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Regeneration of Perchlorate (ClO_4^-)-Loaded Anion Exchange Resins by a Novel Tetrachloroferrate ($FeCl_4^-$) Displacement Technique

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Selective ion exchange is one of the preferred treatment technologies for removing low levels of perchlorate (ClO_4^-) from contaminated water because of its high efficiency and minimal impact on water quality through the addition or removal of chemicals and nutrients. However, the exceptionally high affinity of ClO_4^- for type I anion-exchange resins makes regeneration with conventional NaCl brine extremely difficult and costly for practical applications. The present study entails the development of a novel regeneration methodology applicable to highly selective anion-exchange resins. Tetrachloroferrate ($FeCl_4^-$) anions, formed in a solution of ferric chloride and hydrochloric acid (e.g., 1 M $FeCl_3$ and 4 M HCl), were found to effectively displace ClO_4^- anions that were sorbed on the resin. A mass-balance analysis indicated that a nearly 100% recovery of ion-exchange sites was achieved by washing with as little as ~5 bed volumes of the regenerant solution in a column flow-through experiment. There was no significant deterioration of the resin's performance with respect to ClO_4^- removal after repeated loading and regeneration cycles. Thus, the new methodology may offer a cost-effective means to regenerate ClO_4^- -loaded resins with improved regeneration efficiency, recovery, and waste minimization in comparison with conventional brine regeneration techniques.

Introduction

Perchlorate (ClO_4^-) has been widely used as a rocket propellent and in munitions in the United States and abroad, and improper disposal of perchlorate-containing materials has resulted in a significant new threat to groundwater and drinking water supplies (*1–3*). Because ClO_4^- ions are nonvolatile, highly soluble, and kinetically inert in dilute aqueous solution, they cannot be effectively removed from water by conventional carbon filtration or sedimentation methodologies or by chemical reduction with such reducing agents as elemental iron or dithionite (*1, 4*). Recently, catalytic reduction of ClO_4^- using organic sulfides and oxorhenium-(V) complexes and titanous ions has been reported to be successful (*3, 5, 6*), but the cost or toxicity of the chemicals and/or their effectiveness in treatment of low levels of ClO_4^- (at sub-ppm levels) in contaminated groundwater render these technologies questionable for large-scale field applications. On the other hand, treatment by ion exchange, using highly selective anion-exchange resins in particular, has proven to be an effective technology for removing ClO_4^-, especially at low concentrations (*6–11*). Indeed, the primary motivation for developing anion-exchange resins with enhanced selectivity was to address the need for more efficient and environmentally friendly technologies to treat even more dilute anionic contaminants. As an example, a recent field experiment demonstrated that one bed volume of a bifunctional resin (Purolite D-3696) was able to treat >100 000 bed volumes of groundwater before a significant breakthrough of ClO_4^- occurred (with an initial ClO_4^- concentration of ~50 μg/L or ~0.5 μM/L) (*7*). The use of highly selective ion-exchange resins offers additional advantages including: (1) the treatment process does not change the water chemistry by adding or removing chemicals or nutrients, and (2) the system can be operated at a relatively high flow rate, typically at ~0.5 to 2 bed volumes/ min or higher, and thus requires only a small, simple treatment unit.

However, because ClO_4^- anions are selectively and strongly sorbed as a result of their low hydration energy and large size, regeneration of spent resin becomes a particularly challenging and costly task. The increasing order of affinity of singly charged ions for type I strong-base anion-exchange resins is well-known: bicarbonate < chloride < nitrate < perchlorate. The exceptionally high affinity of ClO_4^- for resins requires the use of large volumes of concentrated salt solutions for regeneration (e.g., by using 12% NaCl brine) (*10–12*). This translates into high operating cost and waste-disposal problems associated with the brine containing ClO_4^-. For example, Tripp and Clifford recently reported that, even with a relatively nonselective resin and with counterflow of the brine, regeneration required a large excess of NaCl (*10*). With relatively selective anion-exchange resins, many bed volumes of 12% NaCl were able to remove only ~6% of the loaded ClO_4^- from the resin, and heating the ClO_4^- -laden resins during regeneration had only limited success (*11*). Similarly, the sorption affinity of pertechnetate (TcO_4^-) anions and corresponding resin regeneration difficulty were found to parallel the case of ClO_4^-, because both anions are large and poorly hydrated with similar chemical properties. A measurement of the distribution ratio of TcO_4^- sorption as a function of NaCl concentration indicated that even resins with a low selectivity (such as Amberlite IRA-900 and a polyacrylic type II resin, Purolite A-850) could not be regenerated with reasonable volumes of NaCl brine (*6*). Note that, although polyacrylic type II resins have been shown to be readily regenerated with NaCl brine, they are nonselective in removing ClO_4^- and thus require a frequent regeneration, particularly in the presence of a high ratio of competing anions to ClO_4^- as commonly observed in groundwater (*9–11*). It has therefore been suggested that the high costs for resin regeneration and regenerant disposal would render the ion-exchange technology unattractive unless the two issues of resin regeneration and final waste disposal could be resolved (*10, 11*).

