Arsenic removal from groundwater by ion exchange and adsorption processes: comparison of two different materials
Agostina Chiavola, Emilio D’Amato, Renato Gavasci and Piero Sirini

ABSTRACT
Among the different technologies for reducing arsenic concentration in drinking water, adsorption has demonstrated in many cases to be superior in terms of performance and costs. However, there are numerous types of commercial adsorbents potentially capable of treating arsenic-contaminated groundwater. The present paper compares arsenic uptake efficiency of two different commercial media, one (FerriX™) using mainly the adsorption process, and the other (IRA 400) working as an ion-exchange resin. Firstly, batch studies with artificially contaminated solutions were run to determine the isotherm equations and the theoretical uptake capacity. The following values of the equilibrium coefficients were determined: for IRA 400, using a two-site model $K = 1.749$; for FerriX™, using the Freundlich isotherm model $n_{50} = 3.02$ mg L/g and $k_{50} = 12.07$ mg L/g, and $n_{100} = 2.32$ mg L/g and $k_{100} = 6.75$ mg L/g, for 50 mg L/g and 100 mg/L initial arsenic concentrations, respectively. Then, a series of experiments were carried out on column plants using real contaminated feeding solutions to determine the breakthrough curves. Both media showed very high duration of the cycle run. However, performance of IRA 400 was negatively affected by the presence of interfering ions, such as sulfates, which accelerated the achievement of the breakthrough condition. Instead, FerriX™ removed arsenic for a much higher number of bed volumes than IRA 400, but it was ineffective against the other contaminants of the solution.

Key words | adsorption, arsenic, batch, column, drinking water, ion exchange

INTRODUCTION
Arsenic is a metalloid widely diffused in the environment, as a consequence of either natural or anthropogenic processes. For instance, geothermal activities, dissolution and leaching phenomena occurring in the aquatic environments have led arsenic concentration to significantly rise in some aquifers. Owing to the high toxicity, the World Health Organization recommended reduction of the maximum allowable concentration (MAC) in drinking water to at least 10 μg/L (Viaraghavan et al. 1999). In Italy, the new limit was adopted in 2001.

Many aquifers have shown arsenic contents above this limit, e.g., in Argentina, Bangladesh, Chile, China, Hungary, India (Smedley & Kinniburgh 2002). Also in Italy, arsenic-contaminated groundwaters have been found in some regions (Ergul et al. 2013).

When contamination is due to natural processes, arsenic is mainly present in the inorganic form and with oxidation state $+3$ or $+5$. In the oxidizing environments, such as surface waters, the most common form is the arsenic acid ($\text{H}_3\text{AsO}_4$), which can dissociate into $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ or $\text{AsO}_4^{3-}$. The trivalent form ($\text{H}_3\text{AsO}_3$) is mainly found in reducing environments, such as deep groundwaters, where it can give rise to $\text{H}_3\text{AsO}_5^-$, $\text{HAsO}_3^{2-}$ or $\text{AsO}_3^{3-}$. Distribution of arsenic among the different forms and its toxicity depend on the oxidation–reduction potential as well as the pH value (Sharma & Sohn 2009). In the typical pH range of drinking
water, As(III) is almost totally undissociated, whereas As(V) assumes an ionized form. These characteristics significantly affect the selection of the technology to be used for reducing arsenic content in the drinking water below the MAC level. Among the available techniques, adsorption and ion exchange have been demonstrated to be highly efficient for this purpose; they are often preferred to other technologies also because they are relatively easy to be implemented at the full-scale and operated, and do not affect drinking water quality through the addition of other salts (Choong et al. 2007; Awual et al. 2012). However, their effectiveness strictly depends on the characteristics of the water to be treated and on the arsenic form. Much effort has been spent in the investigation on the best media to be used, and recently new innovative materials with a higher affinity for arsenic have been proposed (Mohan & Pittman 2007). However, much research is required to determine the optimal design parameters and operating conditions which would allow selection of the best materials to be used for the different water qualities.

