Ion exchange process in the presence of high sulphate concentration: resin regeneration and spent brine reuse

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Abstract
This paper provides new insights on the regeneration step of an ion exchange process for the treatment of surface and ground water characterized by high sulphate concentration. Repeated regeneration of ion exchange resin with a sodium chloride solution (brine) did not alter the resin performances with respect to the fresh one. Besides, neither the sodium chloride concentration of the brine, which was varied between 1 and 3 M, nor the presence of sulphates at concentrations up to 20 g/L in the brine, did notably affect the regeneration efficiency. The brine was effectively treated by adding calcium or barium chloride, in order to remove the sulphates and re-establish the original chloride concentration. Calcium chloride was allowed to obtain up to 70% sulphate precipitation, whereas an almost 100% precipitation efficiency was obtained when barium chloride was used. The precipitation step was described by a model based on the mass action, coupled to the Bromley model for the description of the non-ideal behaviour of the electrolytic solution. This model was shown to give correct, or at least conservative, estimates of the equilibrium sulphate concentration when either calcium or barium chloride was used as precipitating agent.

Keywords
Brine; ion exchange; regeneration; sulphate

Nomenclature

- $K_{sp}$: solubility product (mol L$^{-1}$)$^2$
- $\gamma_z$: activity coefficient of the generic electrolyte in aqueous solution
- $Z_+$: charge of the generic cation in solution
- $Z_-$: charge of the generic anion in solution
- $I$: ionic strength of the solution (mol L$^{-1}$)
- $B$: coefficient of the Bromley equation

Introduction
Ion exchange has been proposed for the removal of trace anionic contaminants from surface water and groundwater. Namely, its application for arsenic removal has been investigated in great detail (Vagliasindi and Benjamin, 1998, 2001; Viaraghavan et al., 1999). In water supplies, arsenic is generally present in its inorganic form. In surface waters, being an oxidizing environment, the pentavalent form As(V), i.e. arsenic acid H$_3$AsO$_4$ and the arsenate species, prevail. On the contrary, in groundwater, being an anaerobic reducing environment, the trivalent form As(III), i.e. arsenious acid H$_3$AsO$_3$ and the arsenite species, are predominant. At typical pH of natural waters, As(III) is commonly found in the undissociated form, whereas As(V) in the monovalent or divalent ionic form. Since arsenic may be found in, or eventually converted to, the ionic form, ion exchange has already been considered in the literature among the feasible treatment of arsenic contaminated water. One of the main drawbacks to the use of ion exchange...
for arsenic removal from potable water, as well as for the removal of other trace contaminants, is due to the presence of other ions, such as sulphates or nitrates, that can effectively compete with As(V) and other anions for ion exchange sites (Kim et al., 2003). This results in a fast saturation of the ion exchange column, reducing to unacceptable levels the lifetime of the ion exchange column before its regeneration.

Recently, Kim et al. (2003) have proposed a novel process based on advanced ion exchange operation (AIXO), where two ion exchange columns are operated in series. The upstream column is regenerated after the As(V) rich zone has been completely eluted from the upstream column, but long before As appears in the effluent from the downstream column. The regenerated column is then returned to the system in the downstream position and the process is then repeated. Using this configuration, arsenic is accumulated in the system, cycle after cycle. The regeneration step is performed by feeding a sodium chloride solution (brine) to a column saturated by sulphates, whereas the spent brine is recycled after sulphate removal by precipitation obtained by addition of barium or calcium chloride. The precipitation step is one of the key issues of the whole AIXO process.

In order to design it properly, Kim et al. (2003) collected solubility data of both calcium sulphate and barium sulphate systems and modelled them by applying the mass action law, where the activity coefficients were estimated through the Langmuir model. Unfortunately, the agreement between model and experiments was rather poor, thus making the proposed model unfeasible for predictive purposes. The authors suggested that a more comprehensive model for the description of non-idealities in solution was required, but in a following paper (Kim and Benjamin, 2004) still used the same approach for predictive purposes.