A new paradigm of resin regeneration is therefore urgently needed before the selective anion-exchange resins can be used cost-effectively for large-scale field applications. The objective of this research was to develop a technique that could be effectively and economically used for regenerating anion-exchange resins that are loaded with ClO_4^- or other strongly held anions. As a general strategy, we considered

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the use of displacement reactions in which the displacing anion could later be decomposed. The displacing anion should not incur excessive cost, nor should its decomposition produce environmental challenges of its own. An attractive candidate meeting these requirements was identified as the tetrachloroferrate anion ($FeCl_4^-$), formed in a ferric chloride ($FeCl_3$) solution in the presence of an excess amount of hydrochloric acid or chloride (eq 1) (*13*):

$$FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^- \quad (1)$$

Like the ClO_4^- ion, the $FeCl_4^-$ is a large, poorly hydrated anion and known as one of the most strongly extracted anions from HCl solutions by either liquid–liquid solvent extraction (*14*) or anion exchange (*15, 16*). It was therefore anticipated to effectively displace ClO_4^- from the resin. On the other hand, the $FeCl_4^-$ ion has a much desired chemical property that it decomposes in dilute HCl solutions according to the following rapidly established chemical equilibria 2–5 (water of hydration not shown) (*17, 18*):

$$FeCl_4^- \rightleftharpoons Fe^{3+} + 4Cl^- \quad (2)$$

$$FeCl_4^- \rightleftharpoons FeCl^{2+} + 3Cl^- \quad (3)$$

$$FeCl_4^- \rightleftharpoons FeCl_2^+ + 2Cl^- \quad (4)$$

$$FeCl_4^- \rightleftharpoons FeCl_3 + Cl^- \quad (5)$$

Accordingly, by decreasing Cl^- concentration, the $FeCl_4^-$ anion converts to positively charged Fe(III) species such as Fe^{3+}, $FeCl^{2+}$, and $FeCl_2^+$, which are readily desorbed from the resin by charge repulsion. Therefore, the resin is regenerated to its original state with Cl^- as the counteranion by charge balance. Because both $FeCl_3$ and HCl are relatively inexpensive and their use in treatment of drinking water is well established, this new methodology may thus offer a cost-effective means to regenerate strong-base anion-exchange resins loaded with ClO_4^- or other strongly held anions (*7, 18*).

Materials and Methods

Anion Exchange Resins. Two anion-exchange resins, Purolite D-3696 and Purolite A-520E, were obtained from Purolite International and used for the present study. The Purolite D-3696 resin is a patented bifunctional anion-exchange resin with both trihexylammonium and triethylammonium functional groups (*19*). Details of the preparation of the bifunctional resins, their characteristics, and their performance were published elsewhere (*6, 20, 21*). The Purolite A-520E is a monofunctional anion-exchange resin with triethylammonium exchange sites and the polystyrene backbone cross-linked with divinylbenzene. It was used as the baseline for assessing the performance of the bifunctional resin because our initial laboratory screening studies indicated that Purolite A-520E was one of the best monofunctional anion-exchange resins with respect to the removal of ClO_4^- or TcO_4^- from contaminated groundwater (*7, 21*). In fact, Purolite A-520E is currently being used to remove TcO_4^- from the contaminated groundwater at the U.S. Department of Energy's Paducah Gaseous Diffusion Plant site in Kevil, Kentucky (*8*).

Kinetics of ClO_4^- Desorption. The effectiveness of the ClO_4^- desorption by both the $FeCl_4^-$ reagent and the conventional NaCl brine (2 M, ~12%) was determined in experiments using two resins, which had been loaded with ClO_4^- either in the laboratory or during a field trial at the Aerojet site in Rancho Cordova, California (*7*). In the laboratory, sorption of ClO_4^- on resins was first determined by contacting 0.1 g of resin (dry weight equivalent) with a 50-mL test solution containing 200 mg/L ClO_4^-. The test solution, a simulant of the contaminated groundwater at the Aerojet site (*17*), consisted of 3 mM $NaHCO_3$, 1 mM $CaCl_2$, 0.5 mM $MgCl_2$, 0.5 mM Na_2SO_4, and 0.5 mM KNO_3. Samples were agitated overnight, and the supernatant was then decanted and analyzed for ClO_4^- content by means of ion chromatography equipped with a Dionex IonPac AS-11 analytical column and an AG-11 guard column (Dionex DX-500, Sunnyvale, California). The detection limit was approximately 4 μg/L ClO_4^- (or ~4×10^{-8} M) (*7, 22*). The amount of ClO_4^- adsorbed by the resin was calculated as the difference between the amount of ClO_4^- added and the amount found in the equilibrium solution.

