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Existing and Prospective Sorption Technologies for the Removal of Arsenic in Water

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ABSTRACT

The present article is devoted to a review of existing and emerging sorption technologies for the removal of arsenic in water. After presenting the traditional sorbents used in arsenic removal, experimental studies to characterize the adsorptive capacities of sorbents are detailed. In a second part, metal-loaded polymers, which are among the prospective technologies for arsenate and arsenite removal in drinking water, are introduced. Finally, the design of new metal-loaded polymers to treat arsenic in drinking water is discussed.

Key Words: Arsenic removal; Arsenate; Arsenite; Adsorption; Ion exchange; Metal-loaded polymers; Water treatment.

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INTRODUCTION

Arsenic is a naturally occurring contaminant widely present in the environment. It can originate either from anthropogenic activities (pesticides, wood preservatives, mining activities, and electronic industry) or from natural erosion of arsenic containing rocks. Arsenic contamination in groundwater has become a worldwide environmental issue, especially in the West Bengal area.[1,2] There is still, however, a controversy about arsenic mobility in groundwater. Some investigators suggest that pyrite oxidation is the main mechanism, whereas others think that oxyhydroxide reduction plays an important role.[1,2]

Currently, Bangladesh experiences the biggest human contamination, with more than 70 million people affected.[3,4] On February 2002, the United States Environmental Protection Agency (USEPA) implemented a new arsenic rule in drinking water, decreasing the permisssible level from 50 to 10 $\mu g/L$. Water treatment systems must comply with this guideline by January 2006. This new regulation has challenged the research of new sorption technologies capable of removing selectively low levels of arsenic, including As(III), which can be predominant in anaerobic groundwater and also more difficult to remove than As(V). Besides strongly basic anion exchange resins and activated alumina, many polymers have been prepared these past few years and among them, metal-loaded polymers have received attention. These sorbents can be classified into two classes, metal-loaded chelating resins and metal-loaded ion-exchange resins. After introducing traditional sorbents, this article will focus on procedures used to test the adsorbents and on the review of metal-loaded polymers prepared so far by research groups.

GENERAL CHEMISTRY OF ARSENIC

In natural waters, inorganic arsenic can be found mainly in trivalent (arsenite) and pentavalent (arsenate) oxidation states. As(V) occurs as H_3AsO_4, with 3 pK_a values of 2.19, 6.94, and 11.5[5] and in this respect, is similar to H_3PO_4 with pK_a values of 2.2, 7.2, and 12.4. As(III) occurs solely as H_3AsO_3, with a pK_a of 9.1. Knowledge of the speciation of arsenic, i.e., the repartition of the different species as a function of pH, is fundamental to understand the sorption process. In the typical pH range of natural waters, arsenate ions are present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Fig. 1) and arsenite is found mostly as the uncharged species H_3AsO_3 (Fig. 2).

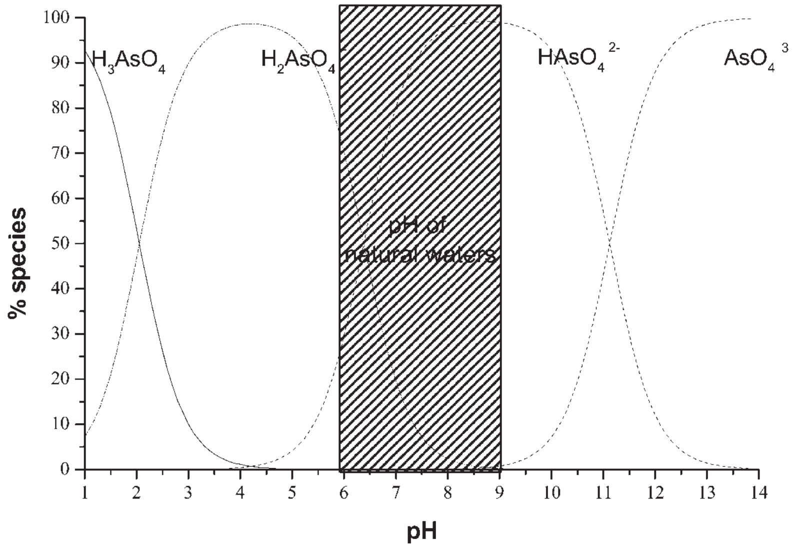


Figure 1. As(V) species repartition as function of pH.

SORPTION TECHNOLOGIES FOR ARSENIC REMOVAL

Strong Base Anion Exchange Resins

Strong base anion (SBA) exchange resins have quaternary ammonium groups connected to the polymer matrix and differ by the nature of the group attached to the nitrogen. They can be classified in two classes: type I resins with three methyl groups connected to the nitrogen and type II with two methyl and one ethanolamine group. Anion exchange resins have more affinity for divalent anions than monovalent anions, therefore, $HAsO_4^{2-}$ will be preferentially adsorbed over $H_2AsO_4^-$. Thus, according to the speciation diagram reported in Fig. 1, arsenate removal is expected to increase between pH 6 and 9.

On the other hand, due to its weak dissociation constant, As(III) cannot be removed. A preoxidation step is necessary to treat an arsenite solution with ion exchange technology.

Korngold et al.[6] investigated As(V) removal with two different type I SBA resins: Purolite A-505 (Purolite Co.), with three methyl groups connected to the nitrogen and Relite A-490 (Mitsubishi Co.), with longer chain groups such as ethyl or propyl. All experiments were conducted using 100 mL of resin packed in a column of 70-cm high. The number of bed volume

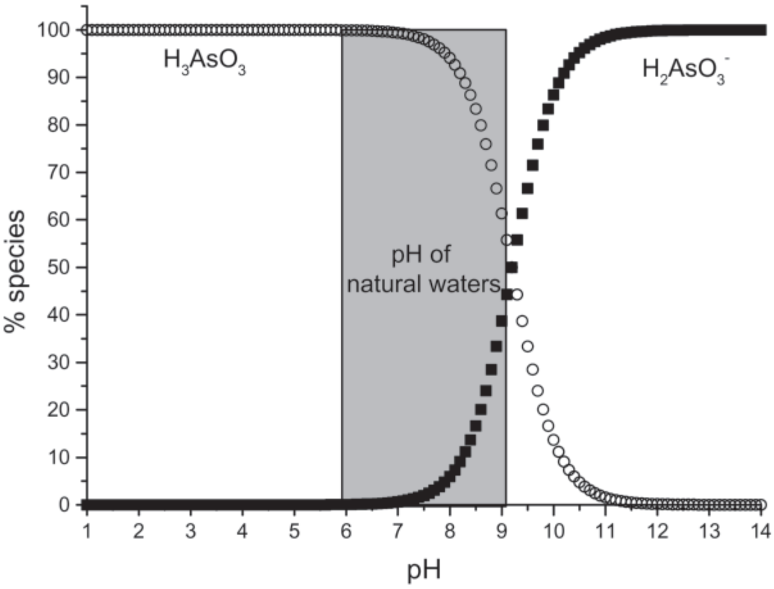


Figure 2. As(III) species repartition as function of pH.

