Modeling a novel ion exchange process for arsenic and nitrate removal

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Abstract

Arsenate and nitrate can be removed quantitatively from drinking water by anion exchange. However, if the raw water contains substantial concentrations of sulfate or nitrate, the resin becomes exhausted quickly, and the requirements for regenerant (brine) can make the process unattractive. Previously, we described a modified ion exchange operating procedure for arsenic removal from solutions containing sulfate that could overcome this problem. This paper extends that work to solutions containing nitrate, and presents a mathematical model for the process.

The selectivity coefficient for sulfate over nitrate of a strong base anion exchange resin increased dramatically with increasing ionic strength, partially counteracting the decrease in \( \text{SO}_4/\text{NO}_3 \) separation factor predicted from mass action considerations. The value of this selectivity coefficient in different solutions can be used in conjunction with mass balances and solid/liquid equilibrium considerations to explore the brine requirement when the modified treatment process is applied to influent waters with various compositions.

The modeling results indicate that, for relatively low influent nitrate concentrations, the volume of water treated per unit volume of brine used can be increased greatly by using the modified ion exchange process. At higher influent nitrate concentrations, the modified process remains advantageous, but is less so. The use of separate brine solutions to regenerate the upstream and downstream columns magnifies the benefits of the modified process significantly. If the sulfate in the brine is precipitated as \( \text{CaSO}_4(s) \) rather than \( \text{BaSO}_4(s) \), the brine usage rate increases by only 30–40%, even though the former solid is orders of magnitude more soluble than the latter.

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1. Introduction

Anion exchange is an attractive technology for removing arsenate from drinking water and is the preferred technology for removing nitrate, because of its ability to remove these ions almost quantitatively from solution, the insensitivity of the process to solution pH, and the long effective lifetime of the resins [1]. However, the economics of the process are very sensitive to the concentration of competing ions in the solution [2]. In particular, at the concentrations present in many water supply sources, sulfate occupies the majority of the binding sites on such resins and thereby decreases the volume of influent that can be treated before regeneration is required; in cases where arsenate is the target contaminant, nitrate can also be an important competing species [3]. In addition to the loss of production during regeneration, the costs of brine preparation and disposal diminish the attractiveness of ion exchange if the competing ions are present at high concentrations.

In prior work [4,5], we described a treatment process for arsenate in which two ion exchange columns are used in series and, in each cycle, the arsenate
chromatographic peak is allowed to pass entirely into the downstream column before the upstream column is regenerated. The regenerated column is then returned to the treatment train in the downstream position. In this way, virtually all the arsenate entering the system is retained within the columns for long periods of time. When the process was tested using a laboratory-scale treatment system fed an influent containing 40 \( \mu \text{g/L} \) As(V) and 80 mg/L SO\(_4\), the effluent As(V) concentration was typically <1 \( \mu \text{g/L} \), and a negligible fraction of the sorbed As(V) was released during column regeneration in tests treating >36,000 bed volumes (BV) of water. That work also demonstrated that sulfate could be removed from the regenerant brine by precipitation of either BaSO\(_4\)(s) or CaSO\(_4\)(s), so that the brine could be reused numerous times. A similar process for removing sulfate from regenerant brines has been described by Bae et al. [6].

In the prior research, sulfate was the only competing anion that was considered. If nitrate is the target contaminant, or if it is a significant competitor for binding sites when the target is As(V), removing it from the brine could also dramatically decrease the requirement for preparing fresh brine and disposing exhausted brine. Prior researchers [7–9] have focused on biological denitrification as the approach most likely to accomplish this goal. Unfortunately, the reliance on halophilic organisms and the need to provide a biodegradable carbon source and to separate the organisms from the water before the brine can be reused all complicate such a process.

The current research comprised experiments and modeling that explored the effect of nitrate on the modified ion exchange process studied previously, focusing on approaches that might allow the regenerant brine to be used more efficiently without removing nitrate from it.

