal adsorbed by P4VPyC8 was obtained by difference between the initial and the remaining concentration of the metal in solution. The latter was determined by fluorescence measurements of Rhodamine B, which interacts with the arsenate ions. This interaction decreases the fluorescence intensity of Rhodamine B, allowing the measurement of arsenic remaining in solution. The solid phase with adsorbed arsenic was measured by fluorescence allowing the determination of As (V) by direct measurement.

## 2.5. Characterization

Characterization of P4VPyC8 as solid phase was carried out in the absence and presence of adsorbed As (V) which was carried out with solutions of As (V) with a concentration of  $1000\text{ mg L}^{-1}$  at pH  $9.0 \pm 0.2$  and a stirring time of 120 min. Then the solid phase was lyophilized and analyzed by FT-IR, TGA, SEM-EDS. Polymer matrices with and without metal were characterized by infrared spectroscopy in the range of

**Table 1**  
The optimization variables for acid zone.

Constant variables		Value	
P4VPyC8 (g)		0.2	
Concentration		$400\text{ }\mu\text{g L}^{-1}$	
Variables studied	Minimum point	Central point	Maximum point
pH	3	4.5	6
Stirring time (min)	1	30.5	60

**Table 2**  
The optimization variables for alkaline zone.

Constant variables		Value	
P4VPyC8 (g)		0.2	
Concentration		$400\text{ }\mu\text{g L}^{-1}$	
Variables studied	Minimum point	Central point	Maximum point
pH	7	8.5	10
Stirring time (min)	1	30.5	60

$200\text{--}4000\text{ cm}^{-1}$  using a Bruker Fourier transform spectrometer model Vector 22. The infrared spectra were obtained by using KBr pellets. Thermogravimetric analysis was performed on a Mettler calorimetric TGA/SDTA851e system. Samples were heated from 298 to 600 K under  $\text{N}_2$  atmosphere at heating rate of  $20\text{ }^\circ\text{C/min}$ . A SEM Jeol (model JSM 5410) and microprobe EDS NORAN, were used to determine the surface morphology and chemical characterization of P4VPyC8 and P4VPyC8-As (V) samples.

## 2.6. Determination of As (V) by direct fluorescence measurement on the solid phase

Once the experimental retention variables such as pH and best agitation time were determined, the calibration curve was constructed by direct measurement of fluorescence on the solid phase. This curve was obtained by means of a batch method using 0.2 g of the solid phase at an optimal stirring time in all cases. The slope, the intercept and the standard deviation were established by employing 10 control samples, which corresponded to the solid phase samples without metallic ion.

## 2.7. Analytical application of the determination method of As (V) by direct measurement on solid phase

In order to fulfill with this purpose, the standard addition method was used. Thus, variable volumes ( $V_S$ ) of a standard As (V) solution of known concentration ( $C_S$ ) were added to a constant volume of tap water ( $V_M$ ) and diluted to a total volume ( $V_T$ ). The pH of the solution was adjusted to  $9.0 \pm 0.2$  in all cases. 200 mg of the polymer matrix were added to each solution. Then, these mixtures were agitated for one hour and the fluorescence of the solid phases was registered by using an excitation wavelength of 248 nm. The fluorescence intensity was plotted against  $V_S$  and the experimental points adjusted to a linear relationship. Then the concentration of As (V) in the sample of tap water was determined by using the slope and the intercept of the calibration curve. In order to corroborate the accuracy of this data, the sample was analyzed in an external certified laboratory.

## 3. Results and discussion

Previous to the selection of P4VPyC8 as solid phase, P4VPyC6 and P4VPyC10 were also analyzed as adsorbents. All polymer matrices were sieved before they were placed in contact with the solutions containing As (V) ions. The remaining As (V) was determined by fluorescence using Rhodamine B. Thus, the adsorbed As (V) concentration in the solid phase was determined. P4VPyC10 showed the highest adsorption capacity for As (V). However, this polyelectrolyte forms larger particles which impede the analytical quantification of As (V). On the other hand, P4VPC6 swells when contacted with the As (V) solutions, thus in the latter two cases the solid phases do not show regular, homogeneous colors. P4VPyC8 is a highly homogeneous solid phase with a regular color in the whole phase, compared with P4VPyC10. These properties are fundamental for the determination of metallic ions. Therefore, P4VPyC8 was used as solid phase for the retention of As (V).