Desorption of ClO_4^- from the ClO_4^- -loaded resins (either prepared in the laboratory or obtained from the field experiment) was then initiated by rinsing with ~5 mL of deionized water to remove residual ClO_4^- in the resin after sorption; it was followed by equilibrating 50 mL of either a solution of 2 M NaCl or the $FeCl_4^-$ regenerant composed of 0.35 M $FeCl_3$, 2 M HCl, and 35% alcohol. Note that alcohol (either ethanol or methanol) was used to decrease the dielectric constant of the regenerant solution. At different time intervals, an aliquot (0.1–0.2 mL) of supernatant solution was sampled, and after proper dilution with deionized water or 0.1 M NaOH (to remove Fe^{3+} ions by precipitation), the clear supernatant solution was analyzed for ClO_4^- content by ion chromatography as previously described.

Regeneration and Mass Balance. Evaluation of resin regeneration by $FeCl_4^-$ displacement was performed in small chromatographic glass columns (10 × 22 mm). Resins were wet-packed to avoid entrapped air bubbles within the column, and a high-precision HPLC pump (Alltech 426, Deerfield, Illinois) was used for both the sorption and the desorption (or regeneration) cycles of the experiment (*7*). For the sorption phase of the experiment, the ClO_4^- -test solution (which consisted of ~10 mg/L ClO_4^-) was fed into the resin column at a constant flow rate of ~17 bed vol/min (or ~38 cm/min with a residence time of <4 s) until an ~35 to 50% breakthrough of ClO_4^- was observed. The high initial ClO_4^- concentration and a high flow rate were used to accelerate the ClO_4^- sorption and breakthrough in these laboratory column studies and to minimize waste generation. For the desorption or regeneration phase of the experiment, the ClO_4^- -loaded resin column was first washed with ~5 bed volumes of deionized water to remove any residual ClO_4^- in the column pore water. The desorption of ClO_4^- was then initiated by pumping the $FeCl_4^-$ regenerant through the resin column at a flow rate of 0.06 to 0.13 cm/min or a residence time of ~10 to 21 min. A low flow rate was necessary to allow a sufficient time of equilibration for the displacement of ClO_4^- by the $FeCl_4^-$ anions. The effluent was collected continuously by means of a fraction collector and analyzed for ClO_4^- content after the regenerant solution was neutralized with dilute NaOH to precipitate out the ferric hydroxides. The success of the resin regeneration was measured through a mass-balance analysis of ClO_4^- sorbed during the sorption cycle and that desorbed during the regeneration cycle.

After displacement of ClO_4^-, the $FeCl_4^-$ -loaded resin bed was equilibrated with dilute HCl solution (0.01 M), in which $FeCl_4^-$ anions dissociate according to eqs 2–5. Thus, the positively charged or neutral Fe(III) species (i.e., Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, and $FeCl_3$) and excess Cl^- anions are eluted off the resin bed, thereby regenerating the resin to its original state with Cl^- as the counteranion. The regenerated resin bed was again subjected to ClO_4^- sorption, and its performance was evaluated by comparing the ClO_4^- breakthrough curves after regeneration with that of the fresh resin bed (which was never exposed to ClO_4^- sorption). The above sorption and regeneration cycles were repeated several times for additional evaluation. Note that column regeneration was performed only with the $FeCl_4^-$ regenerant because the batch experi-

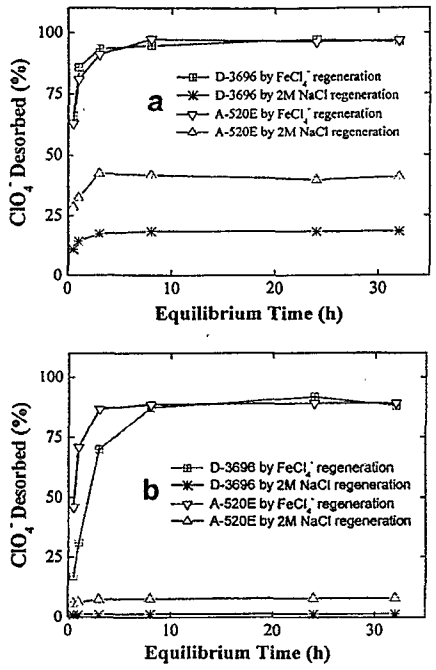

FIGURE 1. Desorption kinetics of perchlorate-loaded resins by both tetrachloroferrate displacement and conventional brine desorption techniques: (a) Clean resins were sorbed with ClO_4^- at ~50% of their anion-exchange capacity in the laboratory; (b) resins had been used for treatment of ClO_4^- -contaminated groundwater (ClO_4^- loading was approximately 10% for the D-3696 resin and ~2% for the Purolite A-520E resin) (*7*).

ments as well as previous studies (*10–12*) indicated that NaCl brine is ineffective for the displacement of ClO_4^- from these selective anion-exchange resins.

