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Treatment of Perchlorate-Contaminated Groundwater Using Highly-Selective, Regenerable Anion-Exchange Resins at Edwards Air Force Base

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EXECUTIVE SUMMARY

Selective ion exchange is one of the most effective treatment technologies for removing low levels of perchlorate (ClO_4^-) from contaminated water because of its high efficiency without adverse impacts on the water quality caused by adding or removing any chemicals or nutrients. This report summarizes both the laboratory and a field pilot-scale studies to determine the ability and efficiency of the bifunctional synthetic resins to remove ClO_4^- from the contaminated groundwater at the Edwards Air Force Base in California. Regeneration of the resins after groundwater treatment was also evaluated using the $FeCl_3$-HCl regeneration technique recently developed at Oak Ridge National Laboratory. On the basis of this study, the bifunctional resin, D-3696 (made by Purolite, Inc.) was found to be highly selective toward ClO_4^- and performed much better than one of the best commercial nitrate-selective resins (Purolite A-520E) and more than an order of magnitude better than the Purolite A-500 resin (with a relatively low selectivity). At an influent concentration of ~450 μg/L ClO_4^- in groundwater, the bifunctional resin bed treated ~40,000 empty bed volumes of groundwater before a significant breakthrough of ClO_4^- occurred. The presence of relatively high concentrations of chloride and sulfate in site groundwater did not appear to affect the ability of the bifunctional resin to remove ClO_4^-. However, the presence of high iron or iron oxyhydroxides and/or biomass in groundwater caused a significant fouling of the resin beds and greatly influenced the effectiveness in regenerating the resins sorbed with ClO_4^-. Under such circumstances, a prefilter (~0.5–1 μm) was found to be necessary to remove these particulates and to reduce the risk of fouling of the resin beds. Without significant fouling, the resin bed could be effectively regenerated by the $FeCl_3$ displacement technique. Nearly 100% of the sorbed ClO_4^- was displaced or recovered after elution with only ~2–5 bed volumes of the $FeCl_3$-HCl regenerant solution. On the basis of both the laboratory and field pilot-scale studies, we therefore anticipate that a combination of the selective ion exchange and the $FeCl_3$-regeneration technologies may offer a cost-effective means to remove ClO_4^- from contaminated groundwater with significantly reduced waste generation and operational cost.

1. BACKGROUND

The perchlorate anion (ClO_4^-) originates as a contaminant in the environment from the disposal of solid salts of ammonium, potassium, or sodium perchlorate. These salts are very soluble in water. The perchlorate anion, although thermodynamically a strong oxidizing agent, is known to be kinetically inert in many redox reactions and noncomplexing in its interactions with typical metal ions found in the environment. These properties make the perchlorate ion exceedingly mobile in the subsurface soil environment. It can persist for many decades under typical groundwater and surface water conditions, due to its kinetic barriers in its reactivity with other organic or inorganic constituents.

Ammonium perchlorate is manufactured for use as a constituent in solid propellants for rockets, missiles, and fireworks. Because of problems with its shelf life, perchlorate-containing propellants must be periodically washed out of the missile and rocket inventory and replaced with a fresh supply. Thus, large volumes of perchlorate-containing compounds have been disposed of in the environment since the 1950's. The presence of this material in the environment poses a threat to ecological receptors and whole ecosystems, either by direct harm to organisms, or by indirectly affecting their ability to survive and reproduce (Urbansky, 1998; Damian and Pontius, 1999). The primary effect of perchlorate on humans is thought to be a decrease in thyroid hormone output due to a competition between perchlorate and iodide sorption in the thyroid gland. Consequently, the California Department of Health Services has set a provisional action level of 18 ppb (or μg/L) for ClO_4^- in groundwater.

Various treatment technologies are being developed for the removal of ClO_4^- from contaminated groundwater or surface water. These include ion exchange, bioremediation, reverse osmosis or membrane-based technologies, chemical precipitation, and catalytic chemical or electrochemical reduction. Each of these technologies has relative advantages and disadvantages as summarized in Table 1.

Oak Ridge National Laboratory (ORNL) recently developed a new class of anion-exchange resins that have a bias for the sorption of large, poorly hydrated anions such as ClO_4^- from contaminated groundwater (Gu et al., 2000a; Brown et al., 2000). These resins are called "bifunctional" anion-exchange resins because they have two quaternary ammonium groups: the first has long alkyl chains for higher selectivity, and the second has shorter alkyl chains for improved reaction kinetics. Treatment by ion exchange using these highly-selective anion exchange resins is one of the most promising methods for removing ClO_4^- at low concentration levels (Gu et al., 2000a,b; Brown et al., 2000; Bonnesen et al., 2000; Venkatesh et al., 2000; Tripp and Clifford, 2000; Batista et al., 2000). In addition to successful benchscale demonstrations, a recent field experiment showed that one bifunctional resin bed (Purolite D-3696) was able to treat more than 100,000 bed volumes of groundwater before a significant breakthrough of ClO_4^- occurred (with an initial ClO_4^- concentration of ~50 μg/L) (Gu et al., 2000a). By comparison, conventional monofunctional resins are usually only effective for treatment of a few hundreds of bed volumes. Additional advantages of using selective ion-exchange include: (1) the treatment process does not change the water chemistry by adding or removing chemicals or nutrients because of its high selectivity towards ClO_4^- anions, and (2) only a small and simple treatment unit is needed because the system can be operated at a relatively high flow rate, typically at ~0.5–2 bed volumes per minute.

Table 1. Comparison of perchlorate treatment technologies for groundwater remediation

	Advantages	Disadvantages
Conventional ion exchange *(non-selective resins)*	• Practical and economical. • Effective and able to remove ClO_4^- below detection limit (<4 ppb). • Fast reaction and simple operation. • Can be operated at a high flow rate.	• Competition by other anions (e.g., Cl^-, NO_3^-, $SO_4^{=}$, HCO_3^-). • Large quantities of brine needed for regeneration. • Remineralization may be needed.
Selective ion exchange	• Efficient and able to remove $ClO4^-$ below detection limit (<<4 ppb). • No changes in groundwater chemistry, and no remineralization is needed. • Only a small treatment unit is needed, and it can be operated at a high flow rate because of its fast reaction. • Low O&M with long resin life(unattended operation)Long waste disposal costs with low volume waste generation.Simple system; practical and economical	• Relatively high cost of resins (depending on production quantity). • Slower regeneration process (~ 2–5 days). This is offset by the dramatic increase in resin life during the treatment phase.
Bioremediation technology	• Practical and economical. • Effective for treatment at relatively high concentrations (e.g., above 10 mg/L).	• Need a highly reducing environment and a continual feed of nutrients. • Competition by other electron acceptors in groundwater and soil. • Not suitable for treatment of water plumes with low concentrations of ClO4- (e.g., <2 mg/L). • Slow reactions, or a large treatment unit is required at the same flow rate. • Microorganisms may be pathogenic or toxic; Requires post-treatment.
Reverse osmosis	• Can be effective.	• Fouling of the membranes. • Remineralization may be needed. • High capital cost and impractical for large-scale applications.
Catalytic chemical reduction	• May work well with highly concentrated $ClO4^-$ in a small volume.	• Relatively slow reduction process. • May generate toxic byproducts. • Impractical for large-scale treatment.
Chemical precipitation	• May work well with high concentrations of $ClO4^-$ in a small volume. • Fast reactions	• Addition of expensive, toxic chemicals (e.g., nitron). • Impractical for large-scale treatment.

