The removal of toxic metals from liquid effluents by ion exchange resins. Part VIII: Arsenic(III)/OH−/Dowex 1x8

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ABSTRACT: The removal of the toxic arsenic(III) from aqueous solutions is investigated using the ion exchange technology and the Dowex 1x8 resin. Different experimental variables which may influence the uptake equilibrium are considered: stirring speed of the system, temperature, NaOH concentration in the solution, and resin dosage. The anion exchange equilibrium is endothermic and non-spontaneous, in the 20 °C - 60 °C range of temperatures the metal uptake onto the resin responded to the pseudo-second order kinetic model, however, the loading mechanism is temperature dependent in the 20 °C - 40 °C range. The linear fit of the experimental data showed that the loading isotherm is best explained by the Freundlich model. The results of arsenic(III) uptake in the present system are compared against the metal uptake which one can obtain with other resins and multiwalled carbon nanotubes. Arsenic(III) loaded onto the resin is eluted by the use of 1M HCl solution.

KEYWORDS: Arsenic(III); Dowex 1x8; Liquid effluents; Multiwalled carbon nanotubes; Removal


RESUMEN: La eliminación de metales tóxicos presentes en efluentes líquidos mediante resinas de cambio iónico. Parte VIII: Arsénico(III)/OH−/Dowex 1x8. En el presente trabajo se utiliza la resina de intercambio aniónico para la eliminación de arsénico(III) de medios acuosos. Esta eliminación se ha investigado teniendo en cuenta diversas variables experimentales como son: la velocidad de agitación del sistema, la temperatura, el pH de la disolución y la dosificación de resina al sistema. El equilibrio de intercambio aniónico tiene un carácter endotérmico y no espontáneo, en el rango de temperaturas comprendido entre 20 °C y 60 °C, la cinética del proceso responde al modelo de pseudo-segundo orden, sin embargo, el mecanismo de carga del arsénico en la resina cambia en el rango de temperaturas comprendido entre 20 °C y 40 °C. La isoterma de carga del metal en la resina responde al modelo linealizado de Freundlich. Se comparan los resultados de carga de arsénico en la resina Dowex 1x8 con los obtenidos con otras resinas y con nanotubos de carbono de pared múltiple. La elución del arsénico se puede realizar con disoluciones acídicas, por ejemplo 1 M HCl.

PALABRAS CLAVE: Arsénico(III); Dowex 1x8; Efluentes líquidos; Eliminación; Nanotubos de carbono de pared múltiple

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1. INTRODUCTION

Though it has several industrial uses and even is necessary for life, arsenic is often related to murder (Emsley, 2005). In any case, arsenic is a toxic element and the need of the removal of its compounds from waters is of a paramount importance. Arsenic is present at various oxidation states and in the form of inorganic and organic compounds, thus, the relative toxicity of arsenic compounds depends on:

- i) inorganic or organic forms
- ii) oxidation state
- iii) others

The hazardousness of arsenic compounds is diverse, generally speaking, arsenic compounds can be ranked as:

- i) inorganic arsenic(III)
- ii) organic arsenic(III)
- iii) inorganic arsenic(V)
- iv) organic arsenic(V)

Upon ingesta, arsenic compounds are responsible of different diseases including cancer, being estimated that millions of persons are in the potential risk of arsenic ingesta from waters, even Spain is one of the countries in which arsenic toxicity has occurred from natural source contamination of well water (Hughes et al., 2011; ATSDR, 2013; Flora, 2015; Yousefsani et al., 2017).

From the various separation methodologies, it appears that ion exchange/adsorption is one of the most widely used procedure for arsenic removal from waters (Ahmad et al., 2017; Inaba et al., 2017; Mal’tseva et al., 2017; Roy et al., 2017; Schouwenaars et al., 2017; Sert et al., 2017; Tavakkoli et al., 2017; Babaei et al., 2018; Kang et al., 2018; Liu et al., 2018; Venkatesan and Narayanan, 2018).

Next in the series of articles published in this Journal focusing in the use of ion exchange technology in the removal of toxic metals (Alguacil et al., 2002; Alguacil, 2002; Alguacil, 2003; Alguacil, 2017a; Alguacil, 2017b; Alguacil, 2018a; Alguacil 2018b), the present work uses the anionic exchange resin Dowex 1x8 in the removal of arsenic(III) from aqueous solutions. Several theoretical models were used to fit the experimental data for a better knowledge of the ion exchange process.