Raman Spectroscopic Analysis. Raman spectroscopic analysis was performed to provide insights into the mechanisms of the formation of $FeCl_4^-$ species in the regenerant solution and consequently into the displacement process. The spectra of the regenerant solutions were collected with a Dilor XY800 Raman microprobe configured as a single-stage spectrograph and by using the macrostage entrance. A Coherent Innova 308C Ar^+ ion laser at 514.5 nm with 100-mW output power was used to excite the sample. Spectra data were recorded between 100 and 800 cm^{-1} from solutions by focusing the laser through the quartz cell and collecting the scattered light 180° back into the focusing lens.

Results and Discussion

Batch Desorption Kinetics. The time-dependent displacement of ClO_4^- by $FeCl_4^-$ and 2 M NaCl brine solutions was examined with the bifunctional D-3696 resin and the monofunctional A-520E resin, both of which had been previously sorbed with ClO_4^- at ~50% of their anion-exchange capacity (Figure 1a). Results indicated that ClO_4^- anions were rapidly desorbed by the addition of $FeCl_4^-$ regenerant. About 60% of the sorbed ClO_4^- was displaced within 30 min, and more than 96% of the ClO_4^- was displaced in 8 h. The desorption appeared to have reached equilibrium after ~8 h. However, less than 20% of the ClO_4^- was desorbed with the 2 M NaCl brine solution from the bifunctional D-3696 resin, even after an extended period of equilibration (32 h). More ClO_4^- (yet only ~40%) was desorbed by the NaCl brine from the monofunctional A-520E resin because of its lower selectivity (K_d) toward ClO_4^- in comparison with that of the bifunctional D-3696 resin. Previous studies have shown that the 24-h K_d value for sorption of ClO_4^- to the D-3696 resin was nearly an order of magnitude higher than that of the A-520E resin (*7*).

Similar batch desorption kinetic experiments were performed with these resins that had been used for the treatment of ClO_4^- -contaminated groundwater at the Aerojet site in the summer of 1998 (*7*). The ClO_4^- loading on these field samples was much lower (~10% of the total anion exchange capacity of the bifunctional D-3696 resin and <2% of the capacity of the monofunctional A-520E resin) despite the fact that a nearly 100% breakthrough of ClO_4^- was observed under field flow-through conditions. This lower loading resulted primarily from the presence of a low ClO_4^- concentration (~50 μg/L) but several orders of magnitude higher concentrations of competing anions (e.g., Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}) and dissolved organic materials in the groundwater (*17*). Results (Figure 1b) also showed that ClO_4^- was readily desorbed from these field resins by $FeCl_4^-$ although the desorption kinetics appeared to be slightly slower than those observed in resins sorbed with ClO_4^- at a relatively high loading rate in the laboratory (Figure 1a). Approximately 90% of the ClO_4^- was desorbed from these field resins after ~8 h of equilibration. Desorption of ClO_4^- by 2 M NaCl brine was essentially ineffective on these field resins. Less than 1.5 and 8% of ClO_4^- was displaced by the brine from the bifunctional D-3696 and the monofunctional A-520E resins, respectively (Figure 1b). It therefore appears that the displacement of ClO_4^- from field resins (with a lower ClO_4^- loading) was more difficult than those prepared in the laboratory, particularly with the NaCl brine. These observations may be partially explained by the fact that these resin samples were subjected to field groundwater treatment and had been stored in a refrigerator for an extended period (>1 year) before these regeneration experiments were performed. Another possible explanation is that different sorption sites with different affinities may exist on the resin beads (particularly in the case of the bifunctional resin). Therefore, at a low ClO_4^- loading, most ClO_4^- ions were sorbed onto the high-affinity exchanges sites, resulting in a lower amount of ClO_4^- desorption from the resin. Nevertheless, the batch desorption experiment demonstrates that the displacement of ClO_4^- by $FeCl_4^-$ technique was highly effective. However, regeneration using NaCl brine was ineffective, as other researchers have reported (*6, 10–12*).