([As] = 600 µg/L) to breakthrough with Purolite A-505 increased from 250 to 300 BV when pH was raised from pH 7.5 to 8.5. The investigators also reported at the same inlet concentration, Relite A-490 was more efficient than Purolite A-505 with 400 and 250 BV treated, respectively. Due its structure with longer alkyl groups, Relite A-490 resin is actually more hydrophobic than Purolite A-505 and improves, somehow, the accessibility of arsenate ions inside the polymer. However, As(V) breakthrough on Relite A-490 occurred after only 300 BV in the presence of 315 mg SO_4^{2-}/L instead of 500 BV, initially. Chloride ions decreased the run length to arsenic breakthrough as well. Ramana and Sengupta,[7] who studied As(V) isotherm sorption at pH 8.5 on type I SBA Amberlite IRA-900, found that arsenate sorption was completely depressed in the presence of 250 mg SO_4^{2-}/L.

Horng and Clifford[8] investigated arsenate sorption at neutral pH on chloride-form type I SBA resin (Amberlite IRA-458) and noticied a significant decrease (2–4 units) of the pH at equilibrium. They demonstrated that in addition to ion exchange, SBA resins can undergo acid base reactions converting $H_2AsO_4^-$ to $HAsO_4^{2-}$ and thus expel protons in solution. As(V) kinetic sorption on IRA-458 was fast, with 90% of arsenic removed from a 1 mg/L As(V) solution in the first 5 min.

Activated Alumina

Activated alumina (AAl), commonly named aluminum oxide (Al_2O_3), is prepared by thermal dehydration of aluminum hydroxide. The AAl has a high surface area (few hundred of $m^2 g^{-1}$) and a distribution of both macro and micropores. The AAl is classified by the USEPA as among the best available technologies for arsenic removal in drinking water. As(V) sorption occurs mostly between pH 6 and 8, where AAl is predominantly positively charged. As pH increases, the AAl surface is less and less positive and As(V) sorption decreases.

At low residual concentration, AAl performs better than other sorbents with uptake capacities of a few mg/g. Gupta and Shen[9] reported that at pH 6–7, a capacity of 4.1 mg As(V)/g on granular activated alumina at $C_{eq} = 50\,\mu g/L$ ($b = 7140\,L/mmol$) was found.

Rosemblum and Clifford[10] investigated arsenate sorption on granular AAl (Alcoa F-1) and reported that at pH 6, loading capacities of 25 and 15 mg/g at $C_{eq} = 1$ and 100 μg/L, respectively, were found. A binding constant calculated from Langmuir isotherm was 766 L/mmol. However, AAl capacity decreased over 50% in solution with 720 mg SO_4^{2-}/L and over 20% with 532.5 mg Cl^-/L. Furthermore, kinetic sorption was very slow, with 7 days to reach equilibrium. As(V) isotherm sorption on granular AAl (Alcoa CPN) at pH 7.7 was characterized by an uptake of 0.68 mg/g at $C_{eq} = 100\,\mu g/L$ with a binding constant of 22.14 L/mmol.[11] The capacity and binding constant, were 20 and 32 times less than those reported by Rosemblum in similar conditions with F-1 type AAl.[10] These results might be explained by a difference in activated alumina grades. During a pilot-scale field test, Wang et al. also noticed a significant decrease of arsenate removal when fluoride and sulfate ions were present in solution.[11]

A study of arsenite and arsenate sorption onto activated alumina grains[12] demonstrated that As(III) and As(V) removal were optimum at pH 6.1 and 5.2, respectively. Kinetic experiments showed a different behavior between the two arsenic forms: As(III) sorption reached equilibrium after 40 hr whereas As(V) needed 170 h. Both As(III) and As(V) isotherms fit a Langmuir model with uptake capacities of 1.69 and 15.90 mg/g, respectively.

The low affinity of As(III) on AAl was confirmed by Gupta and Shen[9] with a capacity of 0.8 mg/g at $C_{eq} = 0.4\,mg/L$. Franck and Clifford[13] demonstrated also that AAl did not remove As(III) at all. Beside a slow sorption kinetic, regeneration of activated alumina can be problematic. Ghosh[14] observed a 3% loss of the adsorptive capacity after each regeneration carried out with a 0.5% solution of sodium hydroxide.

Activated Carbon

Activated carbon (AC) has been extensively used for the removal of organic contaminants in water. Results regarding arsenic removal are quite controversial but most of them show that activated carbon can remove As(V) but not As(III). However, As(V) uptake capacities were low, reaching 20 mg/g on granular activated carbon.[15] The performance of AC depends on its chemical composition: Lorenzen et al.[16] demonstrated that a fly ash content of activated carbon was a critical parameter in arsenate removal. In another study, As(V) sorption was correlated to AC zeta potential values but fly ash content was not consistent with As(V) removal.[17] As(III) was removed significantly only at high initial concentration (>700 mg/L), which was explained by an oxidation from As(III) to As(V) by the oxygenated functional groups present at the surface of the sorbent. Furthermore, Jubinka and Rajakovic[15] demonstrated that activated carbon did not remove As (III) in the pH range of 2–10.