2. EXPERIMENTAL

Dowex 1x8 (Fluka) has the characteristics shown in Table 1. Other resins and chemicals used in the investigation are of AR grade. The multiwalled carbon nanotubes (MWCNTs) present the next characteristics: carbon content > 98%, outer diameter: 10 nm ± 1 nm, inner diameter: 4.5 ± 0.5 nm, length: 3–6 μm (Alguacil et al., 2016).

The batch (loading and elution) experiments was carried out in a glass reactor, the mixture aqueous solution-resin was stirred (four blades glass impeller) at 500 rpm and 20 °C, except when these variables were investigated.

Arsenic in solution was analysed by ICP, whereas metal loads in the resin was calculated by the mass balance.

3. RESULTS AND DISCUSSION

3.1. Arsenic uptake onto the resin

To understand the exchange process, a distribution of arsenic species in solution versus pH is generated using the MEDUSA program (Puigdomenech, 2018). This distribution is shown in Fig. 1, from pH 0 to pH near 9.5, the neutral specimen As(OH)$_3$ or H$_3$AsO$_3$ is predominant, whereas the anionic As(III) species become progressively dominant from pH 9.5 to pH 14. Thus, this alkaline pH range is the one to be investigated when an anionic exchanger, as Dowex 1x8, is used to remove arsenic(III) from aqueous wastes. And the above is corroborated by previous experiments performed with this resin in the pH 1–8 range, resulting in the no-removal of arsenic(III) from the aqueous solutions.

![Figure 1. Distribution of arsenic(III) species with the aqueous pH.](image-url)
Then, at these alkaline pH values, arsenic(III) loads onto the resin via an anion exchange mechanism, such as:

\[
\text{AsO(OH)}_2^- + [\text{R}_4\text{N}^+] \rightleftharpoons \text{R}_4\text{N}^+ \text{AsO(OH)}_2^- + \text{Cl}^- 
\]

where, the subscripts s and r refer to the aqueous solution and resin phases, respectively, and ]- to the non-reactive matrix of the resin.

In these batch experiments, the investigations about the influence of the stirring speed on metal uptake in these ion exchange/adsorption systems are of a paramount importance, because, with this parameter one can find a minimum in the thickness of the aqueous film and thus a maximum in metal uptake onto the resin/adsorbent is reached. The experiments are carried out using aqueous solutions of 0.01 g·L\(^{-1}\) As(III) at pH 12 and resin doses of 10 g·L\(^{-1}\). The stirring speed of the system is varied between 250 and 1200 rpm. The results from these experiments are shown in Table 2. It can be seen that the metal uptake reaches a maximum at 500 rpm, and then decreases, this is probably due to local equilibria between the solution and the resin particles which decrease the corresponding arsenic uptake. The experimental data also indicated that 3 hours are time enough to achieve equilibrium.

The influence of the temperature on arsenic(III) uptake onto the resin is next investigated using the same aqueous solution and resin dosage than above. The results from this investigation are shown in Table 3, it can be seen that the metal uptake increases with the temperature indicating an endothermic reaction, with the plot of log D values against the temperature, one can estimate the corresponding values of \(\Delta H^o = 98 \text{kJ·mol}^{-1}\), \(\Delta S^o = 320 \text{J·mol}^{-1} \cdot \text{K}^{-1}\) and \(\Delta G^o = \text{kJ·mol}^{-1}\) for the present system, whereas D, the distribution coefficient of arsenic between the resin and the aqueous solution, is defined as:

\[
D = \frac{[\text{As(III)}]_{r,e}}{[\text{As(III)}]_{s,e}} 
\]

with \([\text{As(III)}]_{r,e}\) and \([\text{As(III)}]_{s,e}\) the arsenic concentrations in the resin and in the solution at equilibrium, respectively.

The above figures suggested that the metal uptake onto the resin is not spontaneous and that the loading process increased its randomness.

In the 20 °C–60 °C temperature range, the experimental data fit well with the pseudo-second order kinetic model (Akartasse \textit{et al.}, 2017):

\[
t = \frac{1}{k[\text{As}]_{r,e}} + \frac{1}{[\text{As}]_{r,e}} t 
\]

with the data shown in Table 4. In the above equation, \([\text{As}]_{r,t}\) and \([\text{As}]_{r,e}\) are the arsenic concentrations in the resin at a time t and at the equilibrium, respectively, t is the elapsed time and k is the rate constant.