The aim of the present study was to compare the capability of two different materials to reduce the arsenic content in real drinking water: one media was an ion-exchange resin while the other one was considered a hybrid media, using both the adsorption and the ion-exchange process. First, batch studies were run to determine the isotherm equations of both materials, and their theoretical uptake capacity. Then, a series of experiments were carried out on column plants using highly contaminated solutions to determine the breakthrough curves in both cases.

**METHODS**

**Media**

One of the media used was the anionic strong basic resin Amberlite IRA 400 (Rhom and Haas Company, following IRA 400) supplied in the chloride form. It is made of cross-linked polystyrene with a quaternary ammonium functional groups and a percentage of divinylbenzene (DVB) equal to 8% (total operative ion-exchange capacity equal to 3.8 meq/g). FerriX™ A33E (Purolite, following FerriX™) (790–840 g/L as bulk density, particle size distribution in the 300–1,200 μm range, up to 80 °C as operating temperature) was the other commercial media, used in comparison with IRA 400. It is made by deposition and dispersion of nanoparticles of hydrated iron oxides on a porous support made by an ion-exchange resin in the Cl⁻ form. Both media were rinsed with ultrapure water in order to remove any impurities, dried at 50 °C and then used.

**Solutions**

For the batch tests, synthetic arsenic solutions were used. These were made by dissolving in ultrapure water (from Human Power I, Human Corporation, conductivity below 0.05 μS/cm) selected amounts of AsHNa₂O₄×7H₂O, so as to obtain the desired concentrations of arsenic (i.e., 50 and 100 mg/L).

For the column plant tests, two groundwaters were used to provide the feeding solutions; their main constituents are listed in Table 1. The main difference between these solutions was the sulfate and arsenic contents, both being much higher in solution (2). In particular, sulfate is known to compete with arsenic in the ion-exchange removal process (Chiavola et al. 2012); therefore, the use of solution (2) allowed the investigation of the effect of sulfates on the uptake capability of the tested media. Furthermore, the higher arsenic concentration (about 100 μg/L) represented the upper level usually found in the contaminated groundwaters.

The solutions used for both batch and column tests were always spiked with 0.1 mL/L of H₂O₂ (30% v/v) in order to maintain a positive redox. The value of pH in the solutions was always in the range 7.5–7.8. Therefore, as reported by Smedley & Kinniburgh (2002), arsenic was likely to occur in its dissociated pentavalent form (H₂AsO₄⁻) for the duration of the tests, as needed for the ion-exchange removal process to take place.

**Table 1 | Main components of the feeding solutions of the column plant tests**

<table>
<thead>
<tr>
<th>Component</th>
<th>F⁻ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>NO₃ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>As (mg/L)</th>
<th>pH (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution (1)</td>
<td>2.21</td>
<td>11.66</td>
<td>2.04</td>
<td>4.34</td>
<td>0.02</td>
<td>7.8</td>
</tr>
<tr>
<td>Solution (2)</td>
<td>0.20</td>
<td>5.61</td>
<td>3.51</td>
<td>98.85</td>
<td>0.10</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Analytical methods

Anion concentrations in solution were measured by using the Model 761-IC Ion Chromatography system with a Dual One column (Metrohm). Arsenic analyses were carried out with a 3030B Atomic Absorption Spectrophotometer (Perkin-Elmer, USA), using the hydride method as outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). The instrument quantification limit was 0.2 µg/L. Standard solutions were used for calibration. Results obtained were found to be reproducible within ±3%. pH was continuously monitored during the batch tests by means of a standard probe (Hanna Instruments, HI-8418 model), showing values always in the range 7.5–7.8.

Batch experiments

Isotherm equations were obtained for both materials by means of batch experiments performed in a jar test (Velp Scientifica, Italy), stirred at the constant rate of 120 rpm and maintained at 25 ± °C until equilibrium conditions were reached (24 hours). Solid/liquid ratios in the range 0.05–4 g/L were used to investigate the concentration domain of interest. Samples of the solution and the residual arsenic content. The concentration of the i-th ion on the solid phase, \( q_i \), was computed as follows:

\[
q_i = \frac{(C_0 - C_e)V}{W} \tag{1}
\]