2. Materials and Methods

2.1. Preparation and use of the ion exchange columns

A sulfate-selective, strong base anion exchange resin (ASB-1, Sybron Chemicals, Inc., Birmingham, NJ) was used in these studies. Before use, the resin was soaked in 3 M NaCl, rinsed with deionized water, and packed to a nominal volume of 10 mL in a 20-mL polypropylene column.

The breakthrough of sulfate, nitrate, and arsenate from the column was first evaluated for influents with three different compositions (Rows 1–3 in Table 1). The system was operated at room temperature with a feed rate of 2.65 mL/min, corresponding to an empty bed contact time (EBCT) of 3.77 min, until complete breakthrough of all three ions had occurred.

The resin was regenerated with 200 mL of fresh 3 M NaCl after each treatment cycle. One-half of the regenerant solution (100 mL) was circulated through the column for 20 min. The remaining half of the solution was then passed through the column without recirculation, and the two portions of regenerant solution were combined. The EBCT was 3.77 min in both steps. In one experiment, the column was regenerated without a recirculation step (i.e., all the regenerant solution was passed through the column only once). In this test, samples of the solution exiting the column were collected, and the composition of the solution was analyzed as a function of the volume of regenerant used.

The resin regeneration efficiency was assessed as a function of the sulfate and nitrate concentrations in the brine. In these experiments, the influent contained 6000 mg/L SO\(_4\) and 2325 mg/L NO\(_3\) (Row 4 in Table 1). The regeneration protocol after the first cycle was identical to that in the experiments described above. The effect of an additional regeneration cycle on the brine composition was then simulated by adding predetermined amounts of sulfate and nitrate to the solution, which was then used to regenerate the column after the next loading cycle. This procedure was repeated after all subsequent regeneration steps. Thus, between any two real regeneration steps, the composition of the regenerant solution changed twice—once when it was used to regenerate a column that had been loaded with influent solution, and again when sulfate and nitrate were added in a simulated regeneration step. The real regeneration step increased the sulfate and nitrate concentrations in the regenerant, and reduced the chloride concentration, whereas the simulated one increased the sulfate and

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>SO(_4^{2-})</th>
<th>NO(_3^-)</th>
<th>As(V)</th>
<th>pH</th>
<th>Ionic strength (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>meq/L</td>
<td>mg/L</td>
<td>meq/L</td>
<td>µg/L</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>1.67</td>
<td>60</td>
<td>0.97</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>1.67</td>
<td>60</td>
<td>0.97</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>125</td>
<td>2.60</td>
<td>29</td>
<td>0.46</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>6000</td>
<td>125.00</td>
<td>2325</td>
<td>37.50</td>
<td>0</td>
</tr>
</tbody>
</table>
nitrate concentrations but did not alter the chloride concentration.

Whenever the regenerant solution contained > 20 g/L SO$_4$, it was dosed with CaCl$_2$ to precipitate CaSO$_4$(s), and filtered (0.45 μm). Sulfate and nitrate were analyzed after each regeneration cycle and each CaCl$_2$ addition.

2.2. Analysis of water and brine quality

Arsenate was analyzed using an inductively coupled argon plasma (ICP) atomic emission spectrophotometer (Jobin Yvon, Model 138 Ultrace, Edison, NJ). Each 6-mL sample was dosed immediately after collection with 25 μL of 5% sodium hypochlorite and 25 μL of concentrated nitric acid. The sample was mixed on-line with 1.0% sodium hydride (Integra) in 1 M NaOH before injection into the ICP torch.

Sulfate, nitrate, and chloride were analyzed using ion chromatography (Model DX-500, Dionex Corporation, Sunnyvale, CA). When sulfate and nitrate were analyzed in solutions containing a high concentration of chloride, the chloride was removed upstream of the chromatographic column by an OnGuard II-Ag cartridge filter (Dionex).

3. Results and discussion

3.1. Anion breakthrough during resin loading and regeneration

Breakthrough curves for sulfate, nitrate, and arsenate for a run using the influent composition listed in Row 3 of Table 1 are shown in Fig. 1; breakthrough patterns for the feed compositions shown in Rows 1 and 2 were similar. Sulfate was preferentially bound to the resin compared to nitrate and arsenate, leading to chromatographic peaking of both of the latter two ions.