Also, it was investigated the probable mechanism from which arsenic(III) was loaded onto the resin, the results from this fit showed that at 20 °C, the particle-diffusion controlled model (López \textit{et al.}, 2014):

\[
\ln(1-F^2) = -kt 
\]

best responded to the experimental data, however in the 40 °C–60 °C range, the experimental

### Table 2. Arsenic(III) uptake at various stirring speeds

<table>
<thead>
<tr>
<th>Stirring speed (rpm)</th>
<th>As(III) uptake (mg·g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.52</td>
</tr>
<tr>
<td>375</td>
<td>0.57</td>
</tr>
<tr>
<td>500</td>
<td>0.62</td>
</tr>
<tr>
<td>750</td>
<td>0.58</td>
</tr>
<tr>
<td>1000</td>
<td>0.50</td>
</tr>
<tr>
<td>1200</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Temperature: 20 °C; Time: 3 h

### Table 3. Arsenic(III) concentrations in the solution and the resin at various temperatures

<table>
<thead>
<tr>
<th>T, °C</th>
<th>[As(III)] (mg·L(^{-1}))</th>
<th>[As(III)] (mg·g(^{-1}))</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.9</td>
<td>0.62</td>
<td>0.16</td>
</tr>
<tr>
<td>40</td>
<td>0.4</td>
<td>0.96</td>
<td>2.4</td>
</tr>
<tr>
<td>60</td>
<td>0.05</td>
<td>0.99</td>
<td>19.8</td>
</tr>
</tbody>
</table>

Aqueous phase: 0.01 g·L\(^{-1}\) As(III) at pH 12; Resin dosage: 10 g·L\(^{-1}\); Time: 3 h

### Table 4. Experimental data fit on the pseudo-second order kinetic model

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>K (g·mg(^{-1})·min(^{-1}))</th>
<th>[As(_{r,e})] (mg·g(^{-1})) model</th>
<th>[As(_{r,e})] (mg·g(^{-1})) experimental</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.35</td>
<td>0.63</td>
<td>0.62</td>
<td>0.9998</td>
</tr>
<tr>
<td>40</td>
<td>0.094</td>
<td>1.0</td>
<td>0.96</td>
<td>0.9955</td>
</tr>
<tr>
<td>60</td>
<td>0.096</td>
<td>1.1</td>
<td>0.99</td>
<td>0.9969</td>
</tr>
</tbody>
</table>
data best fit to the moving-boundary process (López et al., 2014):

$$3 - 3(1 - F)^{2/3} - 2F = kt$$  \hspace{1cm} (5)

the data from this fit are summarized in Table 5. In Eqs. (4) and (5), F is the factorial approach to the equilibrium, calculated as the relation between the arsenic concentration in the resin at an elapsed time and the arsenic concentration in the resin at equilibrium, t is the elapsed time and k is the rate constant of the corresponding model.

The effect of varying the pH of the aqueous solution on arsenic(III) uptake onto the resin is investigated by the use of aqueous solutions of 0.01 g·L⁻¹ As(III) in the 8–14 pH range and resin dosage of 10 g·L⁻¹. The results show (Table 6) that arsenic(III) is loaded onto the resin as the pH of the solution increases from 8 to 11, then remains constant in the 11–12 pH range, and finally falls off to near 12% at pH 14. These results indicate that (Fig. 1), the As(OH)₃ species is not loaded onto the resin, the negatively charged and hydrogen-containing arsenic(III) species are loaded onto the resin and the non-protonated AsO₄³⁻ species is not loaded onto the resin. Taking into account the fraction of each of the arsenic species present in the aqueous solution at pH values of 9–14 (Fig. 1), Table 6 also presented the corrected percentages of arsenic(III) loaded onto the resin (61–62%) is pH-independent in the 9–14 pH range.