Metal-Loaded Polymers

Metal-loaded polymers were described four decades ago by Helfferich to separate ligands of different coordination.[18] These materials have been used only recently for the treatment of water contaminated with toxic anions like arsenic, selenite, or fluoride. Another domain of application is analytical chemistry, where these sorbents are used to preconcentrate very dilute solutions of arsenic before analysis.[19] One attractive feature of these polymers is that most of the time, they overcome interferences with chloride and sulfate ions generally observed with strong anion exchange resins. Due to the strong interaction between the metal bound onto the polymer and arsenic, uptake capacities can also be increased. The most interesting property may be the possibility to remove both As(III) and As(V). Operating pH conditions can also be less restricted than with SBA because arsenic species do not have to be negatively charged to be removed. However, sorbent has to be carefully designed to avoid any release of the metal in solution and adversely affect the quality of water.

Preparation

Metal-loaded polymers are usually prepared by passing a metal ion solution at a given concentration and pH through a packed column of resins in a downflow or upflow mode.[20] With this method, the operator has control of the pH and concentration of the feed solution. Usually a feeding rate of few mL/H is preferable to correctly load the resin. Channeling or preferential path of the fluid inside the column can be avoided by using a ratio of 1 : 10 between the diameter of the beads and the internal diameter of the column. Analysis of the outlet concentration is necessary to check whether the column is saturated or not: when the outlet concentration is equal to 95% of the inlet, the column is considered saturated. Alternatively, impregnation can be conducted in a batch system by contacting the polymer with the metal ion solution.[21,22] In this case, contact time has to be long enough to allow equilibrium between the solid and liquid phase. pH can be adjusted if necessary by adding small amount of concentrated acids or bases. Although few investigators mention it, final conditioning of the resin with NaOH or HCl can significantly affect arsenic removal performance.

Characterization of Metal-Loaded Polymers

Knowledge of the metal content in the sorbent is critical to optimize its preparation and evaluate its arsenic removal efficiency. For biopolymers, the metal content can be determined easily by disrupting the gel phase by sonication in the presence of EDTA[23] or by using a mixture of H_2O_2/HNO_3 at moderate temperature.[24] For synthetic polymers, mineralization with hot acid and an oxidizing agent like potassium persulfate is necessary to solubilize the polymer. Alternatively, metal content can be calculated from the difference between the initial and final metal solution concentration used for the loading.

FTIR is a quick method to characterize a polymer before and after impregnation and to see how the functional groups are affected by the metal sorption. Advanced solid spectroscopic methods, such as EXAFS or XPS,[25] provide more structural information about the coordination of the metal and the extent of its oxidation degree.

Evaluation of the Adsorptive Properties of Metal-Loaded Polymers

Effect of pH

pH is one of the most important parameter to study because it affects both the nature of arsenic species in solution and the surface of the adsorbent. Experimentally, the same amount of sorbent is contacted with the arsenic solution at a different pH. For each run, pH has to be controlled by the microaddition of concentrated acid or base so that the final volume remains the same. Whenever possible, buffers should be avoided as they can interfere with the sorption process. After filtration, arsenic concentration can be analytically determined using spectrophotometric methods[26] or ICP-AES, depending on the final concentration. Another important variable is the leaching of the metal from the polymer. This can be investigated in conjunction with the pH effect study by analyzing metal leaching. Finally, q_{eq} and percentage metal release plotted against equilibrium pH will give the range of pH where the sorbent can be used.

Selectivity Study

The study of interferences arising from anions, such as phosphate, sulfate, chloride, or nitrate ions, commonly present in natural waters, is very important to evaluate the efficiency of a sorbent for arsenic removal. Additionally, it can provide information about the sorption mechanism.

Because they have a similar chemistry to arsenate, phosphate ions can strongly interfere in the sorption process and can even suppress arsenic sorption if their concentration is high enough. Sulfate ions also strongly interfere with arsenate sorption on SBA and AAl and thus it is important to evaluate their effect on a impregnated sorbent.

This study of selectivity can be carried out in a batch system. Ideally, experimental conditions are set up to saturate the sorbent with arsenic, actually, if arsenic occupies only few binding sites, the effect of co-existing anions might not be noticeable.

Sorption Isotherm

The quality of an adsorbent is judged according to how much metal it can attract and retain. A sorption isotherm defines the distribution of the metal at equilibrium, at given pH and temperature, between the aqueous and the solid phase. Sorption isotherms are plots between q_{eq}, equilibrium uptake capacity and C_{eq}, equilibrium metal ion concentration. The mass balance equation between liquid and solid gives the following equation:

$$q_{eq} = \frac{V(C_0 - C_{eq})}{m}$$

where V is the volume of the solution (L), C_0 and C_{eq} are the initial and equilibrium concentration of the metal in solution, respectively (mg/L), m is the amount of dry sorbent used (g), and q_{eq}, the uptake capacity, is expressed, in mg/g dry sorbent. It can also be convenient to express q_{eq} in mg As/g metal or in mmol As/mmol.

Sorption models like Langmuir and Freundlich allow calculating useful coefficients from the experimental points and quantifying the affinity of the arsenic for the sorbent. Equations, linearization, and coefficients related to each model are reported in Table 1. Isotherms are a powerful tool to compare sorbent performances as long as they are used correctly. Figure 3 reports two isotherms, A and B, which are crossing each other. In this configuration, sorbent A is more efficient than sorbent B to remove metal at low equilibrium although B has a higher saturation capacity. A is, therefore, the best choice for a drinking water application.

Isotherms are more accurate than percentage removal to compare two sorbents because they have more experimental points. For example, if a sorbent A removes 90% of a contaminant and a sorbent B of the same mass as A only 70% (initial arsenic concentration being the same), then it does not mean necessarily that A is a better sorbent. Actually, in this experiment, the two sorbents will lead to different final concentrations but if one reported these values on the configuration depicted in Fig. 3, corresponding q_{eq} values can be in the opposite ranking.

Another example describes two isotherms reaching the same plateau at saturation but with very different slopes at low concentrations (Fig. 4). Isotherm A has a "rectangular shape," characteristic to chelating polymers,[29] which can reach saturation sooner than ion exchange resins.

In this configuration, it will be a misleading conclusion to extrapolate isotherms curve from mg/L to μg/L levels using Langmuir or Freundlich models and conclude that sorbents A and B have the same efficiency to treat μg/L metal solutions.

Table 1. Sorption isotherm models, linearization equations, and coefficients.