Additionally, ORNL recently developed a novel methodology for regenerating the bifunctional resins and other selective anion-exchange resins that are used for ClO_4^- sorption. The new regeneration process uses a sequential chemical displacement with ferric chloride dissolved in hydrochloric acid followed by washing with dilute HCl (p*atent pending*). The new regeneration technique is efficient and cost effective in comparison with conventional brine regeneration. In laboratory tests, less than five bed volumes of the regenerant solution was found to be necessary to recover nearly 100% of sorbed ClO_4^- in the resin bed. The regeneration process thus generates minimal amounts of secondary wastes (<0.05% of treated groundwater). It is anticipated that a combination of the new resin and the new regeneration methodology may offer a promising solution for remediating groundwater or surface water contaminated with ClO_4^-.

2. OBJECTIVES

The overall objective of this project was to evaluate and demonstrate the use of the ORNL-developed bifunctional resin and its regeneration technology to remove ClO_4^- from contaminated groundwater at Edwards Air Force Base (AFB). The work plan included an initial laboratory evaluation using the site groundwater and was followed by a small-scale field evaluation at the Edwards AFB site. This report summarizes the results from both the initial laboratory studies and the pilot-scale field treatability study for evaluation of resin selectivity, capacity, and regeneration effectiveness using groundwater drawn directly from site wells.

3. EXPERIMENTS AND OBSERVATIONS

3.1 LABORATORY BATCH STUDIES

As stated above, initial laboratory experiments were performed to determine the selectivity and sorption capacity of the bifunctional resin (Purolite D-3696) and two commercially available monofunctional resins by using the site groundwater. This experiment was necessary in case the groundwater contained unknown constituents that would interfere with resin performance. Two commercially available monofunctional resins (Purolite A-520E and Purolite A-500) were used to establish baseline for comparison of resin performance and costs. Our previous studies have shown that the Purolite A-520E resin was one of the best commercially available resins with respect to perchlorate removal. The Purolite A-500 resin is functionalized with trimethyl functional groups with a relatively low selectivity to perchlorate. It is a low-cost resin but still performs much better than those non-selective Type II resins.

A total of ~10 gal of the ClO_4^- contaminated groundwater was obtained from the Edwards AFB site by Earth Tech personnel (~5 gal each from Sites #196 and #286). The groundwater was analyzed immediately after receipt with respect to its pH and anion composition. Results are summarized in Table 2. In general, the groundwater contained relatively high concentrations of chloride and sulfate, and a relatively high pH (#286 in particular), as was expected in water taken from these sites. However, both groundwater samples contained a relatively high concentration of ClO_4^- (> 5 mg/L), which may be attributed to the fact that the wells were not purged before sampling. On the basis of prior sampling, it was estimated that ClO_4^- concentration should be stable at around 300–600 µg/L under a continuous flow-through condition (Earth Tech).

Table 2. General properties of groundwater obtained from sites #196 and #286 at Edwards AFB

Property	Site #196	Site #286
HCO_3^- (mg/L)	215	130
Br^- (mg/L)	0.31	0.66
Cl^- (mg/L)	298	312
NO_3^- (mg/L)	2.8	1.9
$SO_4^=$ (mg/L)	141	109
ClO_4^- (mg/L)	>10	5.8
PH	7.2	8.7

Another important observation was that the groundwater appeared to be turbid, containing significant amounts of sediments or clay colloidal materials. This may again be attributed to the fact that the wells were not purged before sampling. As a result, the groundwater had to be filtered before commencing the laboratory batch and column flow-through experiments, as will be discussed below.

Batch equilibrium studies were then performed to determine the distribution coefficients and sorption capacity of the bifunctional resin and two commercially available monofunctional resins (Purolite A-520E and Purolite A-500) for comparison. The distribution coefficient for sorption of perchlorate to the resins, K_d (in mL/g), was calculated as the ratio of the number of moles of perchlorate (expressed as the mass in mg) sorbed per gram of resin divided by the concentration of perchlorate remaining in solution (in mg/mL), i.e.,

$$K_d = \frac{\text{Perchlorate sorbed on resin } (mg/g)}{\text{Perchlorate in solution } (mg/mL)} = \frac{(C_0 - C)/m}{C},$$

where C_0 and C are the initial and final concentrations (mg/mL) of ClO_4^- in solution, and m is the mass of resin per unit volume of test solution (Gu et al., 2000a).

Results are listed in Tables 3 and 4. In general, the new bifunctional resin showed a much better selectivity for sorption of perchlorate from the contaminated groundwater than the Purolite A-520E and Purolite A-500 resins. These results are similar to what we observed previously (Gu et al., 2000a). Although both groundwater samples contained much higher concentrations of chloride and sulfate, perchlorate ions were selectively removed, particularly by the bifunctional resin (Purolite D-3696). At the 1-h equilibration, more than 99% of perchlorate was already removed from the solution (with an equilibrium concentration of only ~0.075 mg/L), although the initial concentration was adjusted at 10 mg/L.

Table 3. Distribution coefficients (K_d)[1] of ClO_4^- on synthetic resins using groundwater from Edwards AFB (#196). Experiments were performed with 100 mL test solution and 0.1g dry resin. The initial ClO_4^- concentration was ~10 mg/L

Resin	1 h K_d (mL/g)	24 h K_d (mL/g)	96 h K_d (mL/g)	168 h K_d (mL/g)
Purolite D-3696	131,750	698,100	883,780	971,920
Purolite A-520E	69,310	176,520	216,250	214,067
Purolite A-500	17,630	41,570	47,670	46,900

[1] All K_d values have a ±5% uncertainty.

Table 4. Distribution coefficients (K_d)[1] of ClO_4^- on synthetic resins using groundwater from Edwards AFB (#286). Experiments were performed with 100 mL test solution and 0.1 g dry resin. The initial ClO_4^- concentration was ~10 mg/L

Resin	1 h K_d (mL/g)	24 h K_d (mL/g)	96 h K_d (mL/g)	168 h K_d (mL/g)
Purolite D-3696	133,080	778,850	826,980	935,690
Purolite A-520E	71,540	174,630	205,855	209,640
Purolite A-500	nd [2]	nd	nd	nd

[1] All K_d values have a ±5% uncertainty.
[2] nd = not determined.

3.2 LABORATORY COLUMN EXPERIMENT

Column flow-through experiments were then performed with the bifunctional D-3696 resin to determine the breakthrough of ClO_4^- in a small column (10 × 22 mm) as a function of the number of bed volumes of contaminated groundwater passed through the column. The initial perchlorate concentration was adjusted to 10 mg/L, and flow rate was maintained at 30 mL/min (or about 17 bed volumes per minute) in order to accelerate the breakthrough experiment in the laboratory. These experimental conditions were intentionally similar to our previous studies using synthetic groundwater to allow comparison of resin performance data with respect to perchlorate removal.

