Full Length Research Paper

Developing new exchanger for removal of inorganic arsenic species from groundwater

Reham S. Hassan[1] and M.R. El-Naggar[2*]

[1]Analytical Chemistry Department, Hot Laboratory Center, Atomic Energy Authority, Post Code 13759, Cairo, Egypt.
[2]Radioactive waste Management Department, Hot Laboratory Center, Atomic Energy Authority, Post Code 13759, Cairo, Egypt.

A new Dowex monospher-BBr exchanger was prepared by the reaction between the conjugated base sulfonic acid $[R\text{-}S\text{-}O_3]^-$ of DOWEX MONOSPHERE MR-450 UPW and the strong Lewis acid BBr_3 forming adduct (coordinated complex) $[(R–S–O_3)_2\ BBr_3]^{+3}$. The prepared resin is a promising exchanger for the removal of inorganic arsenic species from underground water. More than 96% arsenic removal has been recorded using the prepared resin. Effect of pH on the sorption of As(III) and As(V) was studied using VISUAL MINTEQ computer program to determine the optimum pH values at which maximum sorption capacities were obtained. The highest sorption efficiency was obtained at pH 11 and 6 for As(III) and As(V), respectively, which indicate good separation between the two different species. Pseudo-first, pseudo-second order, homogeneous particle diffusion models were applied to analyze the experimentally determined data. Sorption data has been modeled using Langmuir and Freundlich sorption isotherm models and the various model parameters were evaluated indicating that chemisorption was the expected controlling process. The applicability of the prepared resin was tested for the removal of arsenic species from real contaminated groundwater. Results gave an evident to the high sorption efficiency of the prepared resin.

Key words: Dowex monospher 450, BBr_3, As(III), As(V), ground water, kinetic and isotherm modelling.

INTRODUCTION

Arsenic is mostly found in the earth's core and in clay- and sulphide-rich portions of the earth's crust (Henken, 2009). Arsenic is considered to be one of the most toxic elements that are found in groundwater as a result of the strong influence of the water-rock interactions. Concentrations of the generally more toxic inorganic arsenic are highest in underground water in areas with natural geological contamination (Mandal and Suzuki, 2002; Pendias and Pendias, 2000). Groundwater may contain 200 to 1200 µg/L arsenic contrasting with the current World Health Organization (WHO) threshold value for arsenic in drinking water.

The WHO has set a provisional guideline value of 10 µg/L of arsenic in drinking-water and according to the International Agency for Research on Cancer (IARC) there is enough evidence to conclude that arsenic and arsenic compounds can cause cancer in humans, consequently arsenic in drinking water is a global threat to health. In humans, if a large amount of inorganic arsenic is swallowed in a form that is readily absorbed, it can affect the gut, the heart and the nervous system, causing rapid poisoning and death. Drinking water from wells can contain high levels of inorganic arsenic; such levels can harm the skin and are associated with increased risk of cancer in the skin, lungs, bladder and kidney (ATSDR, 2000).

Removal of dissolved arsenic from natural groundwater is linked to the chemistry of As(III) and As(V) compounds and so, to their relative distribution, influenced by pH and redox conditions (Van Elteren et al., 2002). Different

*Corresponding author. E-mail: elnaggar74@yahoo.com. Tel: +20-55-234-5895. Fax: +20-2-462-0796.

Table 1. DOWEX* MONOSPHERE* MR-450 UPW Characterization.

Matrix	Styrene-DVB, gel
Functional group:	Sulfonic acid
Water content:	46 - 53 %
Mean particle size:	360 ± 50 µm
Whole uncracked beads:	95%
Particle density:	1.22 g/ml
Total capacity:	1.9 Eq/L
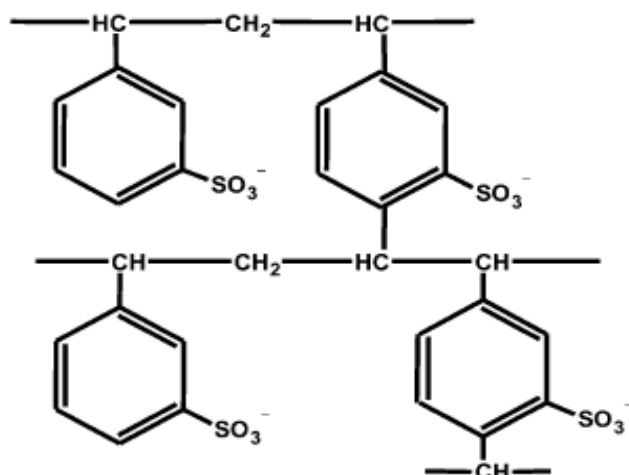
Figure 1. Sulphonated Styrene-Divinyl Benzene.

methods such as precipitation-coprecipitation (Meng et al., 2002; Henken and Hutchison, 2009), sorption (Pattanayak et al., 2000; DeMarco et al., 2003; Henry et al., 2004; Buddhawong et al., 2005; Sarkar et al., 2007; Kröpfelová et al., 2009; Singhakant et al., 2009; Sarkar et al., 2011), methylation (Kosolapov et al., 2004), plant uptake (García et al., 2010), lime softening (Wang and Reardon, 2001), membrane process (Sancha et al., 2000) and ion exchange (Clifford and Lin, 1991; Guenegou et al., 1998) have been used for arsenic removal. However, ion exchange treatment systems are receiving increasing attention for arsenic removal due to their simplicity, ease of operation and handling, regeneration capacity and sludge-free operation (Gupta et al., 2012). It is currently identified as the best available technology for removal of arsenic (EPA, 2002).

This exploratory research addresses the urgent needs for enhanced arsenic removal in small drinking water systems. The research objective is to, develop innovative ion exchange material, that can remove As(III) and As(V) with high efficiency and highly selectively even in the presence of high concentrations of competing ions.

MATERIALS AND METHODS

All chemicals were of analytical grade and solutions were prepared

using de-ionized water. Five liters arsenite stock solution was prepared from sodium meta arsenite ($NaAsO_2$, Fluka, 98%) by dissolving ~ 0.443 g sodium meta arsenite in 5 L bi-distilled water, while five liters arsenate stock solution was prepared from sodium arsenate dibasic hebtahydrate ($Na_2HAsO_4.7H_2O$, Aldrich, 99%) by dissolving ~ 1.05 g of sodium arsenate dibasic heptahydrate in 5 L bi-distilled water. Boron tribromid (≥99.0 %) was obtained from Fluka. The commercial exchanger was purchased from Supelco (Table 1).

Preparation of new exchanger

All three lighter boron trihalides, BX_3 (X = F, Cl, Br) form stable adducts with common Lewis bases. Their relative Lewis acidities can be evaluated in terms of the relative exothermicities of the adduct-forming reaction. Such measurements have revealed a sequence for the Lewis acidity of $BF_3 < BCl_3 < BBr_3$ (strongest Lewis acid). Consequently, the new exchanger was produced by using Dowex Monosphere MR-450 UPW (Figure 1) and boron tribromid. Such new exchanger, Dowex monospher-BBr, was prepared by the reaction between the conjugated base sulfonic acid $[R\text{-}S\text{-}O_3]^-$ of the commercial resin and the strong lewis acid BBr_3 forming adduct (coordinated complex) $(R–S\text{-}O_3)_2BBr$.