The preference for sulfate over nitrate was reversed when the solution contacting the resin contained a high concentration of chloride. As a result, during the one-pass regeneration of an exhausted column, the sulfate concentration peaked and declined to near zero well before the nitrate peak did (Fig. 2).

3.2. Resin regeneration and management of brine composition

Fig. 3 shows the concentrations of sulfate and nitrate in the brine over 20 real and 20 simulated regeneration cycles. CaCl$_2$ was added to precipitate SO$_4$ after the 11th, 18th, 27th, and 36th cycles. Some CaSO$_4$(s) also precipitated after the 15th, 22nd, 30th, and 38th cycles, due to the increase in the sulfate concentration during regeneration and the presence of residual calcium in the regenerant solution. The SO$_4$ concentration in the brine declined after each of these precipitation events.
However, the nitrate concentration increased steadily throughout the test.

Fig. 4 shows the regeneration efficiencies for sulfate and nitrate, defined as in Eq. (1), as a function of brine composition

\[
\eta_X = 1 - \frac{[RX]_{\text{regenerated resin}}}{[RX]_{\text{exhausted resin}}},
\]

where \([RX]\) is the mass of species \(X\) bound to the resin. The progression from lower to higher nitrate concentrations (and higher to lower \(\eta_{\text{NO}_3}\)) in Fig. 4 represents a steady sequence in time and in the number of regeneration steps carried out with the same batch of brine solution. On the other hand, the sulfate data are not sequential—the data points at lower sulfate concentration (and lower \(\eta_{\text{SO}_4}\)) correspond to regeneration cycles shortly after a \(\text{CaSO}_4(s)\) precipitation event, and those at higher sulfate concentration (and lower \(\eta_{\text{SO}_4}\)) correspond to cycles just before a precipitation event.

The regeneration efficiency for sulfate (\(\eta_{\text{SO}_4}\)) could be modeled as a linear function of the sulfate concentration in the regenerant solution over the full-range of concentrations explored. Furthermore, by maintaining the sulfate concentration in the brine below 20 g/L (0.42 equiv/L), \(\eta_{\text{SO}_4}\) was kept above 72% in all experiments.

Up to a concentration of \(\sim 0.18\) equiv/L (11 g NO\(_3\)/L), the plot of \(\eta_{\text{NO}_3}\) vs. nitrate concentration is also linear. However, \(\eta_{\text{NO}_3}\) was more sensitive to nitrate concentration than \(\eta_{\text{SO}_4}\) was to sulfate concentration, as indicated by the steeper decline of the nitrate line in the figure. At nitrate concentrations \(\geq 0.18\) equiv/L, \(\eta_{\text{NO}_3}\) demonstrated a good deal of scatter, but was poor in all cases (15–40%). The direction of the scatter was not correlated with the sulfate concentration and so apparently does not reflect the impact of sulfate concentration on \(\eta_{\text{NO}_3}\).

3. Equilibrium partitioning of ions between solution and the resin

The experiments described above generated data describing the equilibrium partitioning of sulfate and nitrate between solution and the resin in three very different ranges of water quality—Rows 1–3 in Table 1, Row 4 in Table 1, and the regeneration experiments. In theory, the equilibrium between \(\text{SO}_4\) and \(\text{NO}_3\) in all these solutions can be characterized by the single equilibrium reaction and expression shown below.

\[
\text{R}_2(\text{NO}_3)_2 + \text{SO}_4^{2-} \rightleftharpoons \text{R}_2\text{SO}_4 + 2\text{NO}_3^{-}
\]

\[
K_{\text{eq,SO}_4/\text{NO}_3} = \frac{a_{\text{R}_2\text{SO}_4}a_{\text{NO}_3}^2}{a_{\text{R}_2(\text{NO}_3)_2}a_{\text{SO}_4}},
\]

where \(a_i\) is the chemical activity of species \(i\).