Results are presented in Figure 1. The ClO_4^- breakthrough in synthetic groundwater from our previous studies also was included in Figure 1 for comparison. The X-axis shows the bed volumes of groundwater passed through the resin column (plotted on a log scale) whereas the Y-axis was plotted as the ratio of effluent ClO_4^- concentration (C) to the influent concentration (C_0). Results indicate that all three breakthrough curves virtually overlapped, suggesting that the site groundwater had no adverse impact on the performance of the bifunctional resin. The number of treated bed volumes prior to breakthrough appeared similar whether using different site groundwater samples or the synthetic groundwater from previous studies with varying pH and anion compositions (Gu et al., 2000a). In all cases, the resin removed a substantial amount of perchlorate with 10% breakthrough occurring after approximately 2,000 bed volumes of the test groundwater had passed through the column with an initial ClO_4^- concentration of 10 mg/L. It is pointed out, however, at a lower influent ClO_4^- concentration (as is commonly observed in groundwater), more bed volumes of groundwater can be treated. For example, at an initial ClO_4^- concentration of ~0.05 mg/L, approximately 100,000 bed volumes of groundwater may be treated (Gu et al., 2000a).

After completion of the column flow-through experiment, the resin bed with sorbed ClO_4^- was subjected to regeneration using the ORNL-developed tetrachloroferrate displacement technique. The displaced ClO_4^- in the effluent was monitored, and a mass balance obtained for determination of the regeneration efficiency. Results (Figure 2) indicate that the sorbed ClO_4^- was rapidly displaced by the $FeCl_4^-$ ions in the regenerant solution composed of only $FeCl_3$ and HCl; nearly 100% (±2%) displacement of ClO_4^- was achieved after elution with only ~5 bed volumes of the regenerant solution. Both columns (#196 and #286 after perchlorate sorption) performed similarly.

After regeneration, the column (#196) was subjected to the flow-through experiment again (for sorption of perchlorate) under the same experimental conditions as described above. This was to evaluate the performance of the regenerated resin column for ClO_4^- sorption. Results were shown in Figure 3. The breakthrough curve (#196 after regeneration) matched very well with the original breakthrough curves as shown in Figure 1, suggesting that nearly 100% of the exchange sites on the resin were recovered after regeneration. No apparent deterioration of resin performance was observed. Note that the repeated column breakthrough experiments were performed only with the column #196 because of the overall similarities between groundwater at sites #196 and #286 (as shown in Figure 1). Results of the column studies are also consistent with our previous observations that, even after seven repeated sorption and regeneration cycles, we observed no significant decrease in the resin performance (Gu et al., 2000a).

It is therefore concluded that, on the basis of this initial phase of laboratory experiment, a combination of the bifunctional resin and the new regeneration technology is applicable for site groundwater treatment at Edwards AFB.

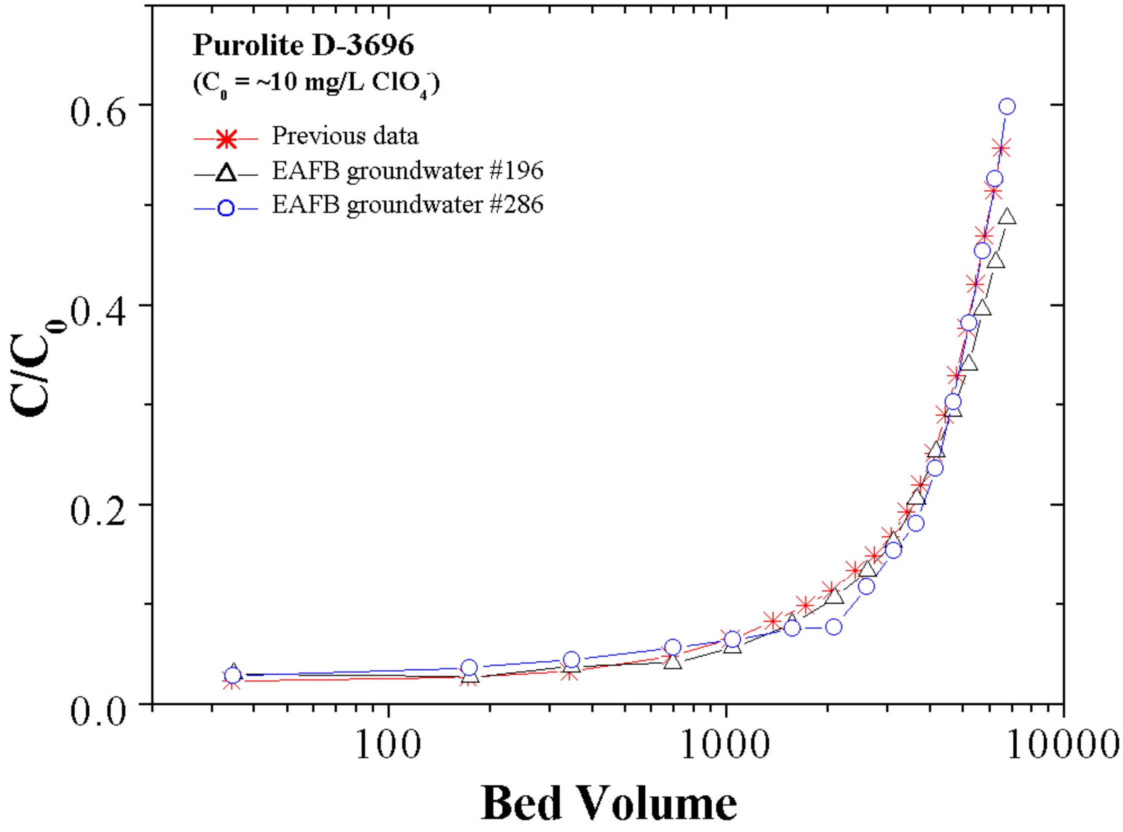

Fig. 1. Breakthrough of ClO_4^- on the Purolite D-3696 resin columns using site groundwater #196 and #286 from Edwards AFB. Note: C/C_0 is the ratio of effluent ClO_4^- concentration to the initial ClO_4^- concentration in the influent water.