In brief, Dowex monospher was first conditioned through base washing using 1 N NaOH then neutralized with 1 N HCl. Upon rinsing using de-ionized water, the resin was equilibrated with 1% BBr_3 (w/w) solution at pH = 4.5 for one week.

Equations (1 and 2) illustrate the expected reaction of the synthesis process.

$$-SO_3H + NaOH \longrightarrow -SO_3^-Na^+ \tag{1}$$

$$2(-SO_3^-Na^+) + BBr_3 \longrightarrow (-SO3)_2BBr + 2NaBr \tag{2}$$
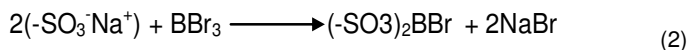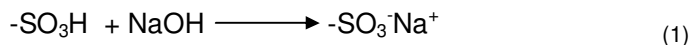
Analytical methods

Ion chomatography (IC) can separate As(III) and As(V) according to their valence states (Sarzanini, 1999). Consequently, analysis was conducted using Dionex-DX150 equipped with conductivity detector. Separation was performed on Dionex Ion-Pac AS-12 Column and 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ were used as an eluent at a flow of 1 mL/min. Arsenite and Arsenate calibration curves were performed using certified standard solutions. The prepared standards solutions (5 to 50 µg/L of As(III) and As(V)) were spiked with the eluent, then measured with IC. Each arsenic species was arranged three times in the concentrations.

Batch sorption studies

Effect of pH

The effect of solution pH on the sorption of As(III) and As(V) was investigated by batch experiments. Series of experiments were initiated by adding 0.2 g of the prepared resin to 100 ml solution containing initial concentration of 50 mg/L of As(III) and As(V) separately. The mixtures were shaking for 24 h, and the pH initial solutions were varied from 2 to 14 using dilute NaOH or HCl and they were kept constant during the equilibration process by the aid of a microprocessor bench top Hanna pH meter model pH211. pH effect was evaluated by calculating the sorption percentage:

$$Uptake(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{3}$$

Table 2. Recovery of arsenic standards in eluent solution.

Compound	5 µg/L	10 µg/L	20 µg/L
As(III)	99.6%	99.4%	99.0%
As(V)	96.2%	97.5%	99.1%

where C_i and C_e are the initial and final concentrations respectively, mg/L, of ions in their aqueous solution.

Selectivity of the prepared resin

The selectivity of the prepared resin was investigated by conducting 0.2 g of the resin with 100 ml solution containing 20 mg/L As(III) and 20 mg/L Cu(II) at pH=11, the mixture was shaking for 24 h, and the uptake percentages were calculated.

Kinetic studies

Kinetic studies were investigated at a constant initial As(V) and As(III) ion concentrations of 50 mg/L using two pH's of 6 and 11, respectively, at room temperature. For these investigations, 0.2 mg of the prepared resin was contacted with 100 ml of aqueous solution containing known concentration of either As(III) or As(V) ions (50 mg/L). A fixed volume (2 ml) of the aliquot was withdrawn as a function of time while the solution was being continuously stirred. Thus, the ratio of the volume of solution to the weight of resin in the beaker does not change from the original ratio. The withdrawn solution was centrifuged to separate the sorbent and a fixed volume (1 ml) of the clear solution was pipetted out for the determination of the amount of un-sorbed metal ion still present in solution.

$$q_e = \frac{(C_i - C_e) \times V}{m} \qquad (4)$$

where q_e is the sorbed amounts in mg/g, V is the volume of the solution in liters and m is the mass of the prepared resin in grams.

Sorption isotherm

Bach isotherm tests were carried out for the prepared resin with As(III) and As(V). In all cases, the testes were initiated by adding known masses (0.03, 0.05, 0.08, 0.1, 0.12, 0.15, 0.18, 0.2, 0.22 and 0.25 g) of the prepared resin to 100 mL of solution containing an initial concentration of 50 mg/L as As(III) and As(V). The mixture was then shaken using platform shaker for 5 h (equilibrium time), which was sufficient to reach equilibrium. The initial solution pH was 11 (for all samples) and it kept constant until final equilibrium was reached. At equilibrium, the aqueous solution of samples were filtered and analyzed for As(III) and As(V) species. The sorbed amounts were then calculated based on Equation (4).

RESULTS AND DISCUSSION

Recovery of arsenic standards

The recovery of arsenic standards was investigated and results obtained are given in Table 2. From this table it could be concluded that, there is no negative effect at the arsenic species was found by spiking the eluent to the standards. The recovery rate of the spiked arsenic standards was between 96.2 and 99.6%. Consequently it was dependable method used to measure the samples.
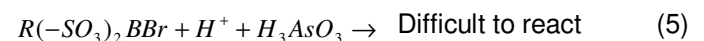
Effect of pH

The pH solution condition has been considered as the most important variable in sorption investigations. It often dramatically affects the amount of sorbed metals as it governs its speciation. The ionic speciation of arsenic in solution was performed with the visual MINTEQA2 computer program version 4.6 (USEPA, 2006) at 50 mg/L initial ionic concentration, calculated mass balance, room temperature and different pH values of the solution ranging from 1 to 14. From the speciation diagram (Figure 2), there are two components of arsenic (H_3AsO_3 and AsO_4^{3-}), the former have three species ($HAsO_3^{2-}$, $H_2AsO_3^-$ and H_3AsO_3) while the later have four species (AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$ and H_3AsO_4) (Ho and McKay, 1999; Plazinski et al., 2009).
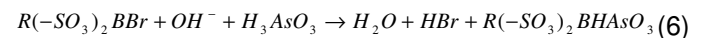
Figure 3 shows the effect of pH solution on the % uptake of both As(III) and As(V) onto the prepared resin. Data obtained reveals that the optimal sorption of As(III) and As(V) were obtained around pH = 11 and pH = 6, respectively. These data are in harmony with those obtained from Figure 2, in which around pH's 11 and 6 the $H_2AsO_3^-$ and $H_2AsO_4^-$ ionic species are the predominant ones for As(III) and As(V), respectively. Furthermore, such effect of pH can be explained though the following equations.
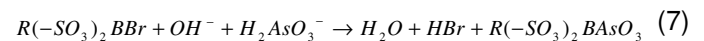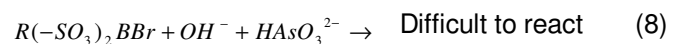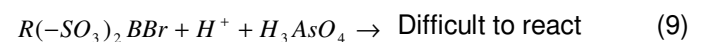
For As (III):

At pH ~ 7:

$$R(-SO_3)_2 BBr + H^+ + H_3AsO_3 \rightarrow \text{ Difficult to react} \qquad (5)$$