The pair of adsorbed \(\text{NO}_3\) ions participating in reaction (2) is shown as \(\text{R}_2(\text{NO}_3)_2\) rather than as two independent \(\text{RNO}_3\) groups, because the two \(\text{RNO}_3\) groups must be adjacent to one another (and not any two \(\text{RNO}_3\) surface groups) to serve as a reactant. Nevertheless, if the resin sites are assumed to be identical and uniformly distributed, \(a_{\text{R}_2(\text{NO}_3)_2}\) is approximately proportional to \(a_{\text{RNO}_3}^2\) over a wide range of surface compositions, i.e. \(a_{\text{R}_2(\text{NO}_3)_2} \equiv k_1a_{\text{RNO}_3}^2\) [10]. Therefore, if the proportionality constant \(k_1\) is combined with the equilibrium constant for reaction (2), an apparent equilibrium constant can be defined that has the same form as if the reaction involved two independent \(\text{RNO}_3\) groups, i.e.

\[
K_{\text{eq,SO}_4/\text{NO}_3}^* = k_1K_{\text{eq,SO}_4/\text{NO}_3} = \frac{a_{\text{R}_2\text{SO}_4}a_{\text{NO}_3}^2}{a_{\text{R}_2(\text{NO}_3)_2}a_{\text{SO}_4}} = \frac{\gamma_{\text{R}_2\text{SO}_4}\gamma_{\text{NO}_3}^2}{\gamma_{\text{R}_2(\text{NO}_3)_2}\gamma_{\text{SO}_4}^2}
\]

where \(\gamma_i\), \(q_i\), and \(c_i\) are, respectively, the activity coefficient, adsorption density, and concentration of species \(i\). Because the activity coefficients of the surface species are impossible to predict, a simplifying assumption is commonly made that the ratio of activity coefficients in Eq. (4) is constant over the range of experimental conditions. With this assumption, the activity coefficients can be combined with \(K_{\text{eq,SO}_4/\text{NO}_3}^*\) to yield a conditional equilibrium constant that is commonly referred to as the selectivity coefficient, \(K_{\text{sel,SO}_4/\text{NO}_3}\)

\[
K_{\text{sel,SO}_4/\text{NO}_3} = \frac{\gamma_{\text{R}_2\text{SO}_4}\gamma_{\text{NO}_3}^2}{\gamma_{\text{R}_2(\text{NO}_3)_2}\gamma_{\text{SO}_4}^2} \frac{q_{\text{R}_2\text{SO}_4}c_{\text{NO}_3}^2}{q_{\text{R}_2(\text{NO}_3)_2}c_{\text{SO}_4}},
\]

\(K_{\text{sel,SO}_4/\text{NO}_3}\) is reported using a wide range of units for the various terms; the values reported here are for \(q\) and \(c\).
expressed in equiv/g and equiv/L, respectively. Note that, unlike \( K_{SelS/N} \), \( K_{SelS/N} \) can vary with ionic strength and other factors related to the composition of the solution.

Rearranging Eq. (5), we obtain

\[
\frac{q_{R,SO_4}}{q_{R,NO_3}} = K_{SelS/N} \frac{c_{SO_4}}{c_{NO_3}^2}
\]  \hspace{1cm} (6)

According to Eq. (6), \( K_{SelS/N} \) can be evaluated from experimental data as the slope of a plot of \( q_{R,SO_4}/q_{R,NO_3} \) vs. \( c_{SO_4}/c_{NO_3}^2 \), for systems that have reached equilibrium. Such a plot, showing the data from all of the regeneration experiments and most of the experiments in which high concentrations of sulfate and nitrate were used to load the resin, is shown in Fig. 5. (Data from four systems at very high values of \( c_{SO_4}/c_{NO_3}^2 \) and \( q_{R,SO_4}/q_{R,NO_3} \) are excluded from Fig. 5, so that the data at lower values can be seen clearly on a single graph. The results from all the systems are included in Fig. 6, which is described below.)