where \( C_0 \) and \( C_e \) are the initial and the equilibrium solution concentrations, respectively, \( V \) is the volume of the solution and \( W \) is the media weight added to the batch. The obtained experimental data were then analyzed using different models depending on the removal process taking place. For instance, the ion-exchange equilibria of IRA 400 were predicted by means of the model proposed by Melis et al. (1995) based on the law of mass action. This model has proven to be the most suitable to represent the ion-exchange process between IRA 400 and arsenic, as described in detail by Chiavola et al. (2014). According to this model, when the resin is heterogeneous and characterized by two different types of functional groups, as in the case of IRA 400, the total resin capacity, \( q_0 \), is given by

\[
q_0 = q_{0,1} + q_{0,2} \tag{2}
\]

where \( q_{0,1} \) and \( q_{0,2} \) refer to the ion-exchange capacity of each type of site on the resin.

Assuming that the functional groups are related to the two copolymers forming the resin skeleton, which are poly(styrene and DVB (Bricio et al. 1998), the distribution of the resin capacity, \( r_j \), between the two active sites is related to the ratio between the ion-exchange capacity of each functional group and the total ion-exchange capacity

\[
\eta_j = \frac{q_{0,i}}{q_0} \tag{3}
\]

with \( j = 1, 2 \) \( r_1 = 1 - r_2 \), \( r_1 = r \), \( r_2 = 1 - r \) and \( r \) being the degree of crosslinking of the resin (percentage of DVB).

The average value of the equilibrium constant of the ion-exchange process is given by

\[
\bar{K} = (K_1)^{r_1}(K_2)^{r_2} \tag{4}
\]

where \( K_1 \) and \( K_2 \) indicate the equilibrium constants of the two types of functional groups.

The best fit was determined based on the average relative error deviation (ARED), which allows calculation of the error deviation between experimental and predicted equilibrium data (\( Y_{i, \text{exp}} \) and \( Y_{i, \text{cal}} \), respectively), as follows:

\[
\text{ARED} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Y_{i, \text{cal}} - Y_{i, \text{exp}}}{Y_{i, \text{exp}}} \right| \times 100 = \frac{1}{n} \sum \delta_i \times 100 \tag{5}
\]

where \( n \) is the number of the experimental data points and \( \delta_i \) is the relative error (Ncibi 2008). The main advantage of the use of \( \delta_i \) is the minimization of the fractional error distribution across the entire concentration range studied.

The results from the batch tests using FerriXTM were analyzed by means of different mathematical models. The best fitting of the experimental data was obtained through
the Freundlich isotherm, whose equation is shown below

\[ q_A = k \cdot (C_A)^{1/n} \] (6)

where \( k \) is the Freundlich adsorption coefficient representing the adsorption capacity, \( n \) is the Freundlich exponent related to the adsorption intensity, \( C_A \) represents the equilibrium concentration of arsenic in solution whereas \( q_A \) is the mass of arsenic on the adsorbent at equilibrium. Goodness-of-fit of the experimental results was made based on the regression coefficient \((R^2)\) value. In Ncibi (2008), the linear approach provided a higher value of \( R^2 \) than the non-linear one in the case of the Freundlich isotherm. Therefore, the linear regression analysis was applied to determine the coefficients \( k \) and \( n \), using the following linearized form of the Freundlich equation

\[ \ln q_A = \ln k + \left(\frac{1}{n}\right) \log C_A \] (7)

Indeed, by plotting \( \log C_A \) versus \( \ln q_A \) it was possible to calculate the values of \( k \) and \( n \) through the intercept and the slope of the fitting straight line, respectively.

**Column plant experiments**

Breakthrough curves were obtained using laboratory-scale column plants, fed using peristaltic pumps with the feeding solutions shown in Table 1. Clean and dry glass columns of 20 cm length and 1.5 cm internal diameter were used, packed with different weights of IRA 400 and FerriXTM, corresponding to different bed volumes (BVs). The columns were continuously fed in a down-flow mode, at a constant flow rate, \( Q \), of 6 mL/min. The resulting empty bed contact time (EBCT = BV/Q) values were: 1.8 and 2.9 minutes for IRA 400 and FerriXTM, respectively, for tests with solution (1), and 2.6 and 4.2 minutes for IRA 400 and FerriXTM, respectively, for tests with solution (2). In the latter case, the EBCT was properly increased to take into account the higher influent loading.