At pH >7 – < 9:

$$R(-SO_3)_2 BBr + OH^- + H_3AsO_3 \rightarrow H_2O + HBr + R(-SO_3)_2 BHAsO_3 \qquad (6)$$

At pH > 9 – < 12:

$$R(-SO_3)_2 BBr + OH^- + H_2AsO_3^- \rightarrow H_2O + HBr + R(-SO_3)_2 BAsO_3 \qquad (7)$$

At pH ~ 12:

$$R(-SO_3)_2 BBr + OH^- + HAsO_3^{2-} \rightarrow \text{ Difficult to react} \qquad (8)$$

For As (V):

at pH ~ 2:

$$R(-SO_3)_2 BBr + H^+ + H_3AsO_4 \rightarrow \text{ Difficult to react} \qquad (9)$$
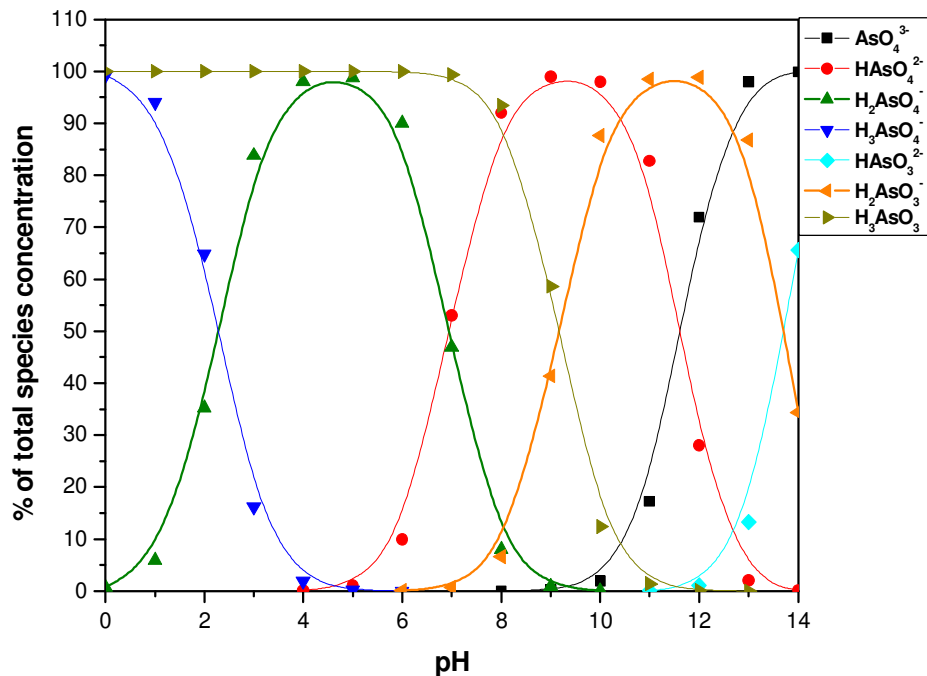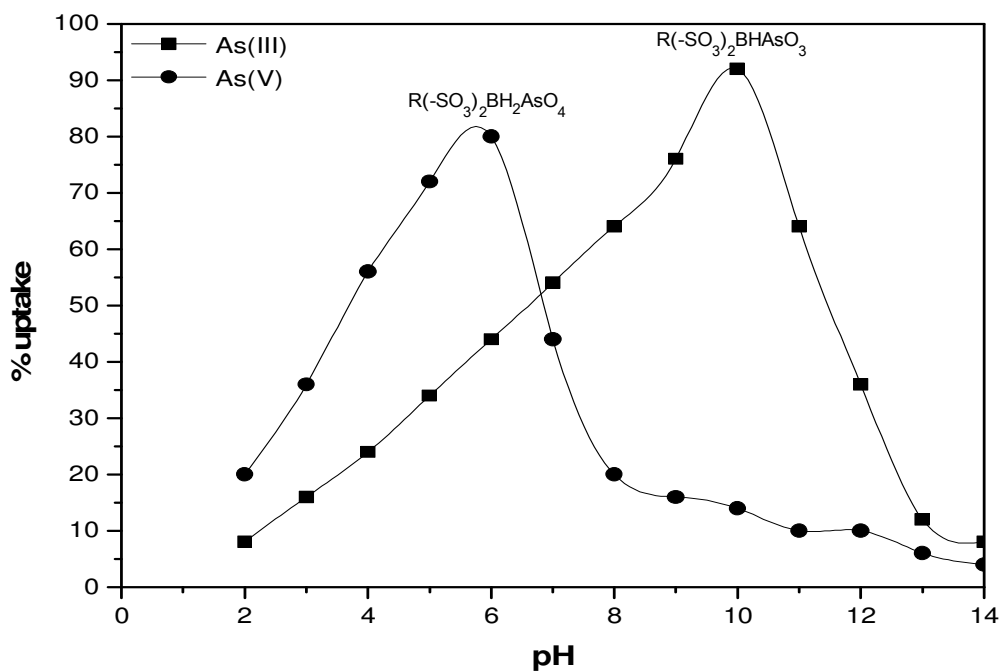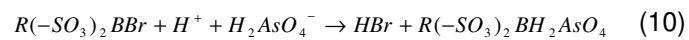
Figure 2. Distribution of As(III) and As(V) ionic species in a bi-component system as a function of pH for 50 mg/L of each at 298K.
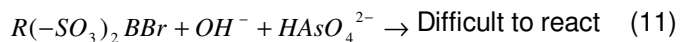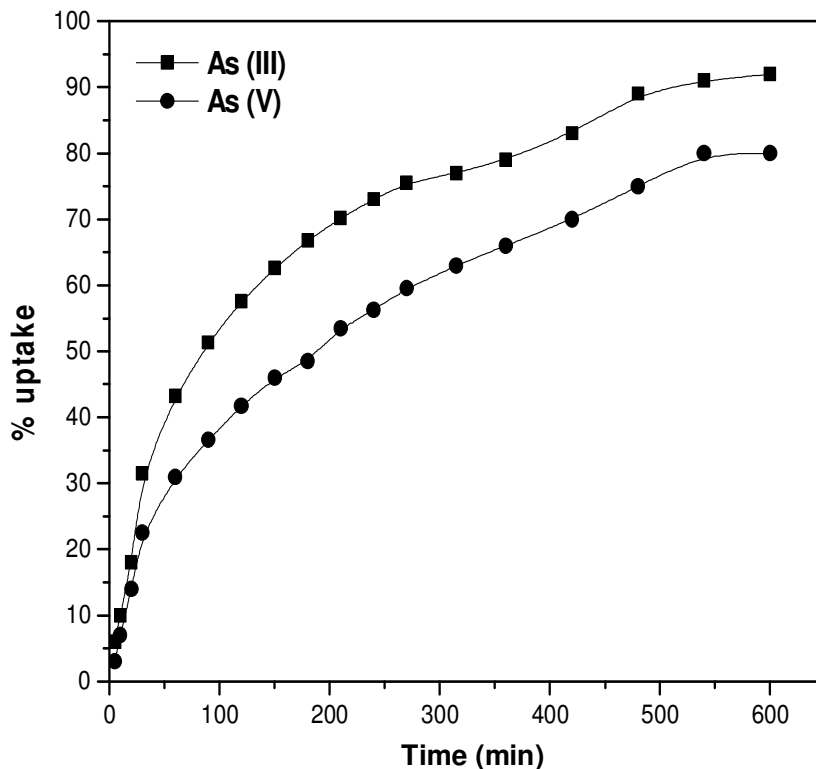