### 3.1. Determination of the adsorption parameters for As (V)

In order to determine the As (V) adsorption parameters, some preliminary fluorescence studies in aqueous solution were performed. The theoretical distribution of As (V) species was considered as a function of the solution pH and the remaining As (V) in solution. Fluorescence can be used to determine several analytes including heavy metals being a selective and sensitive method for detecting this kind of analytes [40]. However, it was not possible to perform these studies for the direct determination of As (V) in solution as effectively occurred in the solid phase, i.e., in the polymeric matrix. For this reason, in this work the “free” concentration of As (V) was determined by detecting the fluorescence intensity of the complex of Rhodamine B with arsenate ions.

#### 3.1.1. Optimization of the stirring time and solution pH for the As (V) adsorption

A screening statistical analysis was performed before the As (V) retention studies in the polymer matrix were carried out. As shown in Fig. 1, in this analysis the pK values and the As (V) distribution species in an acid and alkaline zone was considered. It is well known that in the solid phase extraction the solution pH plays an important role in the adsorption of metal ions [41] because variations in the solution pH can cause changes not only in the adsorbent structure but also in the speciation of the metal ions in aqueous solution. The retention of As (V) is strongly pH dependent, because both, the stability and distributions of species are pKa dependent. It is known that the predominant species at pH values between 2 and 7 is  $\text{H}_2\text{AsO}_4^-$ , whereas at pH values between 7 and 12 the predominant species is  $\text{HAsO}_4^{2-}$ , however at a pH range between 6 and 8 both species coexists [42,43]. A greater retention of divalent species ( $\text{HAsO}_4^{2-}$ ) has been observed in strongly basic anion exchange resins [44].

The effect of the stirring time as well as the solution pH on the fluorescence emission for the acid and alkaline zones is shown by Pareto plots in Fig. 1b and c. As seen in Fig. 1b (acid zone), the stirring time and solution pH have a statistical significance with 95% of confidence limit. Thus, the stirring time and solution pH show a positive effect on the adsorption process, where pH has a higher statistical significance. This greater statistical weight is corroborated with the analysis of the main effect of the studied variables on the fluorescence intensities of the As (V) (see supplementary material).

On the contrary, in the alkaline zone (Fig. 1c) the Pareto plot shows that only the stirring time has statistical significance with a 95% of confidence limit but not only the solution pH or the combination of both variables. This effect is also corroborated with the analysis of the main effects on the fluorescence intensities of As (V) (see supplementary material).

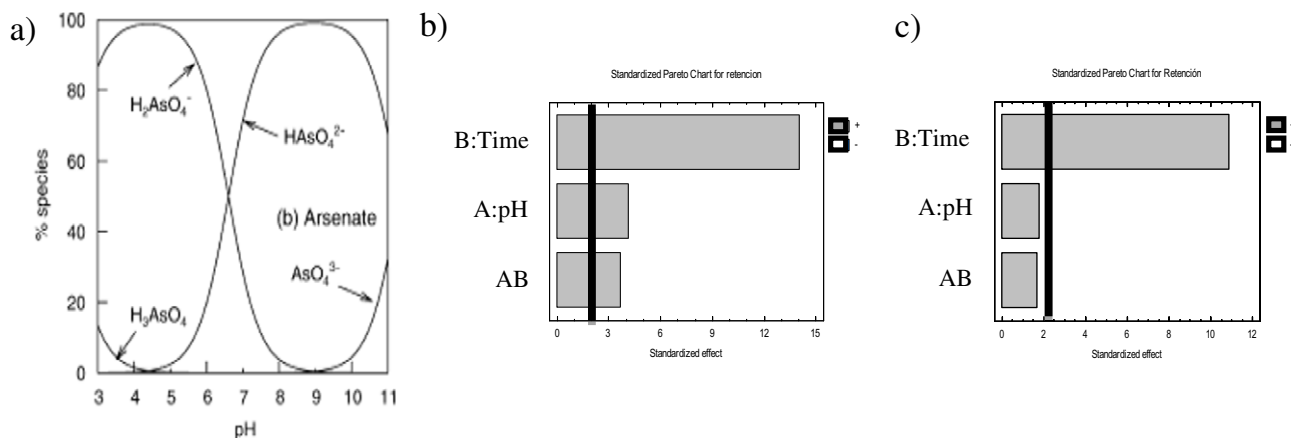


Fig. 1. a) Distribution of As (V) species. Pareto plots: b) acid zone and c) alkaline zone.