Column Breakthrough and Regeneration. In efforts to further evaluate resin regeneration through $FeCl_4^-$ displacement, the adsorption and desorption of ClO_4^- were investigated through the use of columns packed with a sample of the bifunctional D-3696 resin that had been previously used for the treatment of ClO_4^- -contaminated groundwater (*7*). The amount of ClO_4^- desorbed during regeneration was monitored so that a mass balance could be determined (Figure 2). Results indicated that ClO_4^- was rapidly and effectively desorbed from the resin bed. About 98% of the ClO_4^- was eluted off the resin bed with about 10 bed volumes of $FeCl_4^-$ regenerant. The ClO_4^- elution curve reached a maximum concentration of ~23 mM (or ~2300 mg of ClO_4^-/L) after elution with ~5 to 6 bed volumes of the $FeCl_4^-$ regenerant solution. This was equivalent to a concentration factor of nearly 5 orders of magnitude in comparison with the ClO_4^- concentration in the groundwater (i.e., ~0.05 mg/L). Examination of the cumulative ClO_4^- desorption (Figure 2) showed a near 100% recovery or desorption of ClO_4^- after elution with only ~15 bed volumes of the $FeCl_4^-$ regenerant solution.

To reuse the resin bed for ClO_4^- sorption, the sorbed $FeCl_4^-$ and excess ferric chloride regenerant must be washed off the resin bed; this was accomplished by washing with a dilute HCl solution (0.001–0.01 M). An acidic washing solution was used to prevent the hydrolysis or precipitation of Fe(III) species as ferric hydroxides. Results indicated that elution

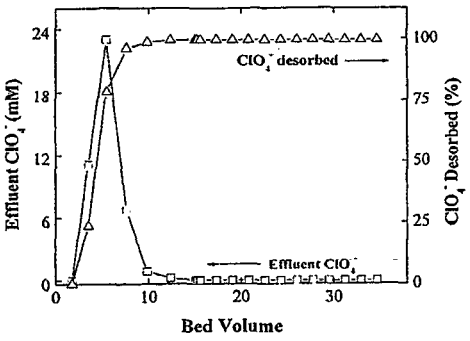

FIGURE 2. Desorption of ClO_4^- and regeneration of ClO_4^- -loaded resin (Purolite D-3696) that had been previously used for the treatment of groundwater contaminated with ClO_4^- at the Aerojet site in the summer of 1998. The regenerant solution consisted of 0.35 M $FeCl_3$, 2 M HCl, and 35% ethanol.

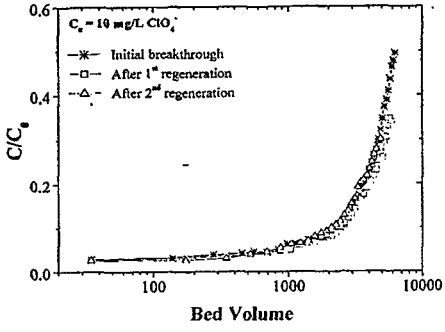

FIGURE 3. Comparison of the breakthrough curves of the bifunctional D-3696 resin (used in the field test in California) regenerated by desorption with a tetrachloroferrate ($FeCl_4^-$) reagent shown in Figure 2. Note: The initial breakthrough curve was obtained with the same D-3696 resin under the same experimental conditions except that the resin was never exposed to ClO_4^- sorption.

with ~20 to 30 bed volumes of the HCl solution was necessary to rinse off ferric ion to a low or nondetectable level (as measured by atomic absorption spectrometry). No mass balance analysis was performed with respect to the sorption or desorption of $FeCl_4^-$ in columns because of a relatively high Fe^{3+} concentration in the regenerant and a rapid equilibrium of $FeCl_4^-$ with other Fe(III) species by washing with an aqueous solution (eqs 2–5). However, no $FeCl_4^-$ ion species were anticipated to be present, nor was ClO_4^- detected in the dilute HCl washing solution, as was fully expected. This washing solution could therefore be neutralized with dilute NaOH (with <0.06% NaCl salt) and readily disposed of along with the treated water or at a municipal water treatment plant.

After regeneration, the same resin column was again subjected to the sorption or breakthrough experiment with the ClO_4^- test solution in the laboratory (Figure 3, after first regeneration). Results indicated that the breakthrough curve after regeneration matched well with the initial ClO_4^- breakthrough curve; this provided additional evidence that a complete regeneration of the spent resin column was achieved (*7*). There was no indication of significant deterioration of the resin's performance with respect to ClO_4^- removal from the ClO_4^- test solution.