Effluent samples were collected at different time intervals and then analyzed to monitor the contaminant concentration, \( C \), leaving the column. The breakthrough curves were drawn by plotting \( C/C_0 \) versus the throughput volumes measured in terms of multiple-values of BV.

**RESULTS AND DISCUSSION**

**Batch experiments**

Figure 1 shows the isotherm curves determined for (a) IRA 400 and (b) FerriXTM, where points indicate the experimental data and the line graphs are the modeled data. It can be noted that there is a change in the concavity in the isotherm curves of IRA 400 at high ionic fractions for both the tested concentrations, due to the heterogeneity of the functional groups on the resin.

The two-site model used in the present study represented this feature well, providing a rather good fit of the experimental data. Further details can be found in Chiavola et al. (2014), where a comparison with the one-site model is also provided. The values of the equilibrium constants relating to the two different exchange sites on the resin were calculated to be \( K_1 = 0.001 \) and \( K_2 = 3.347 \), respectively, giving an average value equal to \( K = 1.749 \).

A quite good fitting of the experimental data of the adsorption tests was obtained with the Freundlich model: the \( R^2 \) values were equal to 0.958 and to 0.961 for 50 mg/L and 100 mg/L initial arsenic concentration, respectively. The fitting provided the following values of the Freundlich equation constants: \( n_{50} = 3.02 \) mg L/g and \( k_{50} = 12.07 \) mg L/g, and \( n_{100} = 2.32 \) mg L/g and \( k_{100} = 6.75 \) mg L/g, for 50 mg L/g and 100 mg/L initial arsenic concentration, respectively.

**Column experiments**

Figures 2 and 3 show the breakthrough curves of the column plants packed with IRA 400 and FerriXTM, respectively, for the different ions present in feeding solution (1), where MAC represents the maximum allowable arsenic concentration in drinking water, which is current law in Italy.

Figures 4 and 5 show the breakthrough curves of the column plants packed with IRA 400 and FerriXTM, respectively, for the different ions present in feeding solution (2). By comparing Figures 2 and 3 with Figures 4 and 5, for the different feeding solutions, it can be noted that the pattern of each ion for every media remained basically unchanged regardless of the influent contaminant loading. In the case of IRA 400 (Figures 2 and 4), the chloride ions were always immediately released as they were exchanged...
with the other ions having higher affinity with the resin. Sulfates were the most preferred species, as these were the last ones to reach the exhaustion condition (effluent concentration equal to the influent concentration). Nitrate removal was also highly favored. When present, the resin was unable to uptake fluorides. For arsenic, the breakthrough curve showed a chromatographic peak pattern, which refers to the concentration peak occurring in the effluent due to the displacement of the lower-affinity ion (in the present case, arsenic) by the resin when a more affine ion is fed to the column (in this case, sulphates). This leads to the release of the displaced ion in the effluent, where it reaches a much higher concentration than in the influent. In the present study, as clearly showed by Figure 4, arsenic concentration in the effluent rose significantly (by a factor of around 3.5) above the value of the feeding (Ghurye et al. 1999). The limit of 10 μg/L, which is the standard to be respected by drinking water according to the law in force in Italy, was rapidly exceeded (after about 350 BVs and 5,600 BVs, for feeding solutions (1) and (2), respectively), and more quickly as the influent concentration increased. This demonstrated that among the ions contained in the groundwaters, arsenic had the lowest affinity with the selected resin. However, when arsenic was present alone in the solution, the resin duration increased significantly.

The breakthrough curves of the column packed with FerriX™ (Figures 3 and 5) highlighted a different behavior of this media compared to IRA 400. Indeed, for FerriX™ arsenic was the mostly preferred ion and the uptake occurred with continuity: the effluent concentration remained far below the MAC value for a very long time of plant operation. For the other ions, FerriX™ were shown to be unable to
remove sulfates (effluent concentration always matched that in the feeding), whereas nitrate uptake was limited and their concentration in the effluent increased and rapidly reached the exhaustion condition. Chlorides immediately showed a peak in the effluent, with C/C₀ above 1, due to both contributions of chlorides in the feeding solution and chlorides being exchanged between the resin matrix of FerriXTM and both arsenic and nitrates. Then, continuous feeding the column with arsenic, which is the mostly preferred ion, likely prevented a further nitrate uptake and therefore the chloride release. Chlorides remained in the effluent at the same concentration as in the feeding solution, without any removal.