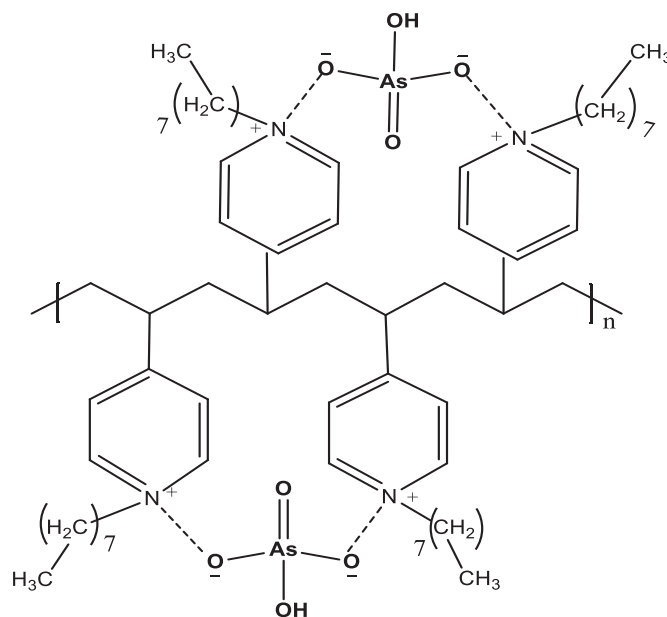


Fig. 2. Interaction model of As (V) with the polymer matrix.

On the other hand, P4VPyC8 presents a formal charge which is independent of the pH. This allows its use as a matrix to retain anions in solution in a wide pH range. Therefore, it can be stated that the interaction between the As (V) and P4VPyC8 is mainly electrostatic involving the positive charge of the polymer matrix and the negative charge of As (V) species. Fig. 2 shows the possible interaction between As (V) and the cationic matrix.

On the basis of the results of the optimization conditions, a univariate study for percentages of the As (V) retention at pH 9 was performed as a function of the stirring time. At this pH only As (V) exists and retention experiments were carried out at the same concentration as the optimization experiments.

#### 3.1.2. Effect of contact time

Fig. 3 shows the effect of the contact time on the retention percentage. A solution of As (V) with concentration of  $400 \mu\text{g L}^{-1}$  was used for this study. This solution was stirred with 0.2 g of P4VPyC8 and the concentration of As (V) remaining in solution was evaluated every 10 min. As shown in Fig. 3, the maximum retention percentage was reached after 60 min of stirring. Thus, in all the adsorption experiments the stirring time was 60 min.

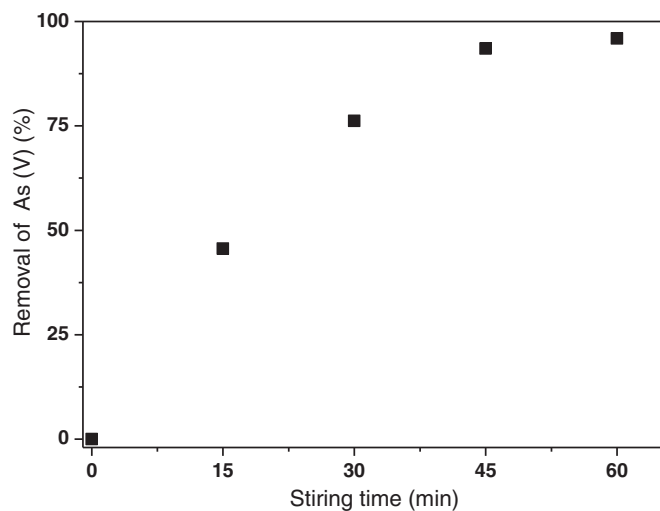


Fig. 3. Dependence of retention of As (V) with the stirring time.