Because a relatively high influent ClO_4^- concentration (10 mg of ClO_4^-/L) was used in these laboratory flow-through experiments, mass-balance analysis indicated that, at an ~35% breakthrough of ClO_4^- (Figure 3, after first regeneration), the resin bed was loaded with ClO_4^- at ~50% of its anion exchange capacity. This loading was substantially

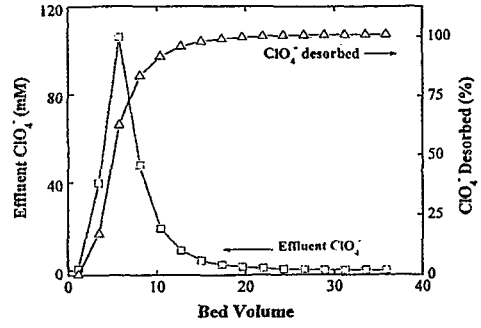

FIGURE 4. Repeated regeneration of the bifunctional D-3696 resin bed by the $FeCl_4^-$ reagent (composed of 0.35 M $FeCl_3$, 2 M HCl, and 35% ethanol). The resin was initially used for groundwater treatment, then regenerated by the $FeCl_4^-$ displacement technique (Figure 2), and reloaded with ClO_4^- in the laboratory column flow-through experiment with a relatively high influent ClO_4^- concentration (10 mg/L) and ClO_4^- loading (Figure 3).

higher than that observed in the field experiment (~10% of the anion exchange capacity) because of a low influent ClO_4^- concentration in the groundwater (~0.05 mg/L) (*7*). To further evaluate the regeneration at a high ClO_4^- loading and the performance of the resin after repeated regeneration, the same resin bed was eluted a second time with the $FeCl_4^-$ regenerant solution, and a mass balance was performed as shown in Figure 4 (the second regeneration). Results again indicated that ClO_4^- was effectively desorbed by $FeCl_4^-$. Nearly 100% of the ClO_4^- was eluted off the resin bed, and a complete recovery of the sorbed ClO_4^- was achieved after elution with ~20 bed volumes of the $FeCl_4^-$ regenerant solution (Figure 4). The displaced ClO_4^- was also found to be concentrated in the first few bed volumes of the regenerant solution and it reached a maximum concentration as high as ~110 mM (or ~11 g of ClO_4^-/L) because of a relatively high initial ClO_4^- loading. However, it is noted that there was a continued desorption or recovery of small amounts of ClO_4^- with an increased number of bed volumes. This tailing was particularly evident at a higher initial loading of ClO_4^- shown in Figure 4 than that shown in Figure 2. An extended elution with the regenerant solution helps to further clean up the resin but is unnecessary when time and economics are in consideration (such as in field applications). This is because only a small fraction of ClO_4^- (<1% in general) may remain on the resin bed and was found not to significantly impact on the performance of the regenerated resin bed (data not shown).

The performance of the resin bed after the second regeneration is also shown in Figure 3 for comparison. Again, the breakthrough curve after repeated regeneration matched well with that of the initial ClO_4^- breakthrough and that after the first regeneration (Figure 3). In fact, previous studies reported that the resin column performed similarly even after seven repeated adsorption and regeneration cycles (*7*). These observations suggest that the acidic regenerant solution and the regeneration process were unlikely to cause deterioration of the resin itself. On the other hand, deterioration may occur with these synthetic resins during an extended water-treatment process, such as when it is operated under high pressure or high shear. However, caution must be taken to ensure a complete elution of ferric ions during regeneration because any precipitation of iron oxyhydroxides may potentially cause the clogging of the resin bed during uptake of ClO_4^- from neutral solution.

Formation of $FeCl_4^-$ and Regeneration Mechanisms. Both the laboratory batch and the column experiments clearly demonstrated the effectiveness of the $FeCl_4^-$ regeneration process. Additional studies were performed to investigate

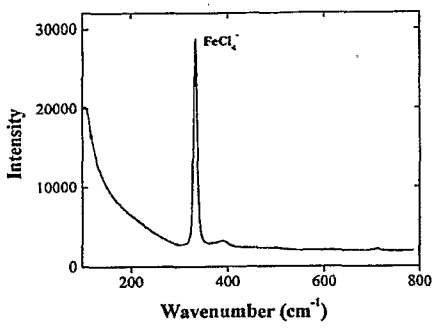

FIGURE 5. Identification of $FeCl_4^-$ species (at ~330 cm^{-1}) by Raman spectroscopy. The test solution consisted of 0.1 M $FeCl_3$, 2 M HCl, and 4 M LiCl in 50% methanol.