Several resin dosages are investigated in order to evaluate their influence on arsenic uptake onto the resin, for these series of experiments aqueous solutions of 0.01 g·L⁻¹ As(III) at pH 12 are put into contact with resin concentrations in the 2.5–50 g·L⁻¹ range. The results of these series of experiments are represented in Fig. 2, it can be seen that the percentage of arsenic loaded onto the resin increases progressively as the resin dosage also increases. From the above experiments, an adsorption isotherm can also be generated by plotting the arsenic concentration in the resin versus the arsenic concentration in the solution at equilibrium, and these data are fitted to the Langmuir or Freundlich adsorption models in their linear forms. The results from this fit showed that the arsenic(III) uptake onto Dowex 1x8 resin was best explained by the Freundlich model (Wang et al., 2017):

$$\ln [\text{As}]_{s,e} = \ln k_F + \frac{1}{n} \ln [\text{As}]_{s,e}$$  \hspace{1cm} (6)

the data from this fit indicated that ln k_F is −1.81, 1/n is 0.97 and r² 0.9831. The Freundlich model proposed that the metal uptake is on a heterogeneous surface of the metal exchanger/adsorbent. In the above equation, [As]_{s,e} and [As]_{s,e} are the arsenic concentrations in the resin and in the solution, respectively, k_F is the Freundlich constant and 1/n is a parameter of the equation.

The performance of the present system is compared against other exchangers/adsorbents by the use of aqueous solutions of 0.01 g·L⁻¹ As(III) at pH 12 and resin dosage of 5 g·L⁻¹. The results from these sets of experiments are summarized in Table 7.

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**Table 5. Influence of the temperature on the mechanism of arsenic uptake onto the resin**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Model</th>
<th>K (min⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>particle-diffusion</td>
<td>0.046</td>
<td>0.9410</td>
</tr>
<tr>
<td>40</td>
<td>moving-boundary</td>
<td>0.010</td>
<td>0.9941</td>
</tr>
<tr>
<td>60</td>
<td>moving-boundary</td>
<td>0.015</td>
<td>0.9974</td>
</tr>
</tbody>
</table>

**Table 6. Influence of the aqueous pH on the percentage of arsenic(III) uptake**

<table>
<thead>
<tr>
<th>pH</th>
<th>% As(III) uptake</th>
<th>% As(III) uptakea</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>9</td>
<td>23</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>53</td>
<td>62</td>
</tr>
<tr>
<td>11</td>
<td>61</td>
<td>61</td>
</tr>
<tr>
<td>12</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>13</td>
<td>52</td>
<td>62</td>
</tr>
<tr>
<td>14</td>
<td>12</td>
<td>61</td>
</tr>
</tbody>
</table>

*aCorrected values taking into account only the fraction of anionic hydrogen-bearing arsenic(III) species in the solution (Fig. 1); Temperature: 20 °C; Time: 3 h*

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**Figure 2.** As(III) uptake at various resin dosages.
It can be seen, that despite of the nature of resins (all quaternary ammonium salts) Ionac SR7, Lewatit MP64 and Amberlite 959, no one of the above load arsenic(III) at any extent, and that in the case of the multiwalled carbon nanotubes this load is extremely low.

3.2. Arsenic(III) elution from the loaded resin

The elution of the arsenic loaded onto the resin is considered by changing the pH of the aqueous solution, thus, 1 M HCl solutions are used as eluent for the system, and the effect of the temperature on the percentage of arsenic released to the aqueous solution is given in Table 8 at various temperatures. It can be seen, that the increase of the temperature increases the percentage of arsenic(III) in the eluate.

Also the effect of the varying relation of volume of aqueous solution to resin weight is investigated. The results of these experiments are shown in Table 9, showing that from the relationship of 20 mL·g⁻¹ the percentage of elution is near constant.

4. CONCLUSIONS

- The hazardous element arsenic(III) can be eliminated from aqueous solutions by the use of Dowex 1x8 resin from alkaline medium. The elimination of the element can be related to an anionic exchange reaction, which is dependent on the stirring speed of the whole system, with best results at 500 rpm, the temperature of the process, being this of an endothermic nature (ΔH° = 98 kJ·mol⁻¹), and the pH of the solution (the resin is only effective from pH 9), but it only removes the arsenic species AsO(OH)₂⁻ and AsO₂(OH)₂⁻ from the solution. In the range of temperatures 20 °C–60 °C, the kinetics of the exchange equilibrium responded well to the pseudo-second order model, but the mechanism is temperature dependent, at 20 °C the data fit to the particle-diffusion model, whereas in the 40 °C–60 °C range the fit is to the moving-boundary model. The arsenic(III) loading onto the resin is best represented by the Freundlich equation.

- Elution of arsenic(III) from loaded Dowex 1x8 resin can be accomplished in hydrochloric acid medium and is temperature dependent, increasing the percentage of arsenic elution from 20 °C to 60 °C (79 to 96% yield, respectively). The arsenic concentration factor reached the value of 4 after a single contact of the arsenic-loaded resin with the eluent.

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REFERENCES