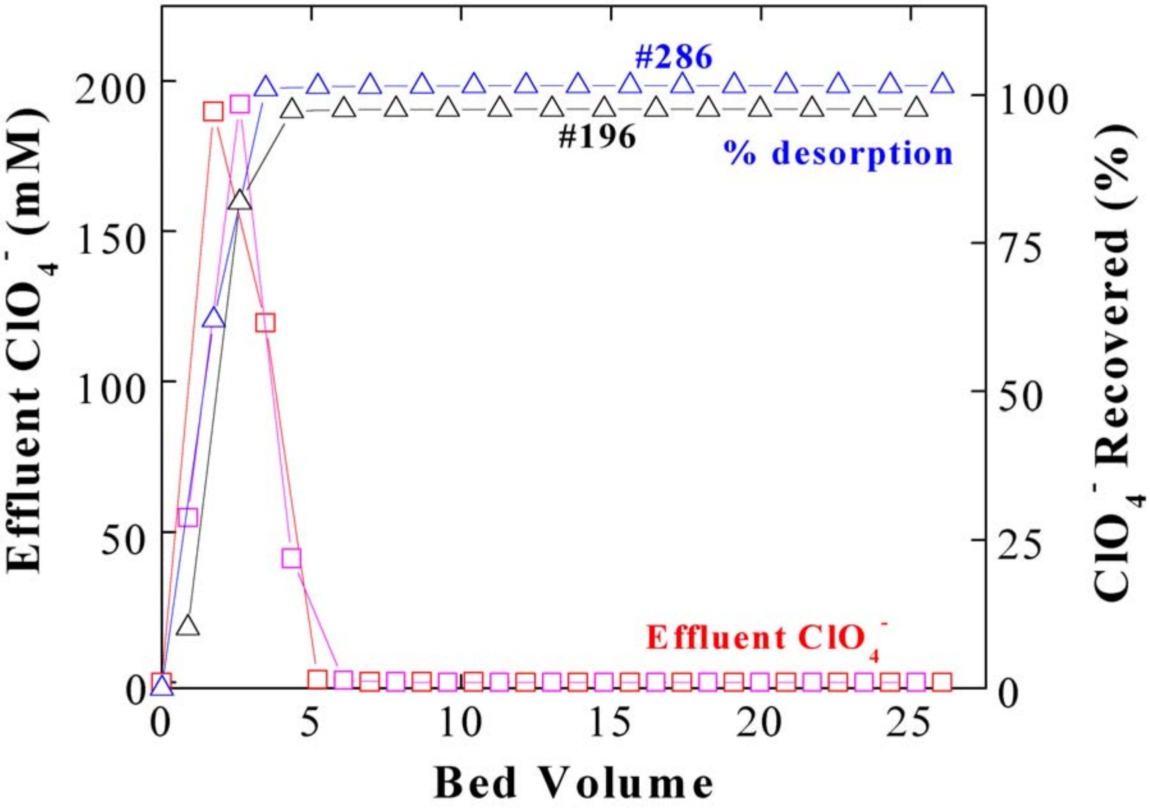

Fig. 2. Desorption of ClO_4^- from the Purolite D-3696 resin bed by displacement with $FeCl_4^-$. Note that the resin bed was first treated with groundwater contaminated with ClO_4^- from Edwards AFB.

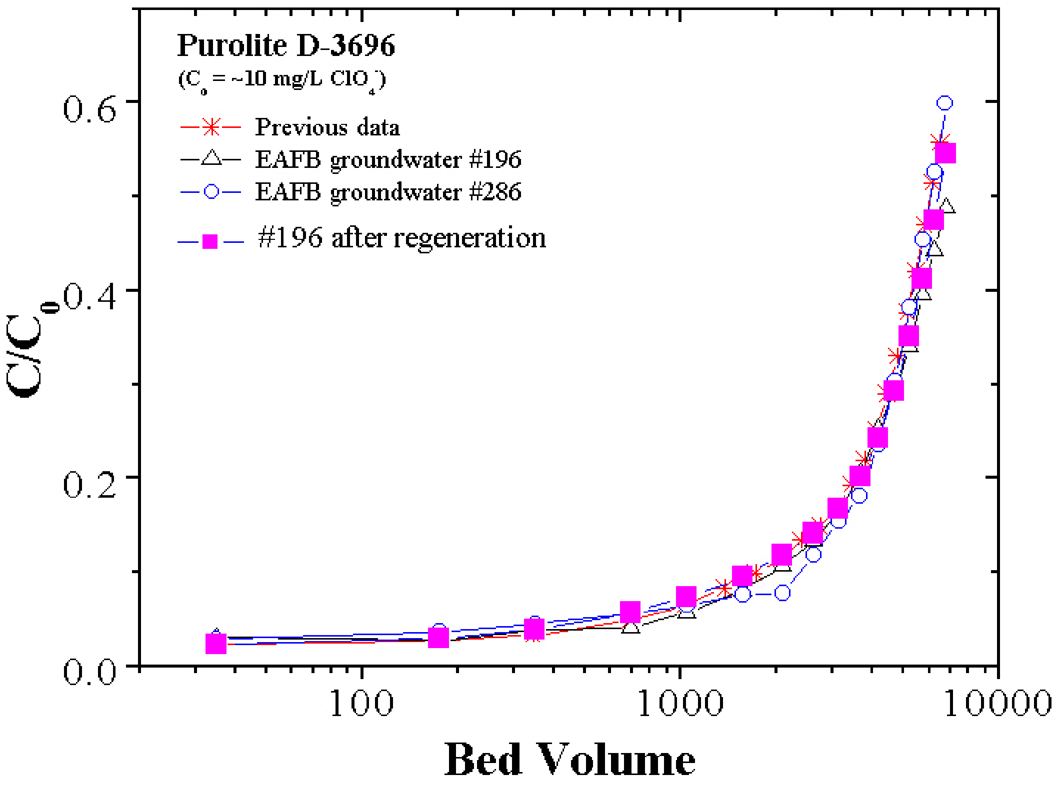

Fig. 3. Performance of the *regenerated* Purolite D-3696 resin column (solid square) after it was used for site groundwater treatment (as shown in Figure 1). Note: C/C_0 is the ratio of effluent ClO_4^- concentration to the initial ClO_4^- concentration in the influent water.

4. FIELD PILOT-SCALE DEMONSTRATION

4.1 INITIAL GROUNDWATER TREATMENT

On the basis of the bench-scale test, a pilot-scale field flow-through experiment was initiated on June 25, 2001, in an attempt to evaluate the performance of the resins before and after regeneration under realistic field conditions. Monitoring well 286 was selected as the source of contaminated groundwater. The general chemical composition and properties of the groundwater are listed in Table 5. A flow diagram of the field experimental configuration is provided in Figure 4. Both the bifunctional (Purolite D-3696) and monofunctional (Purolite A-520E) resins were run in parallel for comparison. The column dimensions were 2" in diameter and ~11.5" in depth, and the flow rate was set at approximately 500 mL/min per column (or ~0.89 bed volumes per minute). A third polishing column was used to capture the residual perchlorate at breakthrough. This ensured that all ClO_4^- was captured before discharging the treated groundwater. The influent perchlorate concentration in groundwater was ~450 μg/L and varied between ~400 and 500 μg/L throughout the experiment.

During the initial setup of the pilot scale test, a large Baker tank (20,000 gal.) was used for water collection and provided for influent water accumulation prior to treatment. It was observed that this tank contained some sediment and/or iron oxide particulates from corrosion. While noted, the tank was not flushed prior to test initiation. In addition, clear plastic tubes used to connect the columns to the influent water were noted to accumulate biological growth during the course of the test.

The breakthrough of perchlorate was continuously monitored by the analysis of effluent perchlorate concentration over time. In addition, perchlorate concentration in the middle-sampling port of the bifunctional resin column was monitored, and the results are presented in Figure 5. The initial breakthrough of perchlorate at the effluent port on the monofunctional resin column occurred after ~14,000 bed volumes of groundwater had been treated in about 2 weeks. However, full breakthrough of the perchlorate did not occur until ~35,000 bed volumes of groundwater had passed through the treatment column. By a mass-balance analysis, it was determined that approximately 3,700 mg of perchlorate was retained by the monofunctional resin column at the initial breakthrough and ~5,400 mg at the full breakthrough.