The upper line in Fig. 5 demonstrates that the equilibrium partitioning of sulfate and nitrate between the resin and solution in the regenerant solutions can be described with good precision by a single selectivity coefficient. The solutions included in this correlation spanned a large range of sulfate and nitrate concentrations (51–347 meq/L and 40–318 meq/L, respectively), but their ionic composition was dominated in all cases by chloride. The straight line providing the best fit to the data in the figure yields a value of \( K_{SelS/N} = 83 \) g/L

\( (R^2 = 0.98) \). The nature of this fitting operation gives extra weight to the data points at high values of \( c_{SO_4}/c_{NO_3}^2 \) and \( q_{R,SO_4}/q_{R,NO_3} \); if each data point is weighted equally (by computing \( K_{SelS/N} \) from each experiment and then averaging the values), the value is 118 g/L. The lower line in the figure indicates that systems in which the high sulfate, high nitrate influent was equilibrated with the resin also could be character-

ized by a reasonably precise, but lower value of \( K_{SelS/N} \) (approximately 20.6 g/L, \( R^2 = 0.97) \).

Computed values of \( K_{SelS/N} \) from all experiments are shown as a function of the solution ionic strength in Fig. 6. This figure demonstrates that, although the experiments at any given ionic strength yielded a reasonably precise value for \( K_{SelS/N} \), the \( K_{SelS/N} \) values at different ionic strengths differed dramatically. Overall, \( K_{SelS/N} \) increased by more than 1.5 orders of magnitude when the ionic strength increased from \( \sim 0.003 \) M (in the simulated drinking water) to \( \sim 3.0 \) M (in the regenerant solutions).

It is important to recognize that this trend is independent of the well established decrease in the \( SO_4/NO_3 \) separation factor, \( 2_{SN}(\equiv (q_{SO_4}/c_{SO_4})/(q_{NO_3}/c_{NO_3})) \) when the concentration of an adsorbable, monovalent ion is increased [11]. In fact, the trend reported here partially counters that effect. That is, even though the separation factor for the systems investigated declined with increasing ionic strength (as indicated by the selectivity reversal in the regenerant solutions, per Fig. 2), the decline was less than it would be if \( K_{SelS/N} \) were constant.

3.4. Development of a model for the treatment process

The values of \( K_{Sel} \) derived from the experimental data were used in conjunction with \( K_{sp} \) values for \( BaSO_4(s) \) and \( CaSO_4(s) \) to model treatment of solutions containing sulfate, nitrate, and arsenate via the two-column ion exchange process described in a prior publication [5]. That treatment process can be represented as a sequence of three steps: feeding the influent to the upstream column until complete breakthrough of sulfate (and, therefore, of nitrate and arsenate as well), regenerating the upstream column, and removing sulfate intermittently from the brine by precipitating \( CaSO_4(s) \) or \( BaSO_4(s) \). Assuming that equilibrium is closely approached in each of these steps, each can be modeled...
using a conditional equilibrium constant to characterize the state of the system when the step has been completed.

For instance, at the end of the treatment step, the resin can be assumed to be in equilibrium with the influent. Because the influent arsenate concentration is typically orders of magnitude lower than that of the other ions, it occupies a negligible fraction of the resin sites at equilibrium, so the composition of the resin phase can be computed using only a site balance and the appropriate value of $K_{\text{eq},S/N}$. In this case, the appropriate $K_{\text{eq},S/N}$ value is the one for a low ionic strength solution, i.e., $K_{\text{eq},S/N} = 2.7 \text{g/L} (=10^{-5.42})$.

During regeneration, the resin equilibrates with a high ionic strength solution, so the appropriate value of $K_{\text{eq},S/N}$ for modeling that step is 118 g/L. The equilibrium condition in the regenerated column can be defined by a site balance, the composition of the regenerant solution, $K_{\text{eq},S/N}$, and either $K_{\text{eq},S/Cl}$ or $K_{\text{eq},S/Ci}$, which can be estimated from the data in Fig. 4.