Figure 3. Effect of pH on the sorption of As(III) and As(V) onto R(-SO$_3$)$_2$BBr exchanger. R= styrene- divinyl benzene.

at pH >3 − < 6:

$$R(-SO_3)_2 BBr + H^+ + H_2AsO_4^- \rightarrow HBr + R(-SO_3)_2 BH_2AsO_4 \quad (10)$$

at pH >7 − < 11:

$$R(-SO_3)_2 BBr + OH^- + HAsO_4^{2-} \rightarrow \text{Difficult to react} \quad (11)$$

Figure 4. % uptake as a function of time for the sorption of As(III) and As(V) ions from aqueous solutions onto prepared Dowex monospher-BBr.

Selectivity of the prepared resin

The selectivity of the prepared resin toward arsenic was investigated. Results obtained showed that the prepared resin removed about 96% of As(III) and 10% only of Cu(II). The substantially As(III) selectivity of the prepared resin is attributed to the concurrent Lewis acid-base interaction and electrostatic interactions between arsenic and the immobilized B(III) at the sorbent-sorbate interface.

Under the experimental conditions, arsenic represented as $H_2AsO_3^-$ so it can react as a strong Lewis base (donor of electron lone pairs). The competing Cu(II) is also a divalent charged ligand, but it is a much weaker Lewis base. Consequently, interaction between arsenic and the immobilized boron involve both Lewis acid-base interaction (or inner sphere complexation) and ion pairing (or electrostatic interactions), while interactions between Cu(II) and boron is predominantly ion pairing.

It is noteworthy that Lewis acid-base interaction also enhances the electrostatic interactions between arsenic and the loaded Boron. This is because the inner-sphere complexation occurs over a much shorter distance than outer sphere complexation, and the electrostatic interactions within the much shortened distance are much stronger in accord with the Coulomb's law. Consequently, the prepared resin offered much greater affinity for arsenic over Cu(II).

**Kinetic studies**

Effect of contact time

The percentages uptake (%) of As(III) and As(V) ions sorbed onto Dowex monospher-BBr and the amounts sorbed at any time, q_t (mg/g) were calculated using Equations (3 and 4), respectively. Figure 4 shows the plots of the % uptake of As(III) and As(V) ions from aqueous solutions onto prepared Dowex monospher-BBr, at initial metal ion concentration of 50 mg/L and at room temperature, as a function of contact time. Figure 4 shows a higher initial rate of removal within the first 50 min followed by a slower subsequent removal rate till reaching equilibrium, for both studied ions. Furthermore, the % uptake of As(III) ions was greater than that of As(V) ones (92 and 80%, respectively).

Sorption kinetic modeling

Results obtained from the effect of contact time on the sorption process were used to gain insights into the nature of the sorption process of As(III) and As(V) ions onto prepared Dowex monospher-BBr, to identify the controlling

Table 3. The calculated parameters of pseudo first-order and pseudo second-order kinetic models of for the sorption of As(III) and As(V) ions onto synthetic Dowex monospher-BBr.

Compound	Pseudo first-order				Pseudo second-order			
	$Q_{e, Exp.}$ (mg/g)	$Q_{e, Cal.}$ mg/g	k_1 (min^{-1})	R^2	$Q_{e, Cal.}$ (mg/g)	h (mg/g min.)	K_2 (g/mg min.)	R^2
As(III)	23.0	18.14	5.23E-3	0.968	26.12	0.272	3.99E-4	0.998
As(V)	20.0	17.59	4.61E-3	0.991	24.56	0.156	2.59E-4	0.997
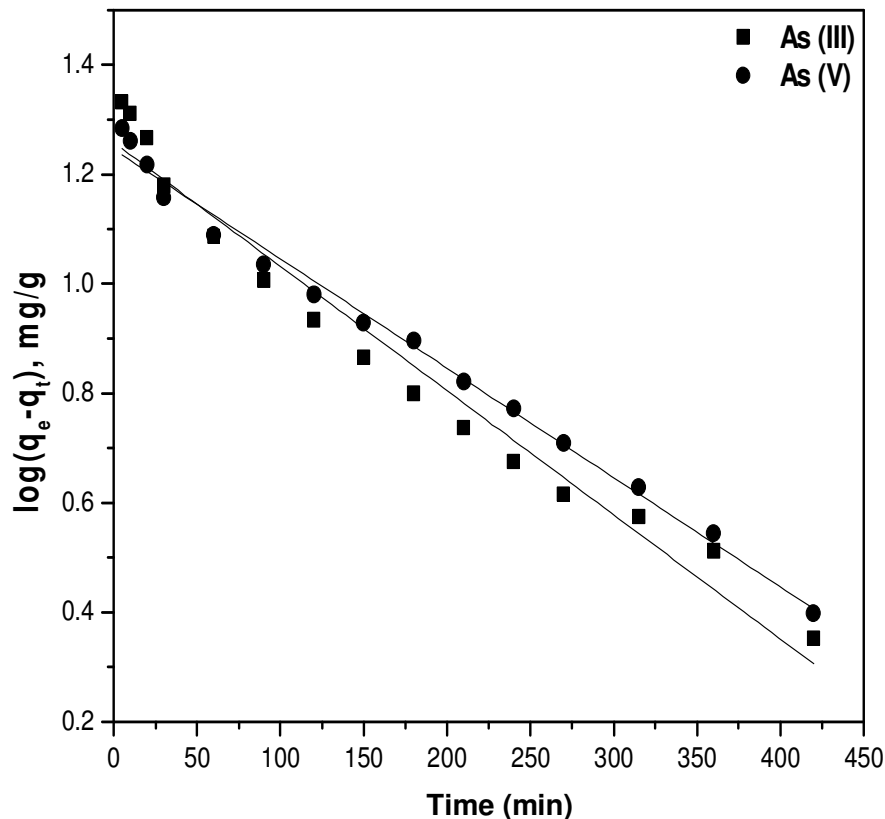
Figure 5. Pseudo first-order kinetic plots for the sorption of As(III) and As(V) ions from aqueous solutions onto prepared Dowex monospher-BBr.

sorption mechanism and to determine the kinetic parameters. Three kinetic models, pseudo-first-order, pseudo-second-order and homogenous particle diffusion, were used to analyze the experimental data.