Model	Equation	Linearization	Coefficients
Langmuir	$q = \dfrac{q_{\mathrm{m}} b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}}$	Type I $\dfrac{1}{q_{\mathrm{eq}}} = \dfrac{1}{q_{\mathrm{m}}} + \dfrac{1}{q_{\mathrm{m}} b C_{\mathrm{eq}}}$[27]	b, binding constant (L/mg or L/mmol)
		Type II $\dfrac{C_{\mathrm{eq}}}{q} = \dfrac{1}{q_{\mathrm{m}} b} + \dfrac{C_{\mathrm{eq}}}{q_{\mathrm{m}}}$[28]	q_{m}, maximum uptake capacity (mg/g or mmol/L)
Freundlich	$q_{\mathrm{eq}} = K_{\mathrm{f}} C_{\mathrm{eq}}{}^{1/n}$	$\log q_{\mathrm{eq}} = \log K_{\mathrm{f}} + \dfrac{1}{n} \log C_{\mathrm{eq}}$	K_{f} relative to the sorption capacity (mmol/g or mg/g) n, affinity coefficient (dimensionless)

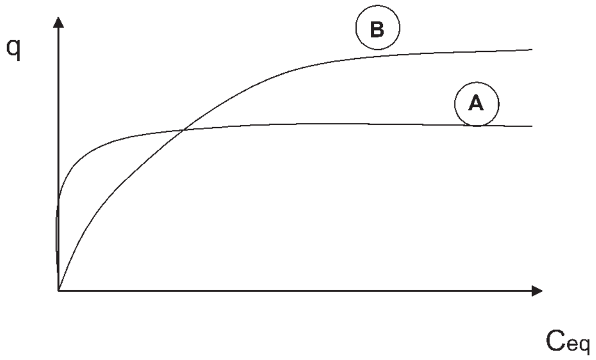


Figure 3. Crossing isotherms sorpiton.

Regeneration and Kinetics

When one considers the final cost of a resin, it might be worthwhile to develop a fully regenerable sorbent. In the case of metal-loaded polymer, a problem can arise from the leaching of the metal, particularly if this one is toxic. Furthermore, if the metal is eluted with the arsenic, then a new impregnation step is required, which can be cost and time consuming.

If the regeneration is carried out in column, arsenic has to be eluted with the minimum volume of eluant. A 40-fold enrichment of the treated solution is commonly observed. Kinetics is also an important parameter to assess the overall performance of an adsorbant. These studies can be carried out in batch by contacting the resin with a large volume of arsenic solution at constant stir

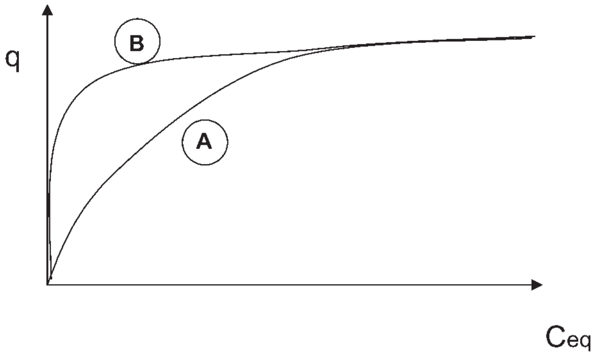


Figure 4. Isotherms sorption with same saturation capacity.

speed, temperature, and pH. Aliquots are withdrawn at regular intervals to study either the decrease of the concentration or the increase of the uptake capacity q vs. time.

By varying parameters like particule size, agitation speed, and mass of sorbent, one can demonstrate if the kinetics of sorption is limited by external or intraparticular diffusion. If kinetics is limited by intraparticular diffusion, an intraparticular diffusion coefficient can be calculated from the slope of $q = f(t^{1/2})$.[30]

On the other hand, if kinetics is limited by external diffusion, a linear relationship is observed between C/C_0 and t.[31] External diffusion coefficient k_i is calculated from the slope $k_i A/V$, where A and V refer to the external surface of the sorbent and the volume of the solution, respectively. More generally, the rate of arsenic sorption k_f can be calculated from Lagergren equation $\log\ (q_e - q) = \log q_e - (k_f t/2.3)$, where q and q_e refer to the equilibrium capacity at any time t and at equilibrium, respectively.

Survey of Metal-Loaded Polymers

Strong cation exchange resins, macroporous polymers, chelating resins, or biopolymer gels have been used in the preparation of metal-loaded polymers. The main advantage of polystyrene- or polyglycidyl methacrylate-based chelating resins are that they are insoluble, nontoxic and chemically resistant as long as the chelating group bound to the polymer is not hydrolyzed in acidic or basic media. Among them, sulfonic acid and iminodiacetic (IDA) resins (Fig. 5), polyhydroxamic (PHA) and lysinediacetic (LDA) resins (Fig. 6) are commonly used. Biopolymers like chitosan or alginate (Fig. 7) usually have a poor chemical and mechanical resistance. However, once metal ions like Mo(VI) are bound into the polymer matrix, they can act as a crosslinking agent and give the structure more strength.[32] This second part of the article presents an extensive list of metal-loaded resins prepared so far by research groups. They are classified according to the metal used for the impregnation. When it was possible, loading capacities at low arsenic equilibrium concentrations (C_{eq}) were reported or calculated using isotherm models and expressed in mg As/g dry sorbent.

Fe(III)-Resins

Fe(III) has been widely used for the preparation of metal-loaded resins. One of the first works reported by Yoshida and Ueno[33] investigated the removal of arsenite and arsenate ions onto a iron-loaded commercially available resin Uniselec UR-10 bearing *o*-hydroxybenzylnitrilodiacetic