In a recent paper, Baciocchi et al. (2005) started a detailed study of the advanced ion exchange process for arsenic removal (AIXO), by investigating the equilibrium behaviour of arsenic in the presence of high sulphate concentrations, i.e. up to 200 mg/L.

This paper reports the results of the activities performed in order to provide a more accurate description of the regeneration step of the ion exchange process, with a specific eye on the recycling of the spent brine. Therefore, as a first step, the regeneration of ion exchange resins was studied. To this aim, ion exchange columns, containing an anionic strong basic resin, were first fed, until breakthrough took place, with water containing high sulphate concentrations, and then regenerated with a sodium chloride solution (brine). There was no need to add arsenic in these experiments, since it is recognized that the resin saturation is regulated only by sulphates. The efficiency of the ion exchange column was then tested after each regeneration cycle; the influence of sodium chloride concentration and the presence of sulphate in the brine on the regeneration efficiency was also investigated. Then, the issue of brine recycle was studied, by adding either calcium or barium chloride to solutions of sodium chloride at different concentrations, and by evaluating the kinetics of either calcium or barium sulphate precipitation. The solubility equilibrium data in each test were also collected and compared with the results provided by application of the mass action law; the activity coefficients needed to describe the non ideal behaviour of the electrolytic solution were estimated through the Bromley model.

**Methods**

**Reagents**

The resin used in this work was an anionic strong basic resin, Amberlite IRA 400, supplied in chloride form and used as received, without any conditioning step. This is a general purpose resin previously applied for arsenic removal studies (Baciocchi et al., 2005).
Column experiments

All experiments were performed on 13 cm length and 15 mm diameter columns, packed with 4.8 g of ion exchange resin.

The breakthrough experiments were performed by feeding the column with 4.8 ml/min solution at 200 g/L sulphate concentration, for an empty bed contact time (EBCT) of 1.46 minutes.

The regeneration experiments were all performed by cocurrent feeding of a sodium chloride solution (brine) again at 4.8 ml/min. The volume of brine fed to the column changed depending on the brine compositions.

Precipitation experiments

Precipitation of sulphate was studied by means of batch experiments performed in 500 ml jar tester, stirred at 100 rpm, on solutions containing 20 g/L sulphate concentration and increasing NaCl concentrations (0–3 M). Sulphates precipitation after calcium chloride addition (equimolar with respect to sulphates) was assessed by sampling after 5, 10, 20, 60 and 120 minutes. The same procedure was used when applying barium chloride, except for sulphate concentration that was set to 2.7 g/L instead of 20 g/L for calcium chloride. This difference is due to the lower value of the barium sulphate solubility product with respect to calcium sulphate.

Modelling of solubility equilibria

The solubility equilibria were described by the following standard mass-action law approach:

\[ K_{sp} = [Ca^{2+}] \cdot [SO_4^{2-}] \gamma^2 \]  
\[ K'_{sp} = [Ba^{2+}] \cdot [SO_4^{2-}] \gamma^2 \]  

where \( \gamma \) is the activity coefficient of the calcium sulphate or barium sulphate electrolyte, that in this work was estimated using the Bromley equation (1973):

\[ \log \gamma_\pm = \frac{1}{Z_+Z_-} \left( -0.511 I^{1/2} + \frac{0.06 + 0.6B}{1 + I^{1/2}} I + \frac{BI}{(1 + 1.5 I^{1/2} I)^2} \right) \]  

where \( Z_+ \) is the charge of the cation (Ca\(^{2+}\) or Ba\(^{2+}\)), \( Z_- \) is the charge of the anion and \( I \) represents the ionic strength of the solution:

\[ I = \frac{1}{2} \sum_i (m_i Z_i^2) \]  

where \( m_i \) is the molarity of the \( i \)th ion.