### 3.2. Characterization of P4VPyC8 and P4VPyC8-As (V)

#### 3.2.1. FT-IR study

Infrared spectroscopy allows identifying the functional groups involved in the interaction between As (V) and the P4VPyC8. A new absorption band at  $384\text{ cm}^{-1}$  in the IR spectrum of P4VPyC8-As (V) appears as compared to that P4VPC8, which can be attributed to As—O bonds [45] (see supplementary material).

#### 3.2.2. Thermal behavior

The thermal degradation profiles of P4VPyC8 and P4VPyC8-As (V) display three regions (see supplementary material). In the first region a decrease of sample weight of 5% between 50 and 100 °C for P4VPyC8 and P4VPyC8-As (V) was observed. This weight loss may be due to evaporation of occluded water. In the second zone, between 250 and 400 °C, a weight loss of 53% for P4VPyC8-As (V) was observed, compared to a weight loss of 63% for P4VPC8. The weight loss of P4VPyC8-As (V) is probably due to the greater thermal stability of

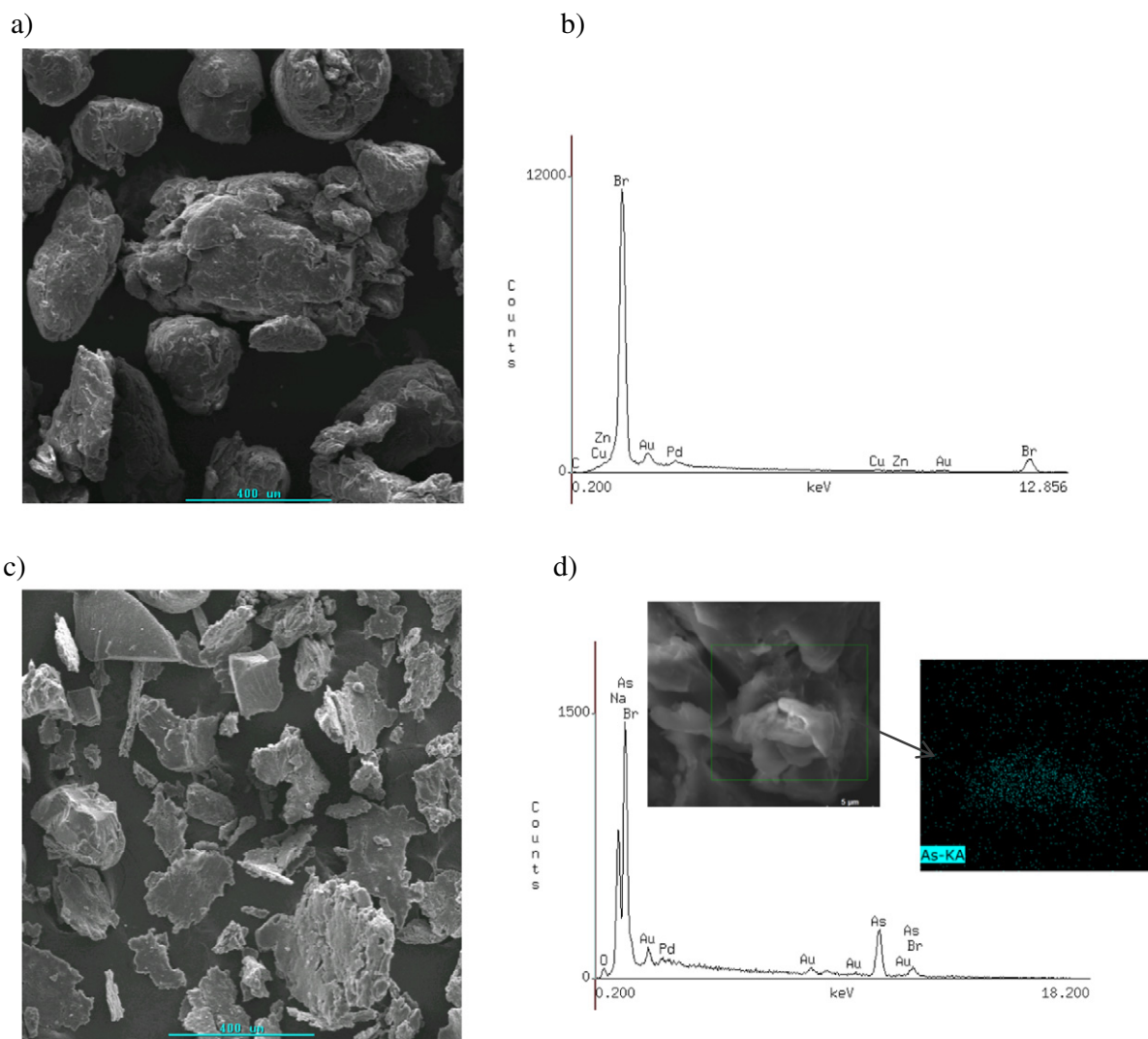


Fig. 4. SEM- images of (a) P4VPyC8 and (c) P4VPyC8-As (V) and their respective EDS analysis (b and d). Figure (d) includes EDS layered image of P4VPyC8-As (V), As (light blue).

P4VPyC8-As (V) as compared with that of P4VPyC8. Moreover, at 600 °C a total weight loss of P4VPyC8 is observed. Similar results have been reported with quaternized poly (4-vinylpyridine) [46], while at this temperature the weight loss for P4VPyC8-As (V) is around 90%. The residue corresponding to 10% of the initial sample weight in this case is probably due to the presence of retained arsenic (V) oxide.

### 3.2.3. SEM-EDS

SEM images of P4VPyC8 and P4VPyC8-As (V) are presented in Fig. 4a and c. No significant morphological differences are observed in the images of P4VPyC8-As (V) samples as compared with the images of P4VPyC8, probably due to the sieving process. Fig. 4b and d shows the EDS analyses performed on P4VPyC8 and P4VPyC8-As (V). The presence of arsenic in P4VPyC8-As (V) sample was observed. In addition, Fig. 4d