Finally, if BaCl$_2$ or CaCl$_2$ is added to the regenerant, the reduction in the concentration of sulfate in the solution can be calculated based on the initial sulfate concentration, the BaCl$_2$ or CaCl$_2$ dose, and the solubility product ($K_{\text{sp}}$) for the solid that precipitates.

The modeling approach described above was implemented to simulate treatment of waters containing 25–200 mg/L SO$_4$ and 0–45 mg/L NO$_3$ (0–10 mg/L NO$_3$–N), using either BaCl$_2$ or CaCl$_2$ as the precipitant for sulfate. $K_{\text{sp}}$ values of $10^{-9.96}$ and $10^{-4.96}$ were used for BaSO$_4(s)$ and CaSO$_4(s)$, respectively, based on the results of our previous study. Based on that same study, the resin was assigned a capacity of 1.28 equiv/L of packed bed. All of the equations and parameter values used in the modeling are summarized in Table 2.

For the first cycle, the simulation assumed that influent would be supplied to the column until the amount of sulfate that entered the system was sufficient to occupy all the resin sites in the upstream column and 25% of those in the downstream column. The composition of the resin in the upstream column was then computed, assuming that it had reached equilibrium with the influent. Next, regeneration of the upstream column with 3 M NaCl was simulated. The mass of sulfate and nitrate entering the brine during this step was calculated by assuming that, by the end of this step, the resin had equilibrated with fresh 3 M NaCl. Finally, a sulfate precipitation step was simulated, based on addition of BaCl$_2$ or CaCl$_2$ to the regenerant at a molar concentration equal to that of sulfate.

During the regeneration step, one equivalent of Cl is expected to be removed from the brine for each equivalent of SO$_4$ or NO$_3$ that is released from the resin. The addition of BaCl$_2$ or CaCl$_2$ would then return an amount of Cl to the brine equal to the amount that had been removed in exchange for SO$_4$ on the resin. However, the amount of Cl used to exchange for NO$_3$ during the regeneration process would not be replenished by BaCl$_2$ or CaCl$_2$ addition, so, in the simulations, one equivalent of NaCl was added to the brine per equivalent of NO$_3$ removed after each regeneration step, thereby maintaining the Cl concentration at 3 M in all cycles.

After the first regeneration step, a second treatment cycle was simulated, with the influent fed to the column that had been downstream during the first cycle. At the beginning of this cycle, approximately 25% of the resin sites in this column were already occupied by sulfate, and some were occupied by nitrate. The duration of the second treatment step was chosen such that the total load of sulfate applied equaled the exchange capacity in one column. As a result, the upstream column had the same composition after the second loading step as after the first, i.e., it was in equilibrium with the influent. However, the regeneration steps after these two cycles were not identical, because, at the beginning of the regeneration step for the second cycle, the regenerant already contained some sulfate and nitrate (acquired during the first regeneration step). The regeneration efficiencies for both SO$_4$ and NO$_3$ were therefore lower after the second cycle than after the first, i.e., some sulfate and nitrate remained in the regenerated column after the second regeneration cycle.

The regenerant composition after the second regeneration step was determined based on mass balance considerations, and another sulfate precipitation step was simulated, again using a BaCl$_2$ or CaCl$_2$ dose equimolar to the sulfate concentration. Thereafter, several more treatment, regeneration, and precipitation cycles were simulated in a similar fashion, with the number of bed volumes fed during the column exhaustion step always the same as in the second cycle, i.e., enough so that the sulfate entering the system was equivalent to the exchange capacity of the resin in one column.

Because nitrate was never removed from the regenerant solution, its concentration in the regenerant increased steadily, as did the mass of nitrate remaining on the resin after regeneration. The sulfate concentration in the regenerant was constant from cycle to cycle, due to the combined constraints of equilibrium with BaSO$_4(s)$ or CaSO$_4(s)$ and the assumption of equimolar dosing of CaCl$_2$ or BaCl$_2$ with SO$_4$. The steady increase in resin-bound nitrate at the beginning of sequential treatment steps caused the sulfate and nitrate wave fronts to move steadily deeper into the downstream column as the simulation progressed.