The following parameter values were used for the system where calcium chloride was added:

\[ B = B_+ + B_- + \delta_+ \delta_- \quad \delta_+ = \delta_{Ca} = 0.0374; \quad \delta_- = \delta_{Ca} = 0.119 \]

\[ B_- = B_{SO_4^{2-}} = 0; \quad \delta_- = \delta_{SO_4^{2-}} = -0.4 \quad K_{sp} = 10^{-4.61} \]

The following parameter values were used for the system where barium chloride was added:

\[ B = B_+ + B_- + \delta_+ \delta_- \quad B_+ = B_{Ba} = 0.0022; \quad \delta_+ = \delta_{Ba} = 0.098 \]

\[ B_- = B_{SO_4^{2-}} = 0; \quad \delta_- = \delta_{SO_4^{2-}} = -0.4 \quad K'_{sp} = 10^{-9.98} \]
Analytical methods
Concentration of all anions was obtained by a Metrohm Ion Chromatography system, equipped with an Anion Dual 1 Metrosep column (3 m length, 150 mm diameter), using an Anion Dual 1 precolumn to determine sulphate concentration in the presence of high chloride concentration. The eluent was a solution of Na₂CO₃ (1.8 mM) and NaHCO₃ (2.4 mM), fed at 0.5 ml/min flowrate. The background conductivity was equal to 16.3 μS/cm. The suppressor module consisted of two peristaltic pumps, feeding a concentrated H₂SO₄ regenerant solution (50 mM) and the rinsing solution (ultrapure water) to the suppressor unit (0.5 ml/min flowrate). Analyses were performed by feeding a 3–4 mL sample volume through the injection system, that was made of a 20 μL injection loop. The method detection limit was found to be 1.0 mg/L for sulphates and 8.0 mg/L for chlorides.

Results and discussion
Ion exchange resin regeneration
The AIXO process, as well as all the ion exchange process, is based on the possibility of using the same resin for several cycles, by performing its regeneration after each use. In this view, assessing the resin performance after each use and regeneration cycle becomes of paramount importance. Figure 1 reports the breakthrough curves of sulphate on a fresh ion exchange resin and on the same resin after one or several regeneration steps performed with a sodium chloride solution. It is worth pointing out that, at least after up to four regenerations, the breakthrough behaviour of the ion exchange columns looks unchanged. Namely, in all tests the sulphate breakthrough takes place always after elution of 550 bed volumes (BV). The regeneration efficiency, calculated as the ratio between the sulphate recovered with the brine after each regeneration step, and those fed to the column, was always near to an average 90% value.

Figure 2 reports the behaviour of the regeneration efficiency obtained with a 3 M NaCl brine containing increasing concentrations of sulphates, up to 20 g/L. It is worth pointing out that even the highest tested sulphate concentrations did not show any effect on the regeneration
efficiency. As far as the effect of NaCl concentration is concerned, it is worth pointing out that using a 1 M NaCl solution caused just a 1% reduction in the regeneration efficiency. In all experiments, the NaCl concentration in the brine after regeneration was reduced by 0.06 M, regardless of the initial concentration used in the brine.

Removal of sulphates by precipitation

After some regeneration cycles, the brine becomes too rich in sulphate and/or too poor in chlorides to be still effective for a proper resin regeneration to take place. At this point, the brine has to be treated in order to precipitate the excess sulphates and to increase the chloride concentration to the starting values. As already discussed above, this is obtained by adding a chloride salt of either calcium or barium, which can precipitate as calcium or barium sulphate, respectively. The result of the precipitation experiments, shown in Table 1, clearly indicate that more than 50% of the sulphate initially present is precipitated within a few minutes, whereas equilibrium is apparently met in less than two hours. The experimental sulphate concentrations achieved after two hours are also compared in Table 1 with the theoretical results obtained by application of the mass action model, coupled with the Bromley equation for the activity coefficients, outlined above. The model predicts an increasing value of the residual sulphate concentration for increasing ionic strength of the solution, i.e. for increasing background chloride concentration. The experimental data do only in part confirm this behaviour, and the quantitative agreement with the model predictions is quite poor. Namely, the model underestimates the equilibrium sulphate concentrations at low ionic strength, but overestimates them at higher ionic strength.