On the bifunctional resin column, we observed an initial perchlorate breakthrough after passing ~14,000 bed volumes of groundwater at the mid-sampling port and after ~20,000 bed volumes at the column effluent. However, a full breakthrough of perchlorate had not occurred after ~56,000 bed volumes of groundwater had been treated (system shut down). The total amount of perchlorate retained on the bifunctional resin was estimated to be ~10,700 mg. The performance of the bifunctional resin therefore appeared only slightly better than that of the monofunctional resin and certainly not as well as anticipated. In particular, the initial perchlorate breakthrough at the bifunctional resin column effluent occurred rapidly (at ~20,000 bed volumes). It was determined that the primary reason for early breakthrough of perchlorate was biofouling and system clogging because of the precipitation and/or deposition of iron oxyhydroxides in the macroporous resin beads. The fouled resin columns are shown in Figure 6.

Because of the large capacity of the Baker tank, groundwater was pumped into and stored in the tank (stagnant) before it was pumped through the resin treatment system. In addition, the tank lid was initially left open, providing an excellent environment for the growth of algae and microorganisms. The tank itself was rusty and probably contributed much of the iron particles or precipitates in the resin column, despite the fact that a 15-µm in-line filter was used initially between the tank and the resin columns. The system clogging was noticed after a few days of operation and the team was notified. System operation was stopped on the seventh day because of a significantly reduced flow rate and an increased pressure drop. The columns were flushed with diluted chlorine bleach (~6%, diluted 1:15), and the in-line filter was changed to 1-µm pore size in order to capture most of iron oxide particles in the influent water stream. The treatment system was then brought back on line until full breakthrough of perchlorate was observed in both the bifunctional and monofunctional resin columns.

Table 5. **General properties of groundwater obtained at the inlet of the treatment system** (Sampling port WSP 1) from monitoring well 286 at Edwards AFB

Property		**Property**	
HCO_3^- (mg/L)	226	**Fe** (mg/L)	0.04
Br^- (mg/L)	0.8	**Al** (mg/L)	0.05
Cl^- (mg/L)	356	**Ca** (mg/L)	21.3
NO_3^- (mg/L)	0.7	**Mg** (mg/L)	9.2
$SO_4^=$ (mg/L)	173	**Co** (mg/L)	nd*
ClO_4^- (µg/L)	460	**Cd** (mg/L)	Nd
TOC (mg/L)	0.94	**Si** (mg/L)	14.9
PH	8.4	**Mn** (mg/L)	Nd

* nd = not detected.

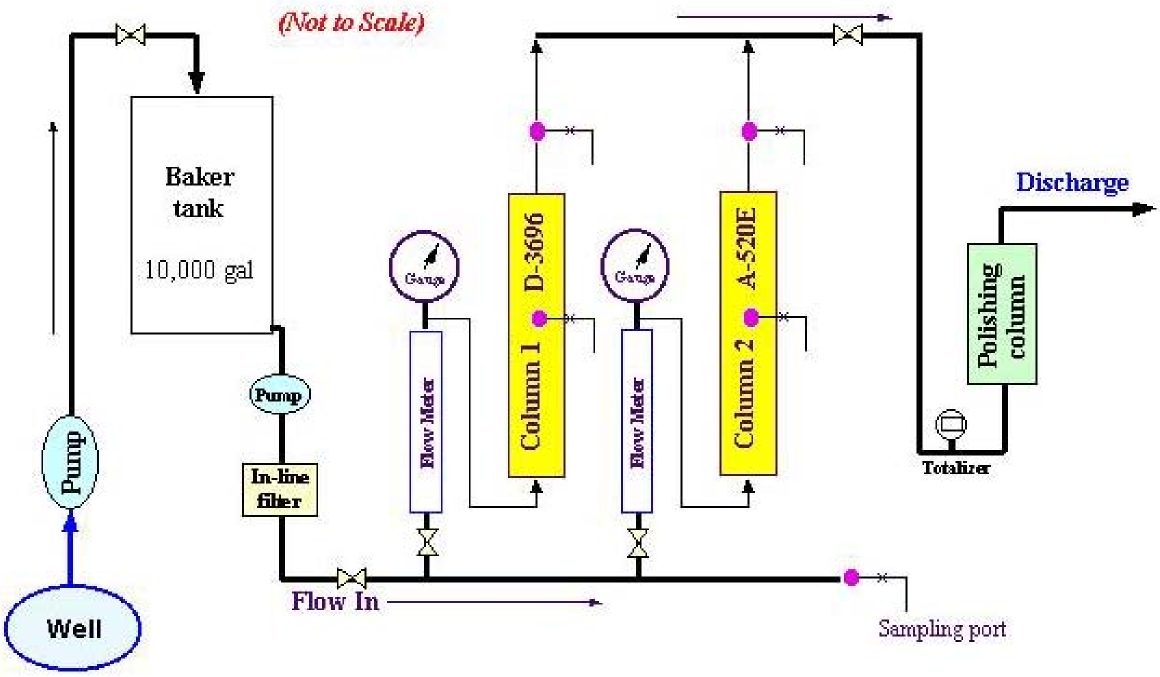

Figure 4. Resin column assembly and flow diagram used for the pilot-scale field experiment at Edwards AFB. Column 1 was packed with the Purolite bifunctional D-3696 resin and the column 2 was packed with the monofunctional A-520E resin. The column dimensions were 2" in diameter and ~11.5" in depth, and the flow rate was set at approximately 500 mL/min per column. The influent perchlorate concentration in groundwater was ~400 µg/L throughout the experiment. A polishing column was used to ensure perchlorate capture before discharging the treated water.