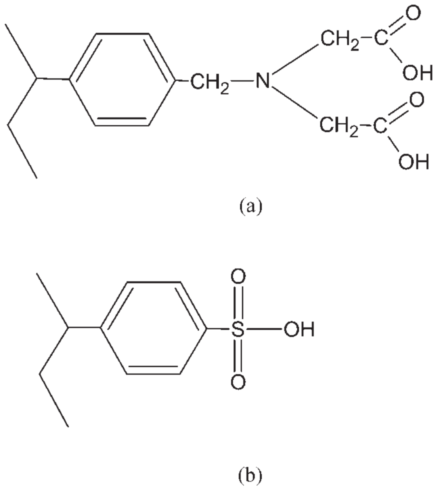
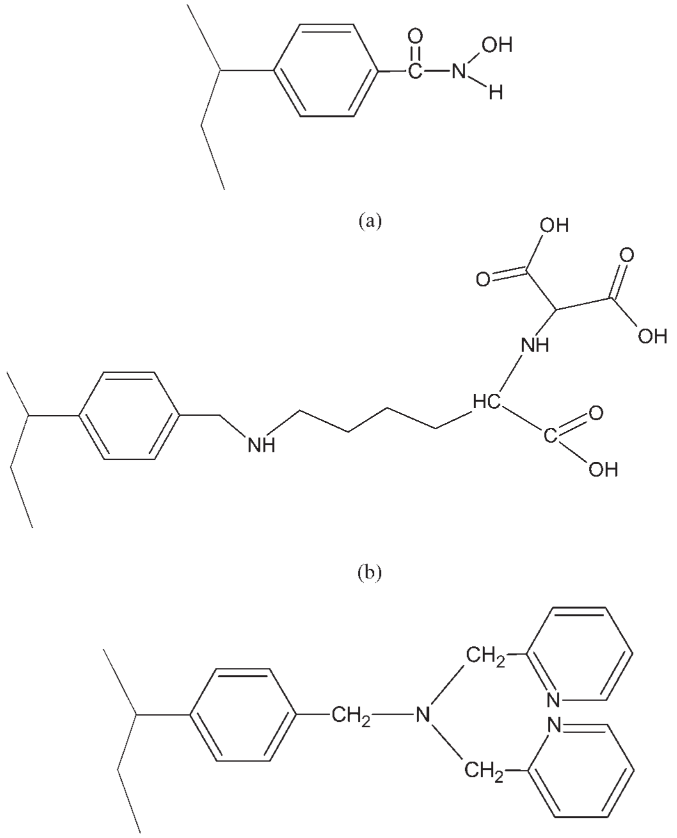


Figure 5. Functionalized synthetic polymers (a) IDA resin (Amberlite IRC-718). (b) Sulfonic acid resin (Bio-rad AGMP-50).

groups. Iron loading was 1.84 mmol/g. As(V) was sorbed between pH 3.6 and 5.5, whereas As(III) sorption occurred at pH 8.5. The investigators did not carry out isotherms but loading capacities of As(III) and As(V) at $C_{eq} = 100$ mg/L were similar, with a value of 35.2 mg/g.

Matsugana et al.[34] prepared a Fe(III)-(lysine-N^{α},N^{α}-diacetic acid) loaded resin [Fig. 6(b)] where iron was believed to be coordinated with one nitrogen and three oxygen of the chelating polymer. Iron loading was 0.89 mmol Fe/g of wet sorbent. Arsenate ions were strongly retained on the resin between pH 2 and 4. According to the As(V) isotherm sorption carried out at pH 3.5, loading capacities were 27.2 and 4.86 mg/g at $C_{eq} = 1$ and 0.1 mg/L, respectively, with a binding constant b of 720 L/mmol. This is by far the highest As(V) sorption capacity observed at low concentration with a metal-loaded polymer and it can be compared to results obtained with AAl. However, as As(V) sorption decreased markedly at neutral pH, Fe(III)-LDA will not be as efficient as it was in acidic media.

Arsenite ions were weakly sorbed on Fe(III)-LDA at pH 9, with an uptake capacity of 1.55 mg/g at $C_{eq} = 10$ mg/L (binding constant, $b = 0.19$ mmol/L). Interestingly, As(III) sorption was faster than As(V), with an equilibrium reached after only 2 h. Both arsenate and arsenite ions were quantitatively eluted from the resin with 0.1 mol/L NaOH solution. Resin was further used for several adsorption–desorption cycles without a noticeable loss of ferric ions.



(a)

(b)

(c)

Figure 6. Functionalized synthetic polymers. (a) Polyhydroxamic acid (PHA) resin, (b) LDA resin, and (c) *bis*(2 picolylamine) resin (Dow XFS- 4195).

Iminodiacetic resin is another functionalized polymer capable of strong coordination of metal ions. Chelex 100 (Bio-rad) loaded in batch with a solution of $FeCl_3$ at pH 2 (Fe loading $= 0.78\,\text{mmol/g}$) removed arsenite at pH 10.5 and arsenate at pH 2.[22]

As(III) sorption was higher than As(V) with saturation capacities of 110.8 mg/g and 71 mg/g, respectively. However, As(III) and As(V) isotherms crossed each other at $C_{eq} = 4\,\text{mmol/L}$ and at low concentrations, Fe(III)-IDA resin removed more arsenate than arsenite. For a equilibrium concentration of 150 mg/L and a pH 2, As(V) loading can be estimated at 49 mg/g. The binding constant for As(V) was 0.993 L/mmol, which is lower than

720 L/mmol reported for Fe(III)-LDA.[34] As(V) capacity is well below the one obtained with Fe (III)-LDA but As(III) capacity, at $C_{eq} = 75\,mg/L$, is similar. Another study regarding arsenite and arsenate sorption on Fe(III)-IDA showed that kinetics was fast for both species, with an equilibrium attained after 4 hr.[35]

Fe(III)-loaded poly(hydroxamic) acid resin [see Fig. 6(a)] was also found to remove both As(III) and As(V).[36] As(V) was favorably sorbed between pH 2 and 4 with a saturation capacity of 86.1 mg/g ($C_{eq} = 2.2\,g/L$), whereas As (III) sorption was two times and a half lower in the same range of pH.

Although no data were available at low concentration, Fe(III)-PHA was considerably less efficient than Fe(III)-LDA in removing arsenate ions; the same loading capacity of 27.2 mg/g was reached at $C_{eq} = 150\,mg/L$ for Fe(III)-PHA and at only $C_{eq} = 1\,mg/L$ for Fe(III)-LDA. Fluoride, selenite, and phosphate ions interfered significantly with As(V) sorption.

Weak base chelating resin with *bis*(2-picolyamine) functional group (Dow XFS-4195) loaded with $FeCl_3$ (0.65 mmol Fe/g) removed both As(V) and As(III) at pH 5 and 10, respectively.[37] Isotherm sorption for both arsenic species fit the Freundlich model and Fe(III)-XFS had a higher saturation capacity for As(III) than As(V). However below $C_{eq} = 74.9\,mg/L$, as observed with Fe(III)-IDA resin,[22] isotherms crossed each other. At $C_{eq} = 15\,mg/L$, As(V) and As(III) capacities were 63.6 and 15.5 mg/g, respectively.

