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EXECUTIVE SUMMARY

The primary objective of this project was to evaluate a novel bifunctional anion exchange resin for the cost-effective, in situ treatment of groundwater contaminated with perchlorate (ClO_4^-). Both laboratory and field studies were performed to determine the selectivity and capacity of the bifunctional synthetic resins to sorb ClO_4^- from simulated or actual contaminated groundwater. A number of synthetic bifunctional resins, including two commercial versions made by Purolite International and three commercially-available, mono-functional resins, were tested. Initial laboratory batch and column breakthrough studies determined the best synthetic resins and the optimal conditions for the field experiment. Laboratory results indicated that the bifunctional synthetic resins, D-3696 (made by Purolite International) and RO-02-119 (prepared at the University of Tennessee-Knoxville), were highly selective toward ClO_4^- and performed ~5 times better than the best commercial nitrate resin (Purolite® A-520E) and more than an order of magnitude better than some nonselective commercial resins (e.g., Amberlite® IRA-900). The bifunctional resins were particularly effective in removing trace quantities of ClO_4^- in groundwater to below the detection limit (~3 μg/L). A field trial demonstrated that the bifunctional resin (D-3696) was able to treat ~110,000 bed volumes of groundwater before a 10% breakthrough of ClO_4^- occurred under the column flow-through conditions (running at ~2 bed volumes per minute). On the other hand, the Purolite® A-520E resin was able to treat ~23,000 bed volumes of groundwater under the same experimental conditions. No pretreatment was needed to remove either dissolved organic matter or other competing anions (such as SO_4^{2-} or NO_3^-) in the groundwater, and the treatment process did not alter the water quality by removing or adding secondary by-products because of the high selectivity of the bifunctional resins. The results thus demonstrated that the new bifunctional resin could provide an efficient and cost-effective solution to the removal of ClO_4^- from groundwater because of its reduced cost in operation and maintenance, resin regeneration, and waste disposal.

INTRODUCTION

The perchlorate (ClO_4^-) anion 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, because of kinetic barriers in its reactivity with other organic or inorganic constituents (Urbansky, 1998). Large volumes of perchlorate-containing compounds have been disposed of in the environment since the 1950s. The presence of this material in the environment poses a potential threat to ecological receptors and the public. The California Department of Health Services has set an action level of 18 μg/L (ppb) for perchlorate in groundwater (Urbansky, 1998).

Treatment technologies capable of removing ClO_4^- from groundwater are urgently needed. Water utilities, in particular, need treatment methods that can reliably reduce ClO_4^- concentrations to low or non-detectable levels. Because ClO_4^- ions are nonvolatile and highly soluble in water, they cannot be removed from water by conventional filtration, sedimentation, or air-stripping methodologies. To be useful, a drinking-water treatment method must be cost effective, acceptable to regulatory agencies and the public, and generate a minimum amount of secondary waste. In addition, a treatment method must not be adversely affected by other components in the water and it must not be responsible for other water quality or distribution system problems. Urbansky (1998) has outlined some candidate treatment technologies and pointed out the drawbacks of each. Membrane-based technologies, such as reverse osmosis, were thought impractical as were conventional anion exchange resins. The cationic chemical nitron precipitates perchlorate efficiently and might be suitable for remediation of high concentrations of perchlorate. However, the cost and waste disposal issues render this technology unacceptable. Given the chemical inertness of ClO_4^- to reduction reactions and the small concentrations involved, it seems clear that chemical reduction is not feasible. Urbansky holds out more hope for electrochemical reduction methods, particularly when catalyzed by a solution redox couple. Bioremediation methods appear to be the most economical and technically feasible remediation methods at the moment. However, a method based on a live bacteria and added nutrient gradients is unlikely to be embraced by the drinking water industry.

Highly selective anion exchange resins offer considerable advantages over conventional (unselective) resins in the treatment of perchlorate contaminated groundwater. Oak Ridge National Laboratory (ORNL) has developed anion-exchange resins that have a bias for the sorption of large poorly hydrated anions such as pertechnetate (TcO_4^-) and ClO_4^- anions from contaminated groundwater (Brown et al., 1995; Brown et al., 1997; Brown et al., 1996). Highly selective bifunctional anion-exchange resins were developed in U.S. Department of Energy (DOE) sponsored work for the sorption of TcO_4^- from contaminated groundwater at the Paducah Gaseous Diffusion Plant site, Kentucky (Gu et al., 1998). Groundwater at several DOE sites is contaminated with the radionuclide Tc-99 which exists in the chemical form of TcO_4^- anions in oxygenated environments (Gu et al., 1996; Gu and Dowlen, 1996). Pertechnetate, like ClO_4^-, is highly mobile in underground aquifers. The concentration of TcO_4^- ion is 4 to 6 orders of

magnitude lower than the other anions found in groundwater, such as chloride, sulfate, nitrate, and bicarbonate. The objectives of this study were to perform both laboratory and field flow-through experiments to determine the selectivity and longevity of the ORNL-developed bifunctional resins in comparison with a small selection of commercially available resins for ClO_4^- removal. The most effective resin was tested in a scale-up field demonstration experiment.