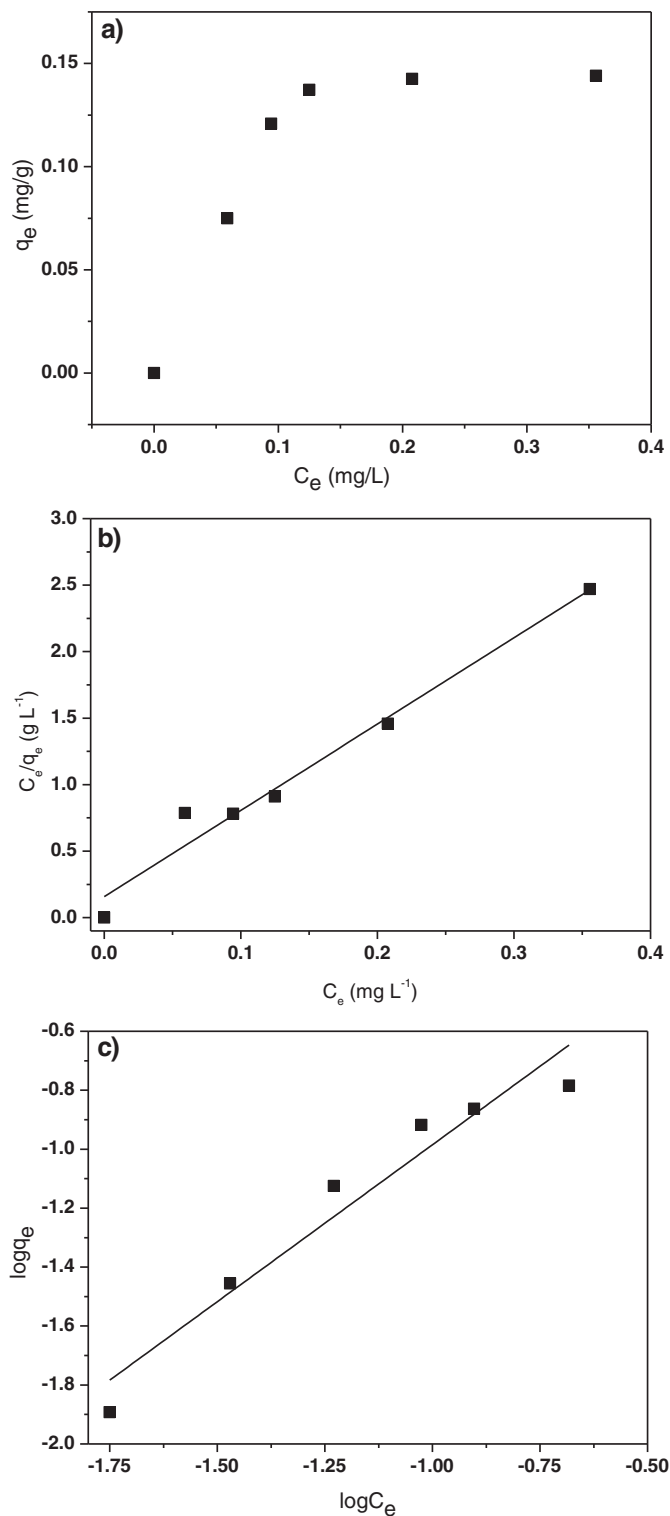


Fig. 5. Adsorbed As (V) ( $q_e$ ) and the As (V) concentration in the equilibrium ( $C_e$ ): a) Adsorption isotherms, b) data adjustment to Langmuir model and c) data adjustment to Freundlich model.

**Table 3**  
Parameters of Langmuir, Freundlich and Dubinin–Radushkevich isotherm.

Metal	Langmuir $\frac{C_e}{Q_e} = \left(\frac{1}{Q_m b}\right) + \left(\frac{1}{Q_m}\right) * C_e$			Freundlich $\log q_e = \log K_f + \frac{1}{n} \log C_e$			Dubinin–Radushkevich $\ln q_e = K e^2 + \ln Q_{DR}$		
	$Q^{\circ}$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$	$Q_{DR}$ (mg/g)	$K$ (kJ/mol <sup>2</sup> )	$R^2$
As (V)	0.154	1.000	0.967	1.201	1.065	0.929	0.459	−0.422	0.878

(light blue EDS layered image) confirms the presence of As (V) retained in the polymer matrix.

### 3.3. Adsorption isotherms

Adsorption experiments of As (V) were performed in optimal conditions of pH, stirring time and polymer mass. The results are presented in Fig. 5a. These results were adjusted to Langmuir (Fig. 5b), Freundlich (Fig. 5c) and Dubinin Radushkevich adsorption models. The latter is not shown due to the low correlation factor between experimental data and the linear prediction of this model (Table 3). The best correlation was obtained by applying the Langmuir model suggesting electrostatic interactions between As (V) and the polymer matrix. On the other hand, it was found that this P4VPyC8–As (V) can be regenerated completely by treating with 0.1 M NaOH solution.