**DISCUSSION**

For the employment of the tested media at the full-scale, it is important to highlight the main advantages and drawbacks of each of these. For IRA 400, regeneration of the exhausted resin is possible and technically feasible; it allows restoration of all or a high percentage of the original exchange capacity, and therefore enables the reuse of the resin for several treatment cycles. The resin is insensitive to pH in the range 6.5–9.0 (EPA 2000a, b). The efficiency of the ion-exchange process is radically improved by pre-oxidation of As(III) to As(V), but the excess of oxidant often needs to be removed before the ion exchange in order to avoid the damage of sensitive resins. The efficiency of the ion-exchange process for As(V) removal depends strongly on the concentration of other anions, most notably sulfates and nitrates. High levels of total dissolved solids (TDS) can also adversely affect its performance. In general, the ion-exchange process is not an economically viable treatment technology if source water contains over 500 mg/L of TDS or over 50 mg/L of sulfate (Jain & Singh 2015). Therefore, the ion-exchange process is particularly suitable when arsenic is the only contaminant.
FerriX™ combines properties of the ion-exchange resin with those of the iron-based adsorbents (granular ferric hydroxide, zero valent iron, iron coated sand). As far as the latter are concerned, the studies conducted have revealed that the affinity of this media for arsenic is very strong and this makes it possible to treat high bed volumes. However, optimal performance is obtained at lower pH values. Therefore, if pH is above the neutral value, a pretreatment of pH conditioning is required. The exhausted iron-based media usually cannot be regenerated; therefore, they need to be disposed of as toxic waste in the proper sanitary landfill (Jain & Singh 2012). Although the very high removal efficiency, cost for FerriX™ purchase is usually higher than those for the iron-based media and the ion-exchange resins.
As far as the other adsorbents is concerned, activated alumina (AA) was the first adsorptive medium to be successfully applied for the removal of arsenic from water supplies (EPA 2000a, b). It is a porous, granular material having good sorption properties. The reported adsorption capacity of AA ranges from 0.003 to 0.112 g of arsenic per gram of AA. The selectivity of AA toward As(III) is poor; therefore, pre-oxidation of As(III) to As(V) is critical. The optimum pH range is 5.5–6.0: greater than 98% arsenic removal can be achieved under these conditions. The arsenic removal capacity of AA is pH sensitive and therefore requires pre- and post-pH adjustment using caustic soda and sulfuric acid. AA is also capable of being chemically regenerated.

Many other adsorbent media have been proposed for arsenic removal: more recently nanostructured metal oxides, such as nanocrystalline titanium dioxide, have also shown to be capable of treating arsenic-contaminated groundwater.

Cost of the media is only a small portion of the cost of the entire treatment plant, which is affected by the size, the composition of the solution to be treated, the duration of the operation before the media reaches exhaustion, and the plant layout (one or more columns, in-series or in parallel). Therefore, a case-by-case technical–economic evaluation is required in order to select the most suitable media as well as the plant configuration.

CONCLUSIONS

Based on the results obtained in the present study, the following conclusions can be drawn:

- batch tests carried out under ideal operating conditions provided the following values of the equilibrium coefficients: for IRA 400, using the two-site model $K = 1.749$; for FerriX™ using the Freundlich isotherm model $n_{50} = 3.02$ mg L/g and $k_{50} = 12.07$ mg L/g, and $n_{100} = 2.32$ mg L/g and $k_{100} = 6.75$ mg L/g, for 50 mg L/g and 100 mg/L initial arsenic concentration, respectively.
- the column plant experiments highlighted the high efficiency of both media.
• performance of IRA 400 was negatively affected by the presence of interfering ions, such as sulfates, which accelerated the achievement of the breakthrough condition.
• FerriXTM removed arsenic for a much higher number of BVs than IRA 400, but it was ineffective against the other contaminants of the solution.

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