the formation of $FeCl_4^-$ in an attempt to confirm both the range of stability of the $FeCl_4^-$ ion in $FeCl_3$ solutions and the displacement mechanism. The $FeCl_4^-$ ion can be observed by the characteristic Raman spectrum which shows a strong and sharp ν_1 band at 330 cm^{-1} (*23*). A series of experiments were conducted to identify the conditions under which the $FeCl_4^-$ ion was present. Initially, aqueous solutions with the composition of 0.1 M Fe^{3+} and from 0.1 to 12 M HCl were examined. Results indicated that $FeCl_4^-$ was present only in the most concentrated HCl solution whereas the other solutions contained predominantly the dichloroferrate ion, $FeCl_2(H_2O)_4^+$, as identified by a band at ~316 cm^{-1} (*24*). Then, experiments were performed with varied concentrations of HCl, chloride ion (as LiCl), and alcohol because decreasing the dielectric constant of the solution by addition of an organic solvent is known to favor the formation of the $(H_3O)^+(FeCl_4)^-$ ion pair (*24*). For example, in a 50-vol % methanol solution with a total ionic strength of 4 M compensated with LiCl and HCl at > 1 M acid concentration, the $FeCl_4^-$ ion became the dominant species. At a total ionic strength of 6 M, the $FeCl_4^-$ ion already appeared to be the dominant species when the HCl concentration was above 0.1 M (Figure 5).

Apparently, the formation of the $FeCl_4^-$ species involves a complex interplay of acid, chloride ion, and media effects caused by the presence of alcohol. Our initial regenerant solution (0.35 M $FeCl_3$, 2 M HCl, and 35% ethanol) was formulated so that a relatively low concentration of $FeCl_3$ and HCl was used, taking into consideration the possible hydrolysis of ferric ion. Alcohol was added to enhance the regeneration efficiency by decreasing the dielectric constant of the regenerant solution. As discussed previously, this regenerant solution was found to be effective in the elution of ClO_4^- (Figures 1 and 3). However, Raman spectroscopic analysis indicated the $FeCl_2(H_2O)_4^+$ ion to be the dominant iron-containing complex in the solution (Figure 6). These results suggest that elution of the ClO_4^- ion from the resin by this solution may involve the displacement by $FeCl_4^-$, present at a small equilibrium concentration (below the detection limit of the Raman spectroscopy), which is then replenished as this ion is removed in the ion exchange process. This observation is also consistent with the known complexation behavior between Fe(III) and Cl^- ions (*15, 16*). In accordance with the classical conceptualization of the anion exchange of complex metal anions, the exchange of resin-bound Cl^- for $FeCl_4^-$ ions in the resin organic phase is a highly favorable reaction that drives the formation of the $FeCl_4^-$ anion on the resin. From our results, it is apparent that this driving force is even sufficient to displace ClO_4^- on the resin. The exchange process is also analogous to the extraction of the $FeCl_4^-$ anion into the organic solvent with protonated amine in an aqueous–nonaqueous liquid–liquid

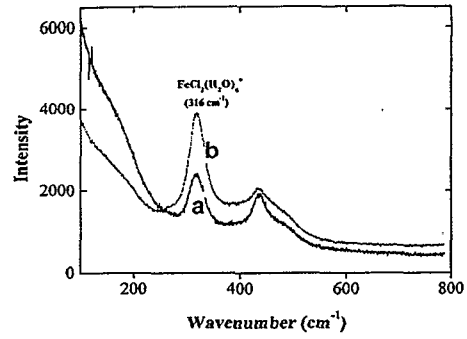

FIGURE 6. Raman spectroscopic analysis of regenerant solutions composed of (a) 0.1 M $FeCl_3$ in 2 M HCl and 35% ethanol and (b) 0.35 M $FeCl_3$ in 2 M HCl and 35% ethanol. Dichloroferrate, $FeCl_2(H_2O)_4^{2+}$, appeared to be the dominant species at ~316 cm^{-1}.

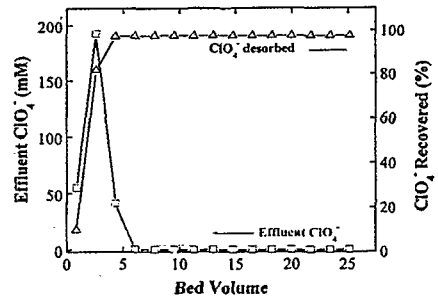

FIGURE 7. Regeneration of the bifunctional D-3696 resin bed that had been treated with ClO_4^- at an influent concentration of 10 mg/L in a laboratory column flow-through experiment. The regenerant solution consisted of 1 M $FeCl_3$ and 4 M HCl.

extraction system. The origin of the driving force has been related to net ion hydration and ion-pairing energies (*15*).