In the presence of 100-fold molar concentrations of Cl^- and SO_4^{2-}, As(V) sorption decreased by 34% and 35%, respectively. In the same conditions, As(III) sorption decreased by 50% and 78%. Kinetic studies showed that for both arsenite and arsenate ions, initial arsenic concentration did not have any effect on the rate of the sorption. As(V) sorption reached equilibrium after 16 min, whereas As(III) needed 64 min. Regeneration was carried out with a acidic solution of $FeCl_3$ to remove both the arsenic and $Fe(OH)_3$ present in the pores of the polymer and reload the resin with active Fe^{3+}. After two regeneration cycles, As(V) and As(III) sorption capacities increased as more and more $Fe(OH)_3$ built up inside the resin. However, for the following regeneration cycles, capacities started to decrease due to the too high concentration of $Fe(OH)_3$ inside the pores.

Alginate, a natural biopolymer, was used to prepare Fe(III)-loaded gel beads. Fe(III)-ALG was prepared by adding, dropwise, an aqueous solution of the biopolymer in a solution of calcium and ferric chloride.[23] Sorption experiments showed that arsenate sorption was optimum between pH 3 and 4. Fe (III)-beads were not stable below pH 3, with a release of 60% of the iron in solution. At pH 4, this release decreased to 4%. Fe(III) leaching determination was carried out by contacting the beads with a low concentration of As(V) (0.4 mg/L), so a higher release of iron can be expected as As(V) concentration increases. At pH 4, for $C_{eq} = 10\,mg/L$, As (V) and As(III) capacities were 352 and 7.5 mg/g Fe, respectively.

Phosphate and sulfate ions did not interfere with As(V) but as a low As(V) initial concentration was used (4 μg/L), interferences may not have been noticeable. Arsenate sorption was relatively slow, with an equilibrium reached only after 24 h. Strong acid cation exchange resins, due to their high affinity for Fe(III) can be used to prepare selective sorbents. Guenegou[38] contacted a sulfonic acid resin (Bio-rad AGMP-50, macroporous) with a ferric chloride solution at pH 1 followed by an elution with 1 mol/L sodium hydroxide solution to precipitate iron inside the pores of the polymer. At saturation, As(V) and As(III) uptake capacities were 11.2 and 10.9 g As/L resin at pH 5.4 and 10.7, respectively.

Fe(III)-resin was used to remove arsenic from an industrial effluent containing 1 mol/L of chloride. In these conditions, arsenate and arsenite sorption were still very close to what was obtained without chloride, giving this Fe(III)-loaded resin a considerable advantage over strong base anion exchange resins.

Very few studies have been dedicated to the study of metal coordination in chelating resins. Fe(III)-IDA properties (Chelex 100) were investigated by wide-angle x-ray diffraction[39] and results showed that Fe(III) could actually be bound to two or three iminodiacetate groups. Among the configurations involving two IDA groups, Fe was bound to two carboxylate oxygen and one nitrogen from one group and two oxygen from the other group, a molecule of water completing the metal coordination sphere.

This review of Fe(III) impregnated sorbent demonstrates that the nature of the chelating polymer can dramatically affect final arsenate sorption capacities. For dilute arsenic concentrations, As(III) sorption was always found to be lower than As(V). Arsenic sorption is highly pH dependant and it is consistent in all studies that As(III) sorption takes place in alkaline conditions and As(V) in acidic media.

Cu(II)-Resins

Ramana and Sengupta[7] prepared Cu(II)-loaded sorbents using two commercially available resins containing IDA (Amberlite IRC-718) and pyridyl/tertiary ammonium groups (Dowex 2N). Copper loadings were 0.85 and 1.6 mmol/g, respectively. Resins were packed in a column and converted into a copper-loaded form by passing a 500 mg/L Cu^{2+} solution at pH 4.5 until saturation.

Cu(II)-Dow2N removed As(V) at pH 8.5 in the presence of 250 mg SO_4^{2-}/L, where SBA Amberlite IRA-900 was totally inefficient. Then 44 mg As(V)/g was sorbed at $C_{eq} = 10\,mg/L$. Unlike Cu(II)-Dow2N, Cu(II)-IDA had a very low affinity for arsenate ions. This result demonstrates, as observed with Fe(III)-resins, that the nature of the polymer ligands strongly influence arsenic removal efficiency.

In addition, if Cu(II)-IDA did not remove As(V), we saw previously[22] that Fe(III)-IDA had a high affinity for As(V). This result can be explained by the difference of electronic configuration between Cu(II) and Fe(III). Actually, once a metal is bound to the resin, it should have at least one coordination left to be able to react with arsenic.

Zr(IV)-Resins

Positive results have been achieved by loading poly(methylmethacrylate) beads (Amberlite XAD-7) with zirconium oxide.[40] Zirconium oxide crystals were immobilized inside the pores of the polymer after hydrolysis and hydrothermal treatment. Zirconium loading was in the range of 2.1–2.6 mmol/g. Pore distribution measurements showed that zirconium oxide was actually trapped in the pores of large diameters (>50 Å). As(III) and As(V) sorption were maximum between pH 2 and 10 and fit a Langmuir isotherm up to a 3 mmol/L residual concentration.[41] Saturation capacities on Zr(IV) resin were 79.4 As(III)/g and 53.9 mg As(V)/g. Using Langmuir equations, we can estimate the loading capacities of 2.5 mg As(V)/g and 4.1 mg As(III)/g for a equilibrium concentration of 1 mg/L. It is still 10 times lower than the capacity reported by Rosemblum and Clifford[10] on AAl. However, the strong affinity of As(III) for Zr(IV)-resin gives this resin interesting features.

Another advantage over AAl is that sulfate and chloride ions did not compete with arsenic sorption. However, significant interferences were observed in the presence of fluoride and phosphate ions in solution. Another alternative to prepare Zr(IV)-loaded resins has been developed by contacting a phosphoric acid resin with a solution of zirconium nitrate at pH 0.8[20] (Zr loading = 0.72 mmol/g wet resin). As(V) and As(III) sorption were investigated using a breakthrough curve. As(V) removal was maximum between pH 1.14 and 2.03, decreasing slightly but being relatively constant between pH 2.03 and 7.53.