If a treatment process such as the simulated one were implemented, the operation would have to be halted when the arsenate wave front, which precedes those of sulfate and nitrate, approached the exit of the
downstream column. At that time, the downstream column would have to be regenerated to prevent the target contaminant (either nitrate or arsenate) from entering the distribution system at unacceptable concentrations. Therefore, when arsenate, sulfate, and nitrate were predicted to occupy 70% of the resin sites in the downstream column, a simulated regeneration of both columns (rather than just the upstream column) was carried out.

Two options were explored for regeneration of the downstream column: use of the same solution as was used to regenerate the upstream column, and use of a separate solution. The latter approach was explored because the downstream column was expected to be highly and selectively loaded with nitrate. If the same solution were used to regenerate both columns, it would acquire a large dose of NO₃ each time the downstream column was regenerated, and that NO₃ could then interfere with regeneration of the upstream column in the subsequent cycle. By using separate solutions to regenerate the two columns, the nitrate concentration in the regenerant used for the upstream column would be minimized, thereby extending the useful life of that solution.
After the two columns were regenerated, the simulation continued as before. Eventually, the accumulation of nitrate in the regenerant solution(s) would cause the regeneration efficiency to deteriorate to the point that the brine would have to be disposed of. In the modeling, the criterion for brine disposal was that the resin regeneration efficiency decreased to <50%. The number of bed volumes treated to that point was the prime basis for comparison of the various runs.

3.5. Model results

The model results for an influent containing 80 mg/L SO₄ and various nitrate concentrations are shown in Fig. 7. The baseline for comparison was a conventional ion exchange process with no brine recycle and hence no sulfate precipitation. For that case, it was assumed that the resin exhaustion step would continue until sulfate and nitrate occupied 90% of the resin sites, and that 3 BVs of brine would be used in the regeneration step. The brine requirement for this scenario was one BV per 160–230 BVs of influent, depending on the influent nitrate concentration.

When the alternative treatment process was simulated for an influent containing no nitrate, and BaCl₂ was used to precipitate sulfate, a single batch of regenerant solution could be used indefinitely. Eventually, of course, if the influent contained arsenate, arsenate would occupy a significant fraction of the resin and would begin to break through the columns, even if essentially all the sulfate were precipitated after each cycle. However, calculations suggest that this would not occur until 2.4 × 10⁶ BVs had been treated for an influent containing 40 μg/L As(V), corresponding to a run time of >9 years for an EBCT of 2.8 min in each column. Other factors would undoubtedly dictate that both columns be regenerated sooner than implied by that calculation. The point is that the effective lifetime of the brine would not be constrained by either accumulation of sulfate or breakthrough of arsenate under these conditions.

If nitrate was present in the influent, the brine requirement increased in both the conventional and modified processes, but the effect on the modified process was much greater. As a result, the benefit provided by the modification declined with increasing influent nitrate concentration. For instance, for systems using a single regenerant solution and in which BaCl₂ was used to precipitate sulfate, the ratio of the brine requirement for the conventional process to that for the modified process was 6.2, 2.6, and 1.3 for influents containing 10, 25, and 50 mg/L nitrate, respectively. That is, the modified process is predicted to provide a substantial benefit over the conventional process (in terms of reduced brine usage) for low-NO₃ influents, but only very modest benefits for high-NO₃ influents.