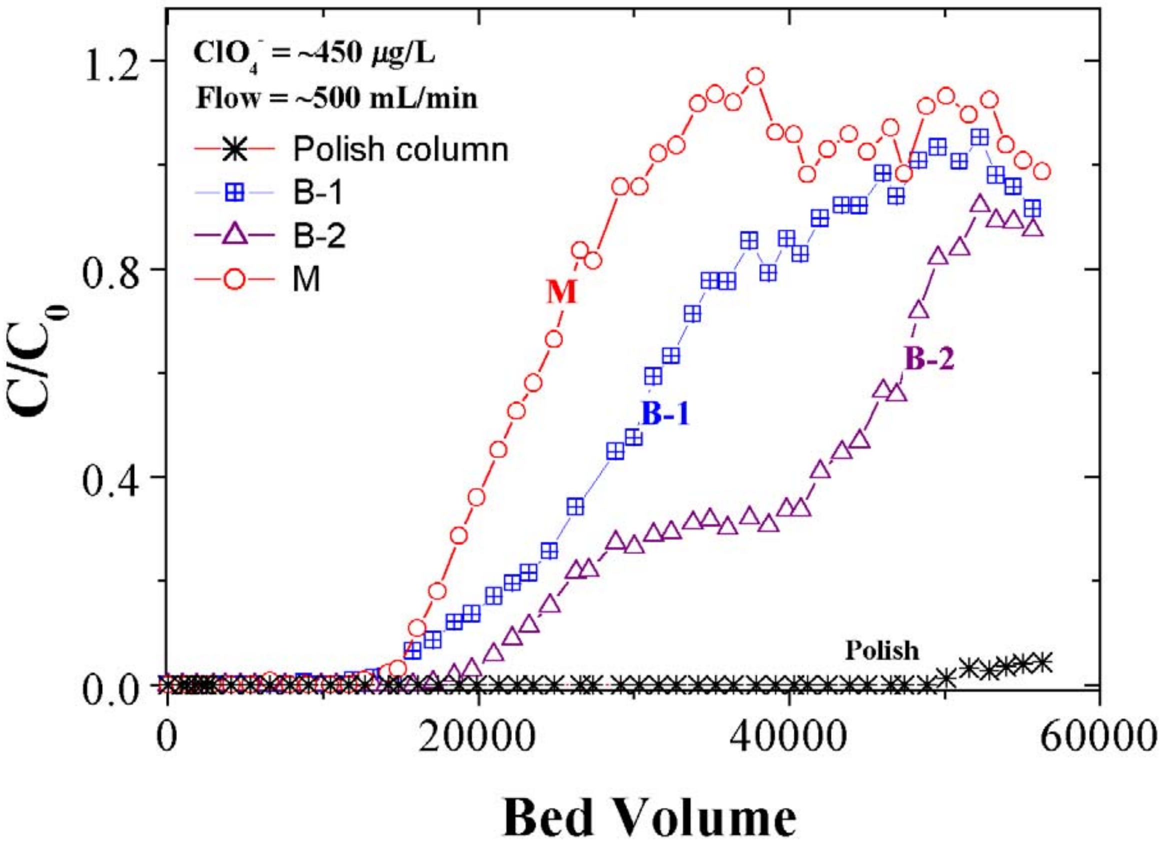

Fig. 5. Breakthrough curves of perchlorate in both the monofunctional (M) and bifunctional (B) resin columns used for groundwater treatment at Edwards AFB. Note: B-1 and B-2 refer to the breakthroughs at the middle and outlet ports of the bifunctional resin bed. Perchlorate breakthrough on the polish column was also plotted.

Fig. 6. Fouled resin columns (A and B) as a result of excessive iron oxide precipitation and/or deposition (from the Baker tank) and bio-fouling. Column C was used in the second run, showing a much lower degree of fouling (used a 1-µm in-line filter).

4.2 REGENERATION OF RESIN COLUMNS

Both the bifunctional and monofunctional resin columns were then subjected to regeneration using ORNL's proprietary $FeCl_3$-HCl regeneration technique. The regenerant solution was comprised of about 1 M $FeCl_3$ and 4 M HCl. The elution profiles of perchlorate in the regenerant solution are shown in Figure 7. As was observed in the initial bench-scale experiment (Figure 2), we found a rapid desorption of perchlorate from the columns, and the maximum effluent concentrations reached as high as ~8,000 mg/L for the bifunctional resin and ~6,000 mg/L for the monofunctional resin column. In comparison with the initial ClO_4^- concentration in groundwater (~0.45 mg/L), this is equivalent to a concentration factor of ~18,000 and ~13,000 for perchlorate, indicating the effectiveness of the $FeCl_3$ regenerant in stripping off ClO_4^- from the resin. Nearly 100% of sorbed ClO_4^- was stripped off the monofunctional A-520E resin bed after eluting with ~6 bed volumes of the regenerant solution. However, only about 76% of sorbed ClO_4^- was stripped off the bifunctional D-3696 resin bed after ~5 bed volumes of the regenerant solution had passed through the column (Figure 7). This observation was attributed to the fact that the resin bed was fouled or clogged with iron oxyhydroxides and/or biomass so that part of the exchange sites on the resin bed was not effectively regenerated. This was especially true for the bifunctional resin, which is macroporous and functionalized with large trihexylamine functional groups (Gu et al., 2000). In other words, the bifunctional resin beads are perhaps more susceptible to fouling and clogging than those of the Purolite A-520E resin. Indeed, further experimentation indicated that a nearly 100% regeneration of the bifunctional resin was achieved when the resin bed was not severely fouled (discussed in the following section).

The regenerated resin beds were washed with dilute HCl solution (<0.01%) and water before they were returned for groundwater treatment. Approximately 20 to 30 bed volumes of dilute acidic washing solution were necessary to rinse off the residual ferric chloride in the resin bed. Analysis of the composite samples indicated that perchlorate was not detected in this acidic washing solution (Table 6), as can be fully expected. Therefore, this acidic washing solution could readily be neutralized with either bicarbonate or hydroxides and be disposed of in situ (e.g., as treated groundwater).

4.3 RE-EVALUATION OF RESIN PERFORMANCE AND REGENERATION

After regeneration, both the bifunctional and monofunctional resin beds were returned for continuation of groundwater treatment at Edwards AFB on August 31, 2001. In addition, a fresh bifunctional resin bed was prepared and run in parallel with the two regenerated columns because these two columns were anticipated to perform poorly as a result of the significant fouling that occurred in the previous run. This would also provide another opportunity to assess bifunctional resin performance without the fouling. The flow rate was again set at ~500 mL/min for the two regenerated resin columns but was at ~700 mL/min for the fresh bifunctional resin bed. A 0.5-µm in-line filter was used to remove most of the particulates and biomass from the Baker tank. Results indeed indicate that, without significant fouling, the fresh bifunctional resin bed (FB, Figure 8)

Table 6. **Analysis of the composite $FeCl_3$-HCl regenerant and dilute HCl washing solutions used for the regeneration of the bifunctional D-3696 resin bed.**

Sample	**Volume** (L)	**ClO_4^-** (mg/L)	**Al** (mg/L)	**Ca** (mg/L)	**Mg** * (mg/L)	**Mn** * (mg/L)	**Ni** (mg/L)
	$FeCl_3$-HCl regenerant solution						
Composite 1	1.13	6450	1.09	5.84	35.1	9.81	0.80
Composite 2	1.01	1750	0.95	0.51	50.5	6.43	0.15
Composite 3	0.42	150	0.71	0.33	44.8	5.17	0.10
	Dilute HCl washing solution						
Composite A	5.45	0	0.12	0.95	74.9	2.47	0
Composite B	6.21	0	0.03	0.01	0	0	0

*Results of Mg and Mn analyses were subjected to the interference by a high concentration of Fe in the regenerant solution as analyzed by the atomic absorption spectrometry.