### 3.4. Determination of As (V) on the solid phase

For the determination of As (V) by direct measurement of the fluorescence emission on the solid phase, a previous study on the P4VPyC8 emission at different excitation wavelengths was performed. A maximum fluorescence emission at an excitation and emission wavelengths of 548 nm and 559 nm, respectively were obtained. Furthermore, a study on opening of Slit was performed, resulting in the optimum slit opening of 10 mm. The P4VPyC8 with increasing retained As (V) was measured. Thus, the fluorescence intensity increases linearly with the As (V) concentration at the established excitation and emission wavelengths. This increase in fluorescence intensity of the polymeric matrix can be used as a new method for the determination of As (V) by direct measurement on the solid phase. The calibration curve obtained based on this method showed a linear behavior in the concentration range of 6.80 to 90.0  $\mu\text{g L}^{-1}$  (see supplementary materials). The linear equation with a correlation coefficient of 0.991 was  $FI = 34.6C - 99.9$ , where  $C$  is the As (V) concentration and  $FI$  is the fluorescence intensity. The relative standard deviation (R.S.D.) was 1.72%. The detection limit was calculated using  $3\sigma/S$ , where  $\sigma$  is the standard deviation of the control sample and  $S$  is the sensitivity of the method calculated by the slope of the calibration curve. The detection limit was 2.24  $\mu\text{g L}^{-1}$ . Some polymeric adsorbents showing high retention capacities such as quaternized P4VPy hydrogels and/or nanoparticles has been reported by N. Sahiner et al. One gram of P4VPy nanoparticles quaternized with HCl is able to remove over 95% of As (V) from a stock solution containing 10  $\text{mg L}^{-1}$  in 15 min, whereas quaternized P4VPy hydrogels removed 82% of the As (V) in ~12 h from a solution containing 10 mg of As (V) per liter. In our study, the adsorbent material exhibits lower adsorption of As (V) than that found by N. Sahiner et al. However, we used As (V) concentration as low as 0.4  $\text{mg L}^{-1}$  for the purpose of performing a preconcentration in solid phase previous to the instrumental determination. It is important to develop an analytical method for the determination of As (V) at trace levels. This will allow to discriminate between the drinking waters that do not meet the rules of arsenic concentration, which should not be greater than 5  $\mu\text{g L}^{-1}$  [42–46]. Some other anions such as Cr (VI) could interfere by competing with As (V) anions for the positive sites in the polymer matrix. However, in natural waters, Cr (VI) is reduced to Cr (III) by the organic material [47]. On the other hand, the interference of organic anions for the As (V) adsorption can be eliminated by a previous acid digestion.

### 3.4.1. Application of method for the direct determination of As (V) on the solid phase

In order to achieve this purpose, the measurement of As (V) was performed by determining the As (V) in a sample of tap water by means of the standard addition procedure. This method is particularly useful to analyze complex samples in order to avoid undesirable effects coming from the sample and the matrix. The total fluorescence intensity ( $S$ ), versus the added volumes of the standard solution of As (V) ( $V_S$ ) yielded the following linear relationship:  $S = 7.91 + 33.51 \times V_S$ . From the slope  $m = 33.51$  and the intercept,  $b = 7.91$ , the concentration of As (V) ( $C_M$ ) in the sample of tap water can be determined with the following relationship [48].

$$C_M = \frac{7.91 \times C_s}{33.51 \times V_M} \quad (1)$$

According to this procedure, the As (V) concentration in the sample of tap water was 2.36  $\mu\text{g L}^{-1}$ . This measurement was compared well with that provided by a certified external laboratory which gives 3.00  $\mu\text{g L}^{-1}$  for the same sample. The certified laboratory used the norm consigned in the NCh N°409/1 Drinking water – Part 1: requirements, which regulates the tap water quality in Chile.

## 4. Conclusions

A screening statistical analysis allowed determining the effect of stirring time and solution pH for the adsorption of As (V) on poly (*N*-octyl-4-vinylpyridinium) bromide used as solid matrix. Pareto plots for acid and alkaline zone showed that in the acid zone, both pH and stirring time has statistical significance with 95% of confidence limit, while in the alkaline zone the stirring time has statistical significance. At pH 9, a univariant study for the retention percentages as a function of the stirring time show a maximum after 60 min of stirring. The high affinity of divalent species of As (V) at pH 9 with positively charged polyelectrolytes is consistent with studies reported in the literature. A possible model for the interaction of As (V) with the polymer matrix was established. Retention of As (V) by the polymer matrix follows the Langmuir model. Moreover, the results suggests that this method can be applied as a screening methodology to detect arsenic concentrations lower than 50  $\mu\text{g L}^{-1}$ , which is the maximum allowed by the Chilean norm. In conclusion, the method developed in this work could have potential application for direct determination of arsenic in tap water.

## Acknowledgements

The financial support of Fondecyt, Projects 1151221, 1100103, 3150241 and ANILLO Project ACT1412 are gratefully acknowledged. Doctoral scholarship and grant support 2009 Thesis AT-24100121.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.reactfunctpolym.2016.10.011>.

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