Pseudo-first-order kinetic model: The analysis of the experimental data using pseudo-first-order kinetic equation has been conducted, where this model has been widely used to analyze the sorption kinetics. It describes the sorption rate based on the sorption capacity and assumes that the reaction rate is limited by only one process or mechanism on a single class of sorbing sites and that all sites are of the time dependent type (Fonseca et al., 2009). The model equation is given by Ho and McKay (1999):

$$log\left(q_e - q_t\right) = logq_e - \frac{k_1}{2.303}t \tag{12}$$

where q_e and q_t (mg/g) are the amounts of sorbed ions onto prepared Dowex monospher-BBr at equilibrium and at time t, respectively and k_1 is the pseudo-first-order rate constant (min^{-1}).

The obtained pseudo-first-order kinetic parameters are given in Table 3. Straight lines (Figure 5) suggest the applicability of pseudo-first-order kinetic equation to fit the experimental data, but the correlation coefficients (R^2) indicated that it is not appropriate to use pseudo-first-order kinetic equation to represent the sorption of the studied ions onto prepared Dowex monospher-BBr for
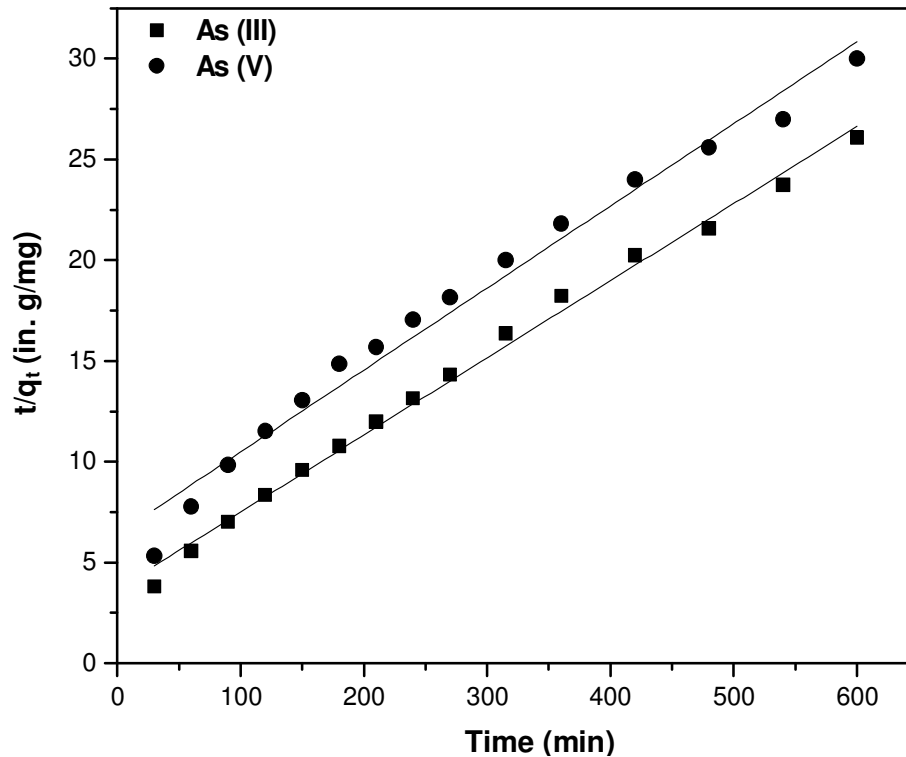
Figure 6. Pseudo second-order kinetic plots for the sorption of As(III) and As(V) ions from aqueous solutions onto prepared Dowex monospher-BBr.

the entire sorption period.

Pseudo second-order kinetic model: Pseudo second-order chemisorption kinetic rate equation is derived on the basis of the sorption capacity of the solid phase (Plazinski et al., 2009). It assumes that the rate of sorption is directly proportional to the number of active surface sites and that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate (Taty, 2003; Hui et al., 2005; Dragan et al., 2010).

The linear form of the pseudo second-order model is expressed as (McKay and Ho, 1999a,b):

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}t \tag{13}$$

where q_e and q_t are the concentrations of As(III) and As(V) ions in the sorbent at equilibrium and at time t, respectively (mg/g) and k_2 is the pseudo second-order constant.

Figure 6 showed that, the relation between t/q_t versus time is linear, and the correlation coefficient (R^2) suggests a strong correlation between the parameters and also explains that the sorption process of each ion follows pseudo second-order kinetics. The product $k_2q_e^2$ is the

initial sorption rate represented as $h = k_2q_e^2$. By the linear fitting of experimentally presented data (Figure 6) we can obtain the pseudo-second-order model parameters (Table 3). The correlation coefficient R^2 has an extremely high value (>0.99), and its calculated equilibrium sorption capacity (q_e) is consistent with the experimental data. These results explain that the pseudo second order sorption mechanism is predominant and that the overall rate constant of each sorption process appears to be controlled by the chemical sorption process (McKay and Ho, 1999b).

Homogenous particle diffusion model

In order to identify the controlling sorption mechanism, kinetic data were analyzed by homogenous particle model equations. This model assumes that, the rate determining step of sorption could be described by either film diffusion, at which the ions diffuse through the liquid film surrounding the particle (Equation 14), or by particle diffusion at which the ions diffuse into the sorbent beads (Equation 15) (El-Kamash et al., 2007).

$$-\ln(1 - x) = \frac{3DC_0}{r_o\delta q_0}t \tag{14}$$
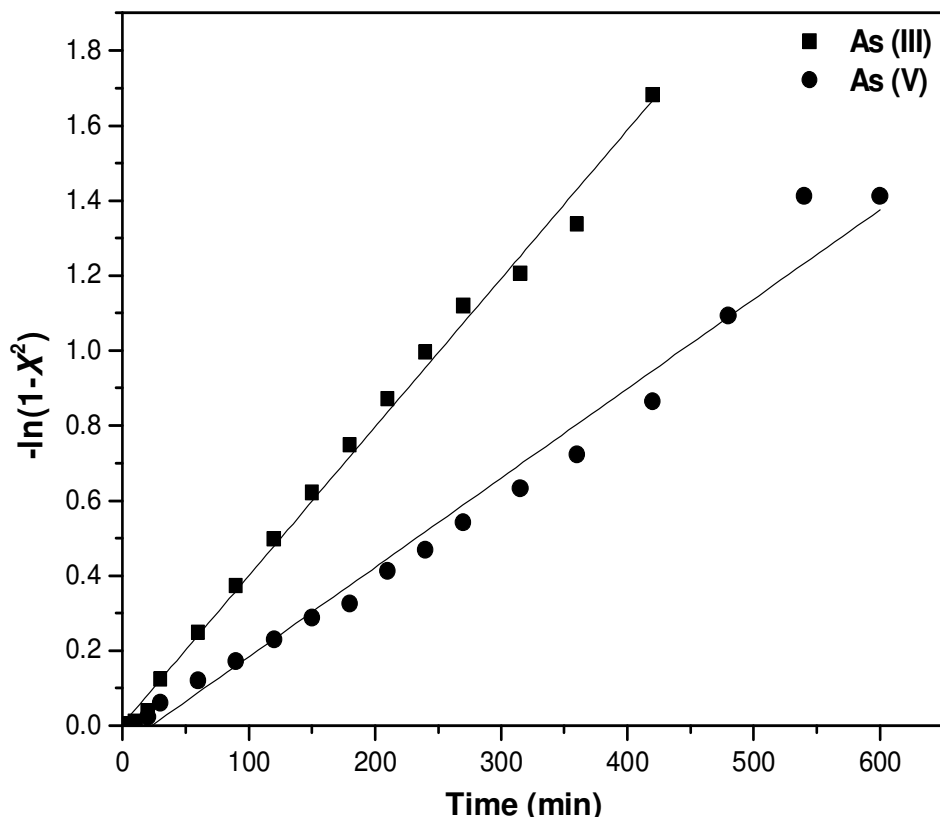
Figure 7. Plots of ln (1-X^2) as a function of time for diffusion of As(III) and As(V) ions from aqueous solutions onto prepared Dowex monospher-BBr.