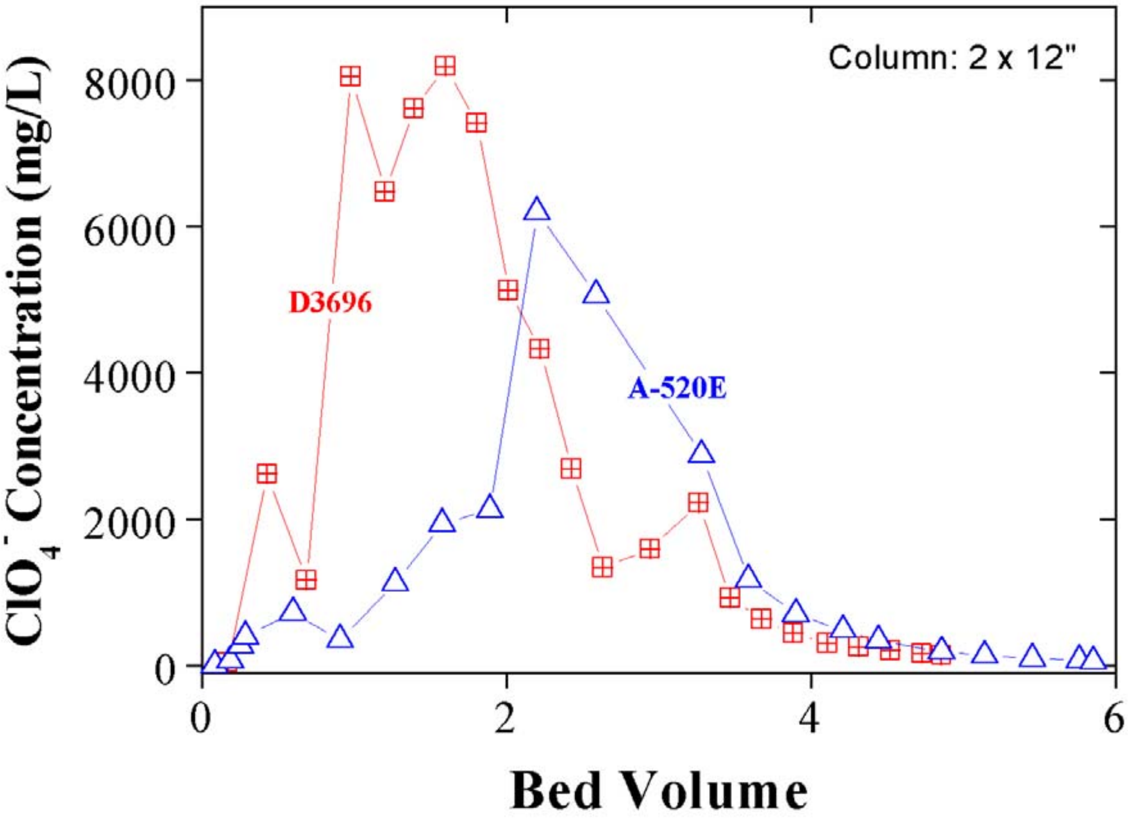

Fig. 7. Perchlorate elution profiles during the regeneration of the bifunctional (D-3696) and monofunctional (A-520E) resin columns used for the pilot-scale field experiment at Edwards AFB.

performed much better than the same bifunctional resin bed from the previous run (with fouling). Significant breakthrough of perchlorate in this fresh bifunctional resin bed occurred after ~40,000 bed volumes of groundwater had been treated, despite that a relatively fast flow rate (~700 mL/min) was used. Again, in the previous run, the same bifunctional resin bed treated only ~20,000 bed volumes of groundwater before a significant breakthrough occurred (running at ~500 mL/min) (B, Figure 8).

The two regenerated resin columns performed fairly well (Figure 8) considering the severe fouling that had previously occurred. The regenerated bifunctional resin bed (BR, Figure 8) actually performed somewhat better than its precursor with respect to the initial breakthrough of perchlorate. However, its performance was about 30-40% lower than that observed on the fresh bifunctional resin bed, which was again attributed to fouling and an incomplete regeneration. Similar results were obtained for the regenerated monofunctional resin bed (MR, Figure 8). From these studies, it is obvious that the effectiveness of regeneration could not be judged solely on the basis of the performance of these two regenerated resin columns.

To further evaluate the regeneration and performance of the bifunctional resin, the fresh bifunctional resin bed used in the second run also was regenerated and re-evaluated. In addition, the monofunctional resin bed was subjected to a second regeneration. The elution profiles of perchlorate in the regenerant solutions of these two columns are shown in Figure 9. Results again indicated a rapid desorption of perchlorate from the column and, with as little as ~2 bed volumes of regenerant solution passed through the column, ~95% of sorbed perchlorate was recovered (Figure 9). To our surprise, the maximum effluent ClO_4^- concentration reached as high as ~60,000 mg/L or ~600 mM. In comparison with the initial ClO_4^- concentration in groundwater (~0.45 mg/L), this is equivalent to a concentration factor of ~133,000 for perchlorate. On the monofunctional resin bed (second regeneration), the maximum perchlorate concentration reached ~18,000 mg/L, which was also much higher than that observed in the previous run (Figure 7). These observations again demonstrate the effectiveness of the $FeCl_3$-HCl regenerant solution in stripping off ClO_4^- from the Type-I resins that are highly selective for ClO_4^- sorption.

5. CONCLUSIONS AND IMPLICATIONS

A pilot-scale field trial at Edwards AFB demonstrated the effectiveness of using *selective* anion exchange resins to remove ClO_4^- from contaminated groundwater and the efficiency of a novel $FeCl_3$-HCl regeneration technology (Gu et al., 2001). At an influent ClO_4^- concentration of 450 μg/L, the bifunctional resin was able to treat about 40,000 bed volumes of groundwater (lasting about 4 weeks) before a breakthrough of ClO_4^- was observed. The spent resin column was successfully regenerated using the $FeCl_3$-HCl regenerant solution, and nearly 100% sorbed ClO_4^- was recovered with as little as about 2 bed volumes of regenerant solution having passed through the column. Obviously, a combination of *selective* ion exchange and the $FeCl_3$-HCl regeneration technologies are promising in remediating groundwater contaminated with ClO_4^- with both a greatly increased treatment efficiency as well as a reduced frequency of resin regeneration compared to the waste brine production and disposal of conventional non-selective ion-exchange