Note that the above regenerant solution may not necessarily be the optimum formulation. Ratios of Fe^{3+} to Cl^-, acid, and alcohol (or other organic solvents) can be changed, depending on the application and such factors as desired regeneration efficiency, the amount of regenerant and type of resins to be used, waste generation, and the overall cost. We realize that the use of alcohol in the regenerant solution could be a major contributor to the cost of the regenerant. In addition, there are also some additional regulatory and waste disposal concerns arising from the use of alcohol in the regenerant. Further studies were therefore performed in which the use of alcohol was eliminated and a counter-flow regeneration technique was employed. Results (Figure 7) indicated that, with an increased concentration of $FeCl_3$ and HCl but without alcohol, the resin bed was effectively regenerated and had a significantly improved regeneration efficiency. Only ~5 bed volumes of the regenerant solution was required to recover ~100% of the sorbed ClO_4^-, and this result was about 2-fold to 4-fold better than that by using the regenerant solution of 0.35 M $FeCl_3$ with 2 M HCl and 35% ethanol, as shown in Figures 2 and 4. The peak ClO_4^- concentration in the regenerant solution was nearly 200 mM or ~20 000 mg/L (Figure 7).

Implications for Field Application. Until recently, the high affinity of ClO_4^- for selective anion-exchange resins had made it impractical to regenerate ClO_4^- -loaded resins by using conventional brine solution. This research developed a new regeneration technique by displacing the sorbed ClO_4^- with $FeCl_4^-$ anions formed in an $FeCl_3$ solution, followed by decomposing the $FeCl_4^-$ ions and eluting the Fe(III) species in a dilute HCl solution (*18*). Both batch and column flow-through experiments demonstrated that the new technique

is highly effective in regenerating selective anion-exchange resins loaded with ClO_4^- and other strongly held anions (*6, 8, 21*). A nearly 100% recovery of ion-exchange sites was achieved by eluting with as little as ~5 bed volumes of the regenerant solution and no apparent deterioration of resin performance observed after repeated regeneration. Since both $FeCl_3$ and HCl are inexpensive and their use in drinking water treatment is well established, the new methodology may thus offer an efficient and economic means of regenerating the spent ClO_4^- -loaded resins. Moreover, the new regeneration paradigm opens the door to the use of new anion exchange materials with enhanced selectivity.

Large-scale field application of this selective ion-exchange and its regeneration technologies is currently under way. On the basis that highly selective anion-exchange resins were able to treat ~100 000 bed volumes of contaminated water (containing ~50 μg/L ClO_4^-) (*7*), the waste regenerant production is estimated to be <0.005% of the amount of water treated. Moreover, additional cost-savings may be realized by (1) reducing regenerant wastes and (2) separating or degrading ClO_4^- in the waste regenerant solution. The former can be accomplished by soaking the spent resin with the $FeCl_3$ regenerant for a sufficient time of equilibration at an increased temperature and/or by segregating the regenerant solutions for repeated use. On the basis of batch equilibrium studies, a longer equilibrium time (>8 h) should result in a more effective desorption of sorbed ClO_4^- and may further reduce the volume of regenerant solution. Additionally, in a view of the relatively small quantities of ClO_4^- (<2500 mg/L) in the regenerant solution (Figure 2, for field samples), the $FeCl_3$ solution could be reused a number of times for additional waste reduction as reported previously (*7*). Therefore, a conservative estimate of the amount of $FeCl_3$ regenerant solution required could be reduced to as low as ~1–2 bed volumes per regeneration cycle. Note that this estimate assumes that the dilute HCl washing solution (~0.01 M) and the follow-on rinse water is neutralized with NaOH in the process so that the neutralized NaCl solution (<0.05%, with no ClO_4^-) can be readily disposed of along with the treated water or at a municipal water treatment plant.

The concentrated waste regenerant solution could be further treated to remove ClO_4^- either by electrochemical reduction, hydrothermal decomposition, chemical precipitation, or biodegradation of the neutralized waste brine solution. Studies are currently being performed to evaluate the destruction of ClO_4^- in concentrated acidic regenerant solutions by either the electrochemical reduction or hydrothermal decomposition techniques (*25*). In both cases, practically no waste brine would be produced if they are successful. Alternatively, potassium hydroxide may be used to neutralize the waste regenerant solution, and the treatment would result in a partial precipitation or coprecipitation of $KClO_4$ with ferric oxyhydroxides sludge (as the final waste form). This is because the solubility of $KClO_4$ is relatively low ($K_{sp} = 1.05 \times 10^{-2}$) in comparison with that of $NaClO_4$ or NH_4ClO_4. On the other hand, the waste regenerant solution may also be neutralized with NaOH so that ClO_4^- will stay in the neutralized brine solution (primarily as NaCl) for further treatment by such techniques as bioreduction (*1, 26*). Recent studies have shown that some microorganisms were able to degrade ClO_4^- anaerobically in highly saline water (*26*). Nevertheless, depending on the regulatory requirements and the cost of waste disposal, additional treatment options of the waste brine are available and could have notable economic implications in that we can significantly reduce the waste brine with ClO_4^- and thus lessen the cost of its disposal.

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