Table 4. Diffusion and correlation coefficient parameters for the sorption of As(III) and As(V) ions from aqueous solutions onto synthetic Dowex monospher-BBr.

Compound	D_r, m^2/s	R^2
As (III)	1.08 E-13	0.998
As (V)	6.51 E-14	0.998

$$- \ln (1 - x^2) = \frac{3D_r \pi^2}{r_o^2} t$$

(15)

where D is the diffusion coefficients in the liquid phase (m^2/s), and D_r is the particle diffusion coefficient (m^2/s), X the fraction attainment of equilibrium, δ is the film thickness and r_o is the radius of the sorbent particle. The results of the analysis of the kinetic data by homogenous particle model equations are illustrated in Figure 7 and the calculated parameters are listed in Table 4. The plots of –ln (1–X) versus contact time are a linear relationship that does not pass through the origin. This means that the film diffusion is not the controlling sorption mechanism. Where the plots of –ln (1–X^2) is a linear relationship that pass through the origin. These results

revealed that the particle diffusion might be the controlling sorption mechanism at all the studied temperatures. The particle diffusion coefficient was calculated from the slope of –ln (1–X^2) versus time as presented in Table 4.

The magnitude of the diffusion coefficients dependent on the nature of the mechanism that control the sorption process. For physical sorption, the value of the diffusion coefficient ranges from 10^{-6} to 10^{-9} m^2/s and for chemisorption the value ranges from 10^{-9} to 10^{-17} m^2/s the difference in these values is due to the fact that in physical sorption the bounds of the molecules are weakly and can easily break and the molecules can migrate, whereas for chemisorption the molecules are strongly bound and mostly localized (El-Kamash et al., 2007). The tabulated value of the diffusion coefficient is in the order of 10^{-12} m^2/s which confirms the result obtained from the analysis of the data to pseudo-second-order that the sorption process is chemisorption process.

Sorption isotherm and modeling

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed
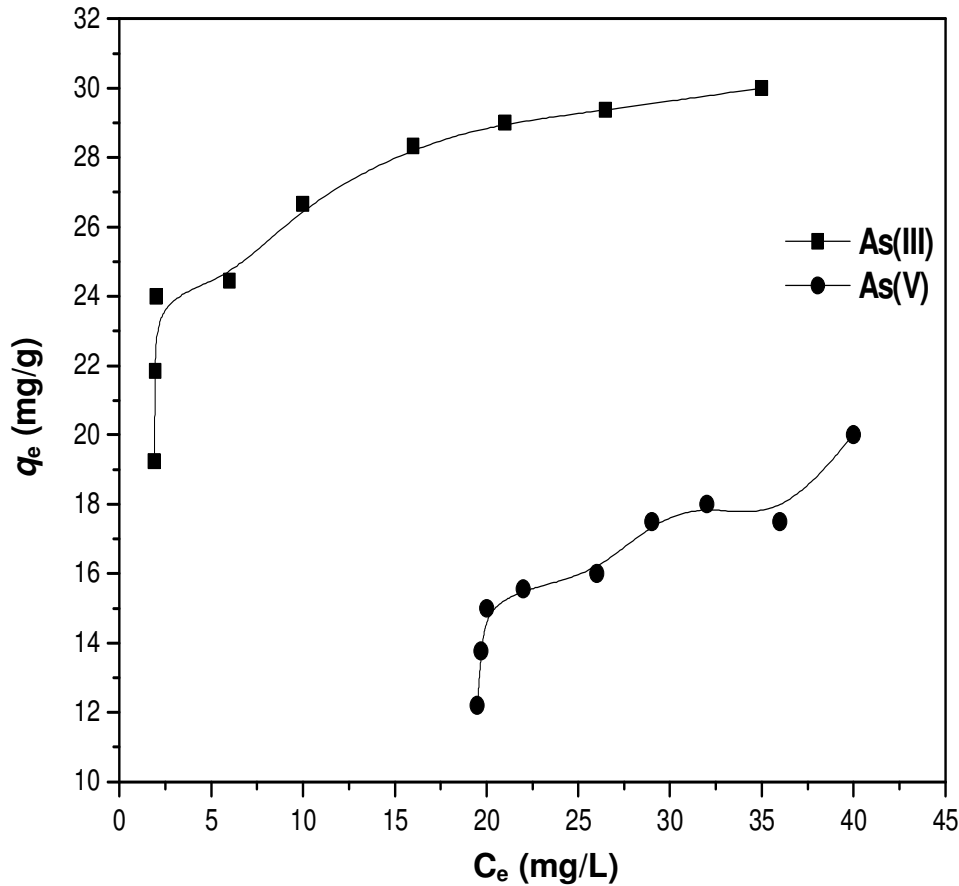
Figure 8. Equilibrium isotherm for the exchange of As(III) and As(V) ions onto prepared Dowex monospher-BBr.

on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption isotherm is very important to design the adsorption systems. Results obtained were illustrated in Figure 8, which showed that the new resin had a high efficiency to remove As(III) from solution otherwise it can remove As(V) but with low efficiency. It means that the new resin is more selective to As(III) at pH 11 than As(V).

Langmuir isotherm model

This model was obtained from assumption that the adsorption occurs at specific homogeneous sites within the adsorbent. Langmuir isotherm model can be expressed by the following equation (Langmuir, 1918):

$$q_e = \frac{Q^o b C_e}{1 + K_L C_e} \qquad (16)$$

where, q_e is the amount of metal ion sorbed per unit weight

of Dowex monospher-BBr (mg/g), C_e is the equilibrium concentration of the metal ion in the equilibrium solution (mg/L), Q^o is the monolayer sorption capacity (mg/g) and b is the constant related to the free energy of sorption (b α $e^{-\Delta G/RT}$). The sorption data were analyzed according to the linear form of the Langmuir isotherm (Equation 17).

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e \qquad (17)$$

The model simulations are shown in Figure 9 for As(III) and As(V) respectively. From these figures it can be concluded that, the prepared resin show good sorption potential, moreover the isotherm for As(III) were better fit than As(V) with the Langmuir equation.

The linear isotherm constants Q^o, b and R^2, were calculated by linear regression and their values were represented in Table 5. This table showed that, the correlation coefficient (R^2) value of 0.999 for As(III) suggests that the Langmuir isotherm provides a good model of the sorption of As(III).