As(V) saturation capacity at pH 3 was estimated to 50.2 mg/g dry resin at $C_{eq} = 374.5$ mg/L. Nitrate and chloride ions did not interfere with arsenate sorption whatsoever. Elution of both arsenate and arsenite ions loaded on Zr-resin using NaOH 0.7 mol/L was found to be more difficult than when Zr-resin was loaded with As(V) alone. This observation made the investigators suggest that Zr-resin exhibits more affinity for As(III) than for As(V), which is consistent with the results obtained by Suzuki et al.[41]

IDA resin was used to prepare Zr(IV)-resins for the selective removal of fluoride.[21] However, little information was given regarding the preparation of the polymer. Zr(IV) can also be loaded on a weakly acidic cation exchange resin bearing carboxylic groups. Amberlite IRC-50, conditioned with sodium hydroxide, was loaded with 1.2 mmol Zr/g at pH 3.[42] IRC-50-Zr(IV) successfully removed phosphate ions between pH 2 and 4. A leaking test performed with HCl 4 mol/L showed that zirconium was eluted completely from the resin. Zr bonding with a carboxylic group is weaker than with IDA groups because zirconium was not removed completely after contact of Zr(IV)-IDA with 4 mol/L HNO_3 for a month.[21]

La(III)-Resins

Trung et al.[19] demonstrated that IDA resin (Muromac A-1) loaded with La(III) could effectively preconcentrate very dilute solutions of As(V) and As(III) before HG-AAS analysis. IDA resin was packed in a microcolumn and loaded with a solution of lanthanum chloride buffered at pH 4. Subsequent washing with NH_3 or NaOH 3.10^{-3} M allowed the resin to convert to the hydroxide form.

Sorption efficiency of La(III)-IDA resin was evaluated by passing a 1 μg/L solution of As(III) or As(V) through a 1-mL resin bed: La(III)-resin removed between 98% and 100% of As(III) and As(V) between pH 4 and 9. Although no sorption capacities were reported, the investigators claimed that La(III)-IDA resin was able to preconcentrate 0.5–20 μg/L solutions of arsenite and arsenate. No information was available regarding the selectivity of the resin.

A short, comparative As(V) removal study was conducted on La(III)-IDA and La(III)-PHA by Haron et al.[43] La(III) was loaded on IDA and PHA by contacting resins with a solution of lanthanum chloride at pH 6 and 5.85, respectively. La(III)-IDA removed 99.4% of the arsenic from a 5-mM solution at pH 3.5, whereas La(III)-PHA removed only 74.7% at pH 2.7.

The content of La(III) on each resin cannot be correlated to the extent of As(V) because La (III) IDA content was only 1.08 against 2.84 mmol/g for PHA.

At $C_{eq} = 2.25$ mg/L, uptake capacity on La(III)-IDA was 18.6 mg/g, which is comparable to results obtained with Ce(IV)-IDA. No information, however, was available on the performance of La(III)-IDA at neutral pH.

If IDA seems to be a good support to prepare La(III)-resins, other chelating polymers can potentially strongly coordinate lanthanum. For example, an amine *N*-phosphonate resin was successfully loaded with 1.1 mmol/g of La(III) at pH 2.5–3.5 and used to remove fluoride at pH 3.5.[44]

Ce(IV)-Resins

Haron et al. prepared Ce(IV)-resins by loading PHA and IDA (Amberlite IRC-718) chelating polymers with cerium chloride at pH 5.65 and 6, respectively.[43] Although the PHA resins contained two times more cerium than IDA resin, Ce(IV)-IDA had the highest affinity for arsenate ions: Ce(IV)-IDA removed 99.51% of As(V) from a 374.5 mg/L solution at pH 3.25, whereas Ce(IV)-PHA removed only 80.60% at pH 2.75. As observed previously for Fe(III) and Cu(II)-resins, coordination state of the metal sorbed on the polymer affects the affinity of the resin for arsenic.

As(V) sorption on Ce(IV)-IDA was maximum at pH 3.25 and decreased slightly at neutral pH. Capacity decreased drastically below pH 2.5 due to the leaching of Ce(IV) from the polymer. As(V) isotherm sorption fit a Langmuir model up to $C_{eq} = 3.4\,\mathrm{g/L}$ with a saturation capacity of 53.2 mg/g and a binding constant of 0.74 L/mmol. This isotherm was not carried out for equilibrium concentrations lower than 74.9 mg/L but one point of the isotherm, calculated from another experiment, gave an uptake capacity of 18.6 mg/g at $C_{eq} = 1.83\,\mathrm{mg/L}$, which can be compared to the results obtained with La(III)-IDA.[40]

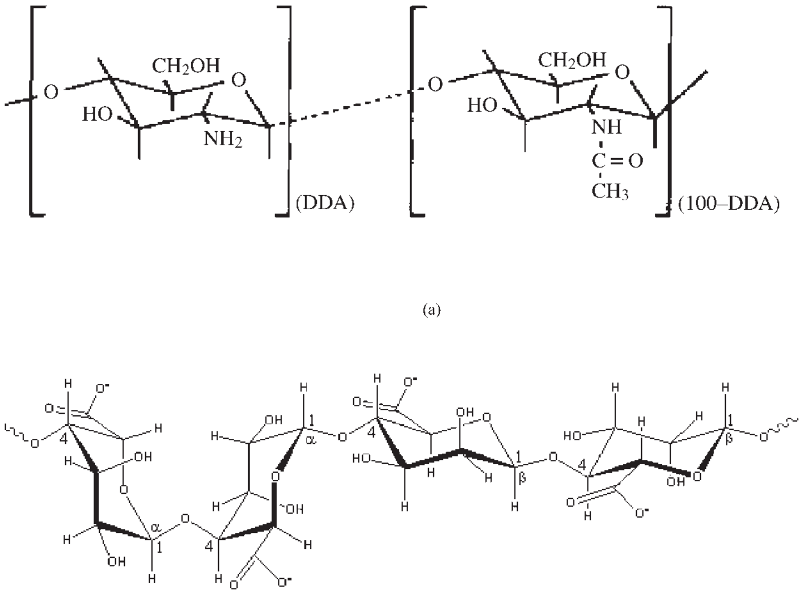
As(V) kinetic sorption on Ce(IV)-IDA was fast, with an equilibrium reached after 2 h. Although bromide, chloride, and nitrate ions did not compete with As(V) sorption, sulfates and phosphates significantly decreased arsenate removal. Finally, a 0.1 mol/L NaOH solution desorbed only 20% of the arsenic, which indicates a strong bonding between As(V) and Ce(IV).