In the simulations described above, the regenerant solution that was used for the upstream column was also used to regenerate the downstream column (albeit only intermittently). As shown in Fig. 7, use of separate solutions to regenerate the two columns reduced the overall brine requirement by a factor of approximately 3–6 compared to when a single batch of brine was used. Interestingly, use of CaCl₂ rather than BaCl₂ to precipitate sulfate increased the predicted brine requirement by only 30–40%, even though CaSO₄(s) is approximately five orders of magnitude more soluble than BaSO₄(s). The result was essentially the same regardless of whether the same or different regenerant solutions were used for the two columns. Therefore, most of the benefits of BaCl₂ addition with respect to reduced brine usage can be achieved by CaCl₂ addition. Given the lower cost of CaCl₂, the smaller mass of solids that would be generated using CaCl₂ (the molecular weights of BaSO₄(s) and CaSO₄(s) are 233 and 136, respectively), and the fact that calcium is considered more environmentally benign than barium, CaCl₂ would probably be the preferred precipitating agent in most situations.

The sensitivity of the brine requirement to the influent sulfate concentration is shown in Fig. 8 for systems regenerated with two brines. At low nitrate concentrations, an enormous volume of influent can be treated per unit volume of regenerant, and the influent sulfate concentration is virtually irrelevant. At higher influent nitrate concentrations, however, the brine requirement decreases with increasing sulfate concentration. For instance, for an influent nitrate concentration of 50 mg/L, approximately 3.3 times as much brine is required if the influent contains 25 mg/L sulfate as if it contains 200 mg/L. This seemingly anomalous outcome reflects the fact that, for the assumed operating procedure, the total number of charge equivalents applied to the
column during a given cycle increases when the sulfate concentration decreases (because the cycle length corresponds to a fixed loading of sulfate, independent of the nitrate concentration). As a result, greater unused resin capacity is required at the beginning of a cycle with a low-sulfate influent than one with a high-sulfate influent, if the cycle is to be completed successfully (without breakthrough), so the low-sulfate system requires more frequent regeneration.

The results presented here have implications for ion exchange for treatment of both nitrate and arsenate. In either case, the proposed process could dramatically reduce the brine requirements and the associated costs for brine preparation and disposal. The process does generate a solid residual (CaSO₄(s)) that is not associated with conventional ion exchange operation. However, in many cases, this residual would be less expensive to deal with than the brine. In practice, separate considerations (e.g., the need to rinse the columns after regeneration) would probably reduce the advantages of the proposed process over a more conventional procedure. Nevertheless, the experimental results and the simulations suggest that the proposed, relatively simple modifications to conventional ion exchange processes are feasible and potentially very attractive.

4. Conclusions

Separation of sulfate from other ions in the brine used to regenerate ion exchange columns, and precipitation of that sulfate as either BaSO₄(s) or CaSO₄(s), can significantly reduce the amount of brine required per unit amount of influent treated. However, nitrate buildup in the brine can limit the regeneration efficiency. The information required to model the process includes the selectivity coefficients for binding of the major ions and any target, minor ion(s) to the resin, both for when the resin equilibrates with the influent and for when it equilibrates with regenerant brines containing a range of target ion concentrations. In the current study, the selectivity coefficient of the resin for sulfate over nitrate increased significantly when the ionic strength of the solution increased from 0.003 to 3.0 M due to addition of chloride, although the SO₄(NO₃) separation factor decreased, to the point where NO₃ was the preferred adsorbate at the highest ionic strength investigated.

To explore the potential benefits of sulfate precipitation from ion exchange brines in systems treating influents that contain nitrate, the proposed process was simulated as a sequence of three steps: equilibration of the upstream column with the influent during resin loading, equilibration of the same column with the brine during regeneration, and equilibration of the brine with CaSO₄(s) or BaSO₄(s) in the sulfate precipitation step. The simulations indicated that the benefits of the proposed operating procedure over a conventional ion exchange process are enormous if the nitrate concentration is low, but they diminish with increasing influent nitrate concentration. The use of separate brine solutions to regenerate the upstream and downstream columns provides additional benefits.

The predicted brine requirement is increased only by approximately 30% if sulfate is precipitated as CaSO₄(s) rather than BaSO₄(s), even though CaSO₄(s) is five orders of magnitude more soluble than BaSO₄(s).

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References

[1] USEPA. Arsenic removal from drinking water by ion exchange and activated alumina plants, EPA/600/R-00/088, October 2000.