The shape of the isotherm is considered to predict whether a sorption process is favorable or unfavorable.
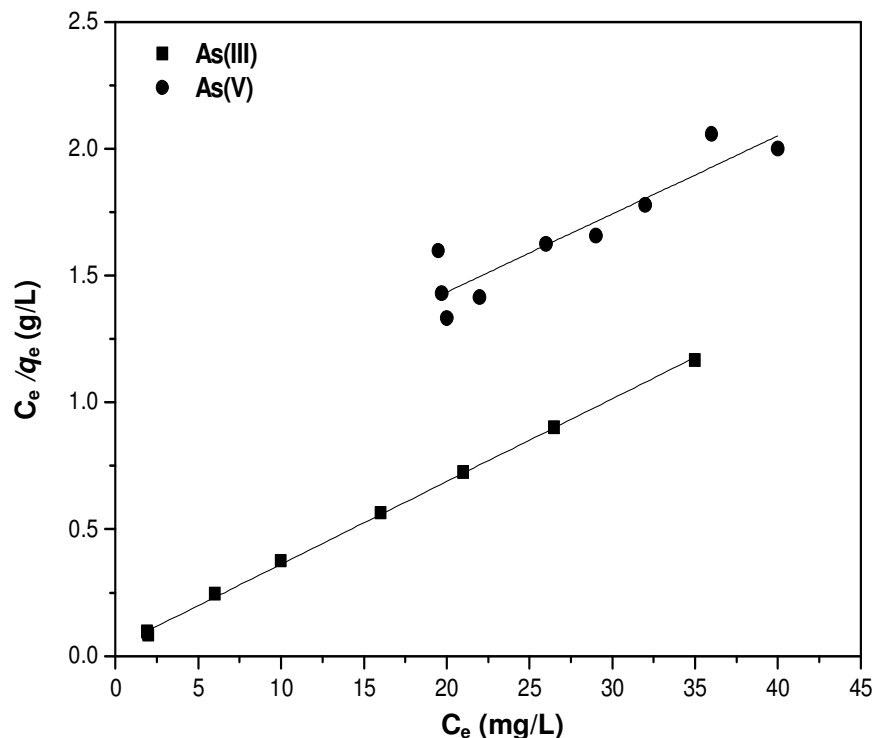
Figure 9. Langmuir isotherm plot for the exchange of As(III) and As(V) ions onto prepared Dowex monospher-BBr.

Table 5. Langmuir isotherm constants for the sorption of As(III) and As(V) onto prepared Dowex monospher-BBr.

As(III)				As (V)			
Q^o (mg/g)	b (L/mg)	R_L	R^2	Q^o (mg/g)	b (L/mg)	R_L	R^2
30.67	0.905	0.022	0.999	32.47	0.38	0.345	0.838

Hereby, a dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti (Webber and Chakkravorti, 1974) can be represented as:

$$R_L = \frac{1}{1 + bC_o} \tag{18}$$

According to the value of R_L, the isotherm is considered to be of the following types:

To be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$). The calculated value of R_L indicated that the sorption of As(III) and As(IV) ions onto Dowex monospher-BBr was favorable as shown in Table 5.

Freundlich isotherm model

Freundlich isotherm (Freundlich, 1906) is the earliest

known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Adamson and Gast, 1997). Freundlich isotherm model can be expressed by the following equation:

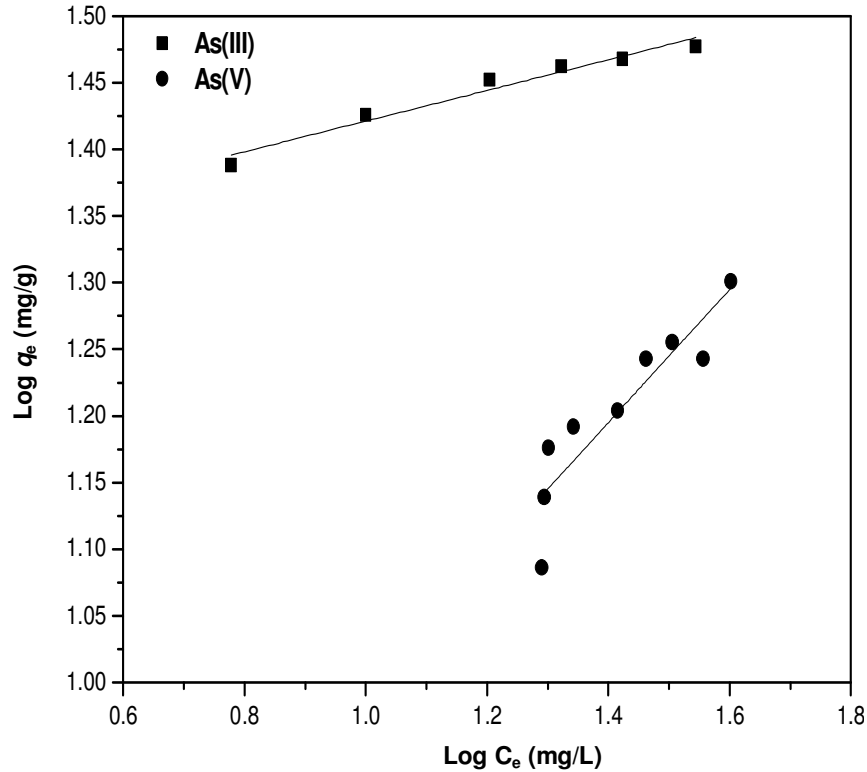$$q_e = K_f C_e^{1/n} \tag{19}$$

where K_f (L/g) and n are Freundlich constants.

The linearized form of the Freundlich isotherm model can be expressed by the following equation:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{20}$$

The Freundlich sorption isotherms of As(III) and As(V) onto prepared Dowex monospher-BBr were shown in Figure 10. Freundlich isotherm parameters are given in Table 6

Figure 10. Freundlich isotherm plot for the exchange of As(III) and As(V) ions onto prepared Dowex monospher-BBr.

Table 6. Freundlich isotherm constants for the sorption of As(III) and As(V) onto prepared Dowex monospher-BBr.

As(III)			As (V)		
K_F (mg/g)	$1/n$	R^2	K_F (mg/g)	$1/n$	R^2
20.24	0.115	0.9541	3.14	0.499	0.807

Table 7. Treatment of arsenic contaminated real life groundwater.

Sample depth	Initial concentration (mg/L)		Final concentration (mg/L)	
(m)	As (III)	As (IV)	As (III)	As (IV)
70	182	198	6.9	82.6
150	156	181	6.2	73.7
300	135	152	ND	67.2

ND: Not detected. Conditions: 0.2 g of prepared resin, total aqueous volume 100 ml, equilibration time 5 h. The sample pH was adjusted at 11.

where the R^2 values were 0.954 and 0.807 for As(III) and As(V), respectively. Data given in Table 6 indicated that the slopes of Figure 10 were ranged between 0 to 1. Thus, the sorption process for both studied ions appear to be chemisorptions (Haghseresht and Lu, 1998) indicating a good harmony with results obtained from the pseudo-second-order kinetic model.