Y(III)-Resins

Basic yttrium carbonate has been reported to remove both As(V) and As(III) from water.[45] Haron et al.[43] compared arsenate sorption on IDA and PHA resins loaded with 1.37 and 2.50 mmol Y/g, respectively. Even though IDA had the lowest yttrium content, Y(III)-IDA had the highest affinity for As(V) at pH 3.6.

Mo(VI)-Resins

Chitosan, a natural occurring biopolymer with a high affinity for molybdate ions has been used to prepare Mo(VI)-loaded chitosan gel beads (Fig. 7).[24] Separation was based upon the reaction of complexation in solution between Mo(VI) and As(V).[46] The structure of these complexes, so called heteropolyanions, is quite complex and depends on both the initial Mo/As ratio and pH.[47]



(a)

(b)

Figure 7. Biopolymers supports: (a) chitosan and (b) alginate.

Mo(VI)-chitosan beads were prepared either by contacting gel beads with a solution of ammonium heptamolybdate at pH 3 or by adding, dropwise, a solution of the biopolymer in a concentrated bath of ammonium heptamolybdate.[48] Subsequent washing with orthophosphoric acid allowed the resin to convert to the phosphate form and removed the fraction of Mo(VI) weakly bound to the polymer. At pH 3, As(III) and As(V) saturation uptake capacities were 20.2 and 61.4 mg/g, respectively.

As(V) was removed with no noticeable loss of performance from solutions containing copper, zinc, lead, and other anions like sulfate or chloride. Phosphate ions strongly interfered with As(V) sorption. Due to the leaching of molybdate ions from chitosan, its utilization was restricted between pH 2 and 4. Arsenate ions were exchanged by ligand exchange with the phosphate ions bound to molybdate. Arsenic was readily desorbed with 0.1 mol/L phosphoric acid and several adsorption–desorption cycles were carried without a noticeable decrease of the performance and a negligeable leaching of molybdate. The reaction between arsenic ions and molybdate in solution being quantitative only at acidic pH, Mo(VI)-loaded polymers will not likely be used for the treatment of drinking water.

CONCLUSION AND PERSPECTIVES

This review demonstrates that many metal-loaded polymers can effectively and selectively remove arsenite and arsenate ions in water and thus be potentially an improvement of AAl and IX technologies. Most of the work on metal-loaded polymers has been done with Fe(III) but these sorbents have limitations for drinking water treatment due to their low operating pH for As(V) removal and a low affinity for As(III). Zr(IV)-loaded chelating resins are promising because they are selective and have an high affinity for arsenite ions at neutral pH. In addition to phosphoric acid resin, Zr(IV) can be loaded on other chelating resins. For example, Zr(IV)-IDA had never been studied for arsenic removal but was found to remove μg/L level of fluoride in solution[21] as well as phosphates.[42]

However, more data are needed at low concentration to demonstrate if the Zr(IV) resins can actually be used in drinking water treatment. Data regarding La(III) resins are scarce and further studies are needed to determine their adsorptive properties vs. As(III) and As(V). Ce(IV)-resins seem to have a high affinity for As(V) at low concentration and at acidic pH, but no data are available at neutral pH. Furthermore, Ce(IV)-resins have not been tested with As(III).

With most impregnated sorbents, saturation capacities for arsenate and arsenite ions are between 74.9 and 112.4 mg/g (1 and 1.5 mmol/g) of dry sorbent. These capacities, however, can drastically decrease at low residual concentration, making the sorbent inefficient for drinking water treatment. It has also been observed for Fe(III)-IDA and Fe(III)-XFS resins, that at saturation, resins removed more As(III) than As(V) but it was the opposite at low arsenic concentration due to the crossing of the respective isotherms. To avoid mistakes, isotherms sorption has to be conducted up to $C_{eq} = 10$ mg/L for a drinking water application. The ideal sorbent will, at neutral pH, have a high sorption capacity at low concentrations as well as a high binding constant *b*.

Studies of the interaction between arsenic and metal oxides can give some insight for the development of new metal-loaded polymers. For example, a mixed rare earth oxide containing 37% of Nd_2O_3 with an affinity for arsenate ions at neutral pH[49] made Nd(III)-resins a potential sorbent to remove As(V). In addition, it has been reported that Nd(III) can be loaded on PHA resin at pH 6.[50] Beside Nd(III), chelating resins loaded with Ti(IV), Hf (IV), Ga(III), or Lu(IV) can also be investigated. By combining these metal ions with different chelating polymers, many new selective sorbents can be prepared.

Successful combination of metal ion and chelating polymer can usually be found by experimentation. It seems, however, that among chelating polymers, IDA, LDA, and phosphoric acid resins are superior to PHA because this latter does not leave enough reactivity to sorbed metals to interact with arsenic in solution. Metal-loaded polymers can be used in a packed column but if operating pH and conditioning are compatible, a mixed bed of resins can be an alternative for a more efficient removal of arsenic.

ABBREVIATIONS AND SYMBOLS

AAl = activated alumina
AC = activated carbon
b = binding constant in the Langmuir model ($\mathrm{L\,mg^{-1}}$)
BV = bed volume
C_{eq} = metal equilibrium concentration ($\mathrm{mg\,L^{-1}}$)
EDTA = ethylenediaminetetraacetic acid
EXAFS = extended x-ray absorption fine structure
FTIR = fourier transform infrared
HG-AAS = hydride generation atomic absorption spectrometry
ICP-AES = inductively coupled plasma–atomic emission spectroscopy
IDA = iminodiacetic
IX = ion exchange
LDA = lysinediacetic
PHA = polyhydroxamic
q_{eq} = equilibrium metal uptake capacity ($\mathrm{mg\,g^{-1}}$)
SBA = strong base anion
USEPA = United States Environmental Protection Agency
XPS = x-ray photoelectron spectroscopy

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