Table 2 reports the results of the precipitation experiments, obtained after two hours, and the model predictions, in terms of sulphate removal efficiency. These data more clearly show that the model fairly well predicts the system behaviour for low to medium ionic strengths, whereas it completely fails to describe the system behaviour for high ionic strengths. This suggests that the Bromley model is somehow not suitable for proper

Table 1 Residual sulphate concentration after addition of calcium chloride. Initial sulphate concentration: 20 g/L. Initial equimolar ratio between sulphate and calcium chloride

<table>
<thead>
<tr>
<th>Cl⁻</th>
<th>Residual sulphate concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 min.</td>
</tr>
<tr>
<td>0 M</td>
<td>8.4</td>
</tr>
<tr>
<td>0.5 M</td>
<td>10.52</td>
</tr>
<tr>
<td>1 M</td>
<td>10.38</td>
</tr>
<tr>
<td>2 M</td>
<td>7.54</td>
</tr>
<tr>
<td>3 M</td>
<td>7.02</td>
</tr>
</tbody>
</table>
use describing the non ideal behaviour of this electrolyte solution at high ionic strengths. These results qualitatively confirm those reported by Kim et al. (2003), where a poor correlation between model predictions and experimental data was observed, even though a different model for activity coefficients was used.

As far as the sulphate precipitation experiments with barium chloride are concerned, the removal efficiency was in this case very high, so that the sulphate concentration always showed a three-fold reduction. For this reason, the experimental results were reported in Table 3 just in terms of sulphate removal efficiency, and here compared with the model estimates. It is worth pointing out that in this case, both experimental data and model estimates were all very near, but basically all data indicated an almost complete removal of sulphates from the brine.

Conclusions

The results reported in this work suggest that even after repeated regeneration, the properties of the ion exchange resin, used for treating water containing high sulphate concentrations, remain very near to those of the fresh one. Within the experimental range tested, neither sodium chloride concentration of the brine nor the presence of sulphate in the brine did notably affect the regeneration efficiency. When required, the brine used for regeneration was effectively treated by adding precipitating agents, in order to remove the sulphates and re-establish the original chloride concentration. Two precipitating agents, calcium and barium chloride, were tested and compared. The former enabled obtaining up to 70% sulphate precipitation. A gypsum sludge is in this case obtained, which can be used for concrete production. An almost 100% precipitation efficiency was observed when calcium chloride was used, but the sludge in this case needs to be treated for barium extraction and its density is higher than that of gypsum, so that also the disposal costs are higher. In view of building a model for the description of the different steps of an ion exchange process, the precipitation step was described by a model based on the mass action law, coupled to the Bromley model for the description of the non-ideal behaviour of the electrolytic solution. This model was shown to give correct or at least conservative estimates of the sulphate concentration when either calcium or barium chloride was used as precipitating agent.

Table 2 Sulphate removal efficiency after addition of calcium chloride: experimental results and model estimates. Experimental conditions: see Table 1 caption

<table>
<thead>
<tr>
<th>NaCl (M)</th>
<th>Experimental removal efficiency (%)</th>
<th>Estimated removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.74–99.85</td>
<td>99.96</td>
</tr>
<tr>
<td>0.5</td>
<td>99.9–99.95</td>
<td>99.73</td>
</tr>
<tr>
<td>1</td>
<td>99.49–99.8</td>
<td>99.55</td>
</tr>
<tr>
<td>2</td>
<td>99.73–99.83</td>
<td>99.01</td>
</tr>
<tr>
<td>3</td>
<td>99.35–99.52</td>
<td>98.41</td>
</tr>
</tbody>
</table>

Table 3 Sulphate removal efficiency after addition of barium chloride: experimental results and model estimates. Experimental conditions: Initial sulphate concentration: 2.7 g/L. Initial equimolar ratio between sulphate and barium chloride

<table>
<thead>
<tr>
<th>NaCl (M)</th>
<th>Experimental removal efficiency (%)</th>
<th>Estimated removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80–81</td>
<td>93.05</td>
</tr>
<tr>
<td>0.5</td>
<td>75.5–78.5</td>
<td>82.10</td>
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<tr>
<td>1</td>
<td>71.5–72</td>
<td>75.30</td>
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<tr>
<td>2</td>
<td>67.5–73</td>
<td>61.40</td>
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<tr>
<td>3</td>
<td>70.5–71.5</td>
<td>46.05</td>
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References