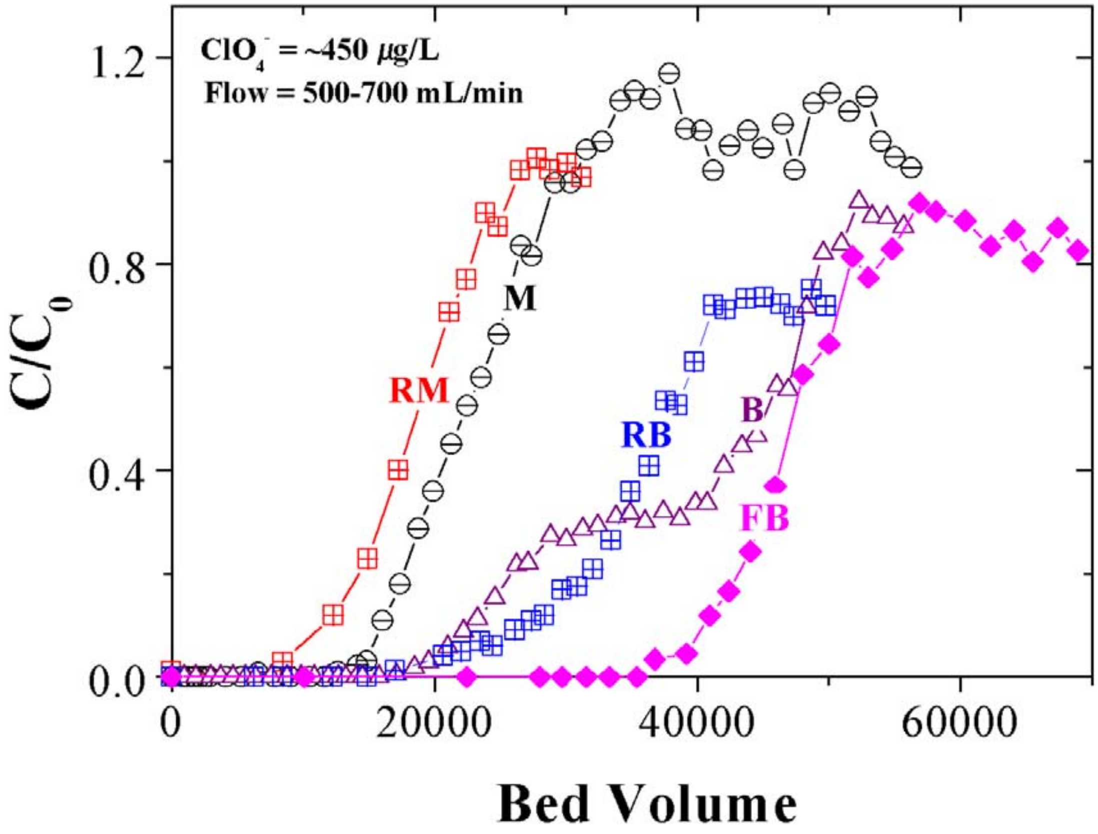

Fig. 8. Breakthrough curves of perchlorate in both the monofunctional (M) and bifunctional (B) resin columns before and after regeneration (R). FB refers to the breakthrough of perchlorate in the fresh bifunctional resin column (without fouling).

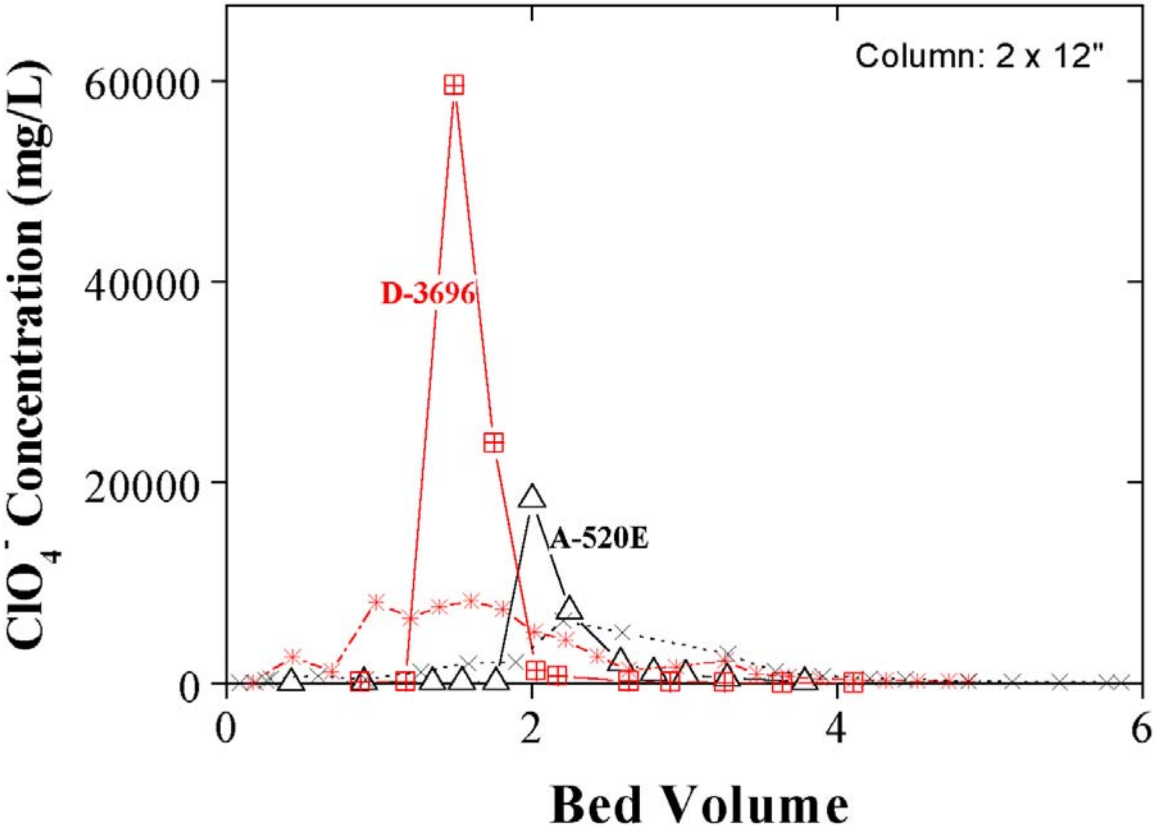

Fig. 9. Perchlorate elution profiles during the regeneration of the unfouled bifunctional resin bed and the second regeneration of the monofunctional resin bed. The dotted lines show the regeneration of those fouled columns for comparison (from Figure 7).

and regeneration techniques. On the basis that the bifunctional resin was able to treat about 40,000 bed volumes of contaminated groundwater containing 450 μg/L ClO_4^- (or about 100,000 bed volumes of water containing 50 μg/L ClO_4^-) (Gu et al., 2000a), the waste regenerant production is estimated to be <0.005% of the amount of groundwater treated. This is approximately 2 orders of magnitude less than what may be produced by using conventional NaCl brine regeneration technique (Batista et al., 2000; Brown et al., 2000).

In addition to a significantly reduced secondary waste production, one of the greatest advantages accrued from using selective ion exchange and its regeneration is perhaps the ability to leave the treatment system operating for months in the field before regeneration is needed, minimizing the operational and maintenance cost, as mentioned previously. Of course, duration of the treatment phase will depend on such factors as the influent ClO_4^- concentration, size of the treatment unit, and flow rate (Gu et al., 2000a). Additionally, only a relatively small treatment unit may be required because the treatment system is highly efficient and can handle a relatively high flow rate (e.g., 1–2 bed volumes per minute). This may translate into a significantly reduced capital cost. As an example, a rough estimate is that a 1000-gpm-treatment unit may cost between \$600,000 and \$1 million, which includes the cost of the resin itself, the treatment and regeneration systems, site preparation, and labor. Additional cost savings may also be realized when several 1000-gpm-treatment units are in operation simultaneously so that only one central regeneration facility may be needed for the regeneration and perchlorate-destruction.

By using the $FeCl_3$-HCl regeneration technique, additional treatment options are available to completely destroy ClO_4^- in the regenerant solution so that the spent regenerant solution can be reused or disposed of without the presence of ClO_4^- as a hazardous component. Recently, a new proprietary methodology also was developed to completely destroy ClO_4^- in $FeCl_3$ solution at ORNL. Perchlorate was found to decompose into non-hazardous Cl^- and water under certain catalytic conditions, and a complete reaction occurs within a few hours to 1 day with an initial ClO_4^- concentration at about 7,000 mg/L. While perchlorate is completely decomposed, the destruction process does not alter properties of the regenerant solution, so it can be reused. Noting that perchlorate is highly concentrated in the first 2 bed volumes of the $FeCl_3$ regenerant solution (Figure 9), only relatively small volumes of the regenerant solution need to be treated. Therefore, depending on the regulatory requirements and the cost of ClO_4^- waste disposal, this additional treatment process may have notable economic implications in that not only is a reduced volume of regenerant solution required but also the disposal of hazardous waste regenerant solutions containing ClO_4^- is eliminated.

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