Applicability of the prepared resin to arsenic contaminated groundwater

The new prepared resin was applied to remove arsenic contaminated groundwater (Table 7). From such table it was evident that removal of As(III) down to WHO drinking water standards was achieved. Regarding the low

removal efficiency of As(V), the later can be reduced to As(III) before contacted with the resin to reach about 96% removal percent.

REFERENCES

Adamson AW, Gast AP (1997). Physical Chemistry of Surfaces, sixth ed., Wiley- Interscience, New York.

Agency for Toxic Substances and Disease Registry (2000). Case studies in environmental medicine: Arsenic toxicity. ATSDR-HE-CS-2002-0003.

Buddhawong S, Kuschk P, Mattusch J, Wiessner A, Stottmeister U (2005). Removal of arsenic and zinc using different laboratory model wetland systems. Eng. Life Sci. 5:247-252.

Clifford D, Lin CC (1991). Arsenic (III) and arsenic (V) removal from drinking water in San Ysidro. New Mexico, EPAy 600yS2-91y011, US EPA, Cincinnati.

DeMarco MJ, SenGupta AK, Greenleaf JE (2003). Arsenic removal using a polymeric/inorganic hybrid sorbent. Water Res. 37:164-176.

Dragan ES, Dinu MV, Timpu D (2010). Preparation and characterization of novel composites based on chitosan and clinoptilolite with enhanced adsorption properties for Cu^{2+}. Bioresour. Technol. 101:812-817.

El-Kamash AM, El-Gammal B, El-Sayed AA (2007). Preparation and evaluation of cerium (IV) tungstate powder as inorganic exchanger in sorption of cobalt and europium ions from aqueous solutions. J. Hazard. Mater. 141:719-728.

EPA (2002). Office of Groundwater and Drinking water. Implementation guidance for arsenic rule, EPA report 816-D-02-005, Cincinnati USA.

Fonseca B, Maio H, Quintelas C, Teixeira A, Tavares T (2009). Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough. Chem. Eng. J.152:212-219.

Freundlich HMF (1906). Over the adsorption in solution. J. Phys. Chem. 57:385-471.

García J, Rousseau DPL, Morató J, Lesage E, Matamoros V, Bayona JM (2010). Contaminant removal processes in subsurface-flow constructed wetlands: A review. Crit. Rev. Environ. Sci. Technol. 40:561-661.

Guenegou T, Tambute A, Jardy A, Caude M (1998). Elimination of arsenic traces contained in liquid effluents by chomatographic treatment. Analysis 26:352-357.

Haghseresht F, Lu G (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. Energy Fuels 12:1100-1107.

Henken KR (2009). Introduction. In: Henken, K.R. (Ed.), Arsenic Environmental Chemistry, Health Threats and Waste Treatment. John Wiley & Sons Ltd., Chichester, pp. 1–7.

Henken KR, Hutchison A (2009). Arsenic chemistry. In: Henken, K.R. (Ed.), Arsenic Environmental Chemistry, Health Threats and Waste Treatment. John Wiley & Sons Ltd., Chichester, pp. 9-68.

Henry WD, Zhao D, SenGupta K, Lange C (2004). Preparation and characterization of a new class of polymeric ligand exchangers for selective removal of trace contaminants from water. React. Funct. Polym. 60:109-120.

Ho YS, McKay G (1999). A kinetics study of dye sorption by biosorbent waste product pith. Resour. Conserv. Recycl. 25:171-193.

Hui KS, Chao CYH, Kot SC (2005). Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. J. Hazard. Mater. B127:89-101.

Kosolapov DB, Kuschk P, Vainshtein MB, Vatsourina AV, Wießner A, Kästner M, Müller RA (2004). Microbial processes of heavy metal removal from carbon deficient effluents in constructed wetlands. Eng. Life Sci. 4:403-411.

Kröpfelová L, Vymazal J, Švehla J, Štíchová J (2009). Removal of trace elements in three horizontal sub-surface flow constructed wetlands in the Czech Republic. Environ. Pollut. 157:1186-1194.

Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40: 1361-1403.

Mandal BK, Suzuki KT (2002). Arsenic round the world: A review. Talanta 58:201-235.

McKay G, Ho YS (1999a). The sorption of lead (II) on peat. Water Res. 33:585-587.

McKay G, Ho YS (1999b). Pseudo-second order model for sorption processes. Process Biochem. 34:451-460.

Meng X, Korfiatis GP, Bang S, Bang KW (2002). Combined effects of anions on arsenic removal by iron hydroxides. Toxicol. Lett. 133:103-111.

Pattanayak J, Mondal K, Mathew S, Lalvani SB (2000). A parametric evaluation of the removal of As(V) and As(III) by carbon based adsorbents. Carbon 38:589-596.

Pendias AK, Pendias H (2000). Trace elements in soils and plants. CRC Press, Boca Raton, FL.

Plazinski W, Rudzinski W, Plazinska A (2009). Theoretical models of sorption kinetics including a surface reaction mechanism: A review. Adv. Coll. Interf. Sci. 152:2-13.

Sancha AM, O'Ryan R, Perez O (2000). The removal of arsenic from drinking water and associated costs: The Chilean case. Interdisciplinary perspectives on drinking water risk assessment and management. Proceedings of the Santiago Symposium, September 1998, IAHS Publ. 260:17-25.

Sarkar S, Gupta A, Biswas RK, Deb AK, Greenleaf JE, SenGupta AK (2007). Use of ArsenX^{np}, a hybrid anion exchanger, for arsenic removal in remote villages in the Indian subcontinent. React. Funct. Polym. 39: 1599-1611.

Sarkar S, Chatterjee PK, Cumbal LH, SenGupta AK (2011). Hybrid ion exchanger supported nanocomposites: Sorption and sensing for environmental applications. Chem. Eng. J. 166:923-931.

Sarzanini C (1999). Liquid chromatography: A tool for the analysis of metal species. Chromatography A, 850: 231-228.

Singhakant C, Koottatep T, Satayavivad J (2009). Enhanced arsenic removals through plant interactions in subsurface-flow constructed wetlands. J. Environ. Sci. Heal. A44:163-169.

Taty VC, Fauduet H, Porte C, Delacroix A (2003). Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*. J. Hazard. Mater. 105:121-142.

United States Environmental Protection Agency (2006). Minteq A2, ver. 4.03, http://epa.gov/ceampubl/ mmedia/minteqA2.

Van Elteren JT, Stibilj V, Slejkovec Z (2002). Speciation of inorganic arsenic in some bottled Slovene mineral waters using HPLC–HGAFS and selective coprecipitation combined with FI-HGAFS. Water Res. 36:2967-2974.

Wang Y, Reardon EJ (2001). Asideritey limestone reactor to remove arsenic and cadmium from wastewaters. Appl. Geochem. 16: 1241-1249.

Webber TW, Chakkravorti RK (1974). Pore and solid diffusion models for fixed-bed adsorbers. AlChE J. 20:228-238.