MATERIALS AND METHODS

Synthetic Resins

All synthetic resins investigated were anion-exchange resins based on a poly(vinylbenzyl chloride) backbone, cross-linked with divinylbenzene (DVB), which contains chloromethyl reaction sites that were functionalized by reaction with various trialkylamine groups to create quaternary ammonium strong-base exchange sites. A systematic study was performed to evaluate the effects of different trialkyl functional groups (or their combinations) in the resin, as well as the percentages of DVB cross-linking, on the resin's reaction kinetics and selectivity for sorption of ClO_4^-. All synthetic resins were prepared in the laboratory of Professor Spiro Alexandratos of the Department of Chemistry, University of Tennessee, Knoxville. A commercial scale-up version of one of Prof. Alexandratos' resins was prepared to our specifications by Purolite International (Purolite® D-3696). It was prepared from a DVB cross-linked polystyrene that was chloromethylated to provide functional sites. This resin backbone has different properties than the resin based on a poly(vinylbenzyl chloride) backbone, and an iterative process of resin synthesis and testing was conducted with Purolite to develop a resin with properties that met our specifications. Details of the preparation of the mono-functional and bifunctional resins prepared at UTK and their characteristics will be published elsewhere (Bonnesen et al., 1999). Three commercially-available anion-exchange resins were also selected for investigation, and the performance of these resins forms a benchmark that is the basis for comparison with the new resins. These commercial resins are Purolite® A-520E (a resin with triethylamine exchange sites), Sybron Ionac SR-6 (a resin with tributylamine exchange sites), and Amberlite® IRA-900 (a resin with trimethylamine exchange sites). The general properties of these synthetic resins are listed in Table 1. Based on the initial laboratory screening test, two synthetic resins and one commercial resin (i.e., Purolite® A-520E) were selected for further laboratory column and field flow through experiments.

Table 1. **General properties of synthetic resins[1]**

Resin	Amine	%DVB	Mesh Size	TAEC [2] (meq/g)
Monofunctional resins, amine chain length				
VP-01-165	$(Methyl)_3N$	10	40 – 60	3.77
VP-01-168	$(Ethyl)_3N$	10	40 – 60	2.84
VP-02-152	$(Propyl)_3N$	10	40 – 60	2.33
VP-02-083	$(Butyl)_3N$	10	40 – 60	1.66
Monofunctional resins, % cross-linking				
VP-02-152	$(Propyl)_3N$	10	40 – 60	2.33
VP-02-138	$(Propyl)_3N$	15	40 – 60	1.58
VP-02-072	$(Propyl)_3N$	25	40 – 60	1.32
Amberlite® IRA-900	$(Methyl)_3N$	5	16 – 50	3.56
Purolite® A-520E	$(Ethyl)_3N$	5	16 – 50	2.80
Sybron Ionac® SR-6	$(Butyl)_3N$	5	16 – 50	1.80
Bifunctional resins, chain length of small amine				
VP-02-092	Me_3N/Hex_3N	5	40 – 60	3.20
RO-02-74	Et_3N/Hex_3N	5	40 – 60	3.04
RO-02-119	Et_3N/Hex_3N	5	40 – 60	2.53
RO-02-61	Pr_3N/Hex_3N	5	40 – 60	2.15
RO-02-217	Pr_3N/Hex_3N	5	60 – 200	2.06

1   All resins had a backbone which was a copolymer of vinylbenzyl chloride and divinylbenzene (DVB), the latter added as a cross-linking agent.

2   TAEC = Total anion exchange capacity.

Determination of Distribution Coefficients (K'_d) for ClO_4^- Sorption on Resins

Perchlorate sorption on synthetic resins was determined by bringing 0.1g resin (dry weight equivalent) of ion exchange resin in contact with a solution containing a varying amount of ClO_4^- (100 mL of test solution). The test solution was a simulant of a typical contaminated groundwater found in Redlands, California, and 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. The initial ClO_4^- concentration varied from 0.1 to 100 mg/L and was therefore about 1 to 4 orders of magnitude lower than that of the background anion concentration. An aliquot of sample was taken at a given time interval and filtered with a PTFE syringe filter (0.45 μm). The samples were then analyzed for ClO_4^- concentration by means of a Dionex ion chromatograph equipped with a GP-40 gradient pump, an ED-40 electrochemical detector, and an IonPac ASA-11 analytical column (Dionex, California). The external water mode was used because a strong base (0.1 M NaOH) was used as the mobile phase (Jackson, 1998). The detection limit is approximately 3 μg/L ClO_4^- (3 ppb).

The distribution coefficient for sorption of ClO_4^- to the resins, K'_d (in mL/g), was calculated as the ratio of ClO_4^- sorbed (expressed as mg per gram of resin) to the concentration of ClO_4^- remaining in solution (as mg/mL), that is,

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

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 solution (expressed as g/mL). The apparent distribution coefficient was measured as a function of time, and equilibrium was assumed to be reached when the apparent K'_d value no longer changed.

Laboratory and Field Column Flow-Through Experiments

Laboratory column flow-through experiments were performed using small glass chromatographic columns (10 x 40 mm). Resins were wet-packed to avoid entrapped air bubbles within the column, and a high precision HPLC pump (ISCO, Model 2350) was used for feeding solutions at a constant rate of 30 mL min^{-1}. The effective linear velocity was ~76 cm/min assuming an effective porosity of 0.5 for the resin bed. The columns were initially equilibrated by pumping the background solution consisting 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 for at least 1 h before an input of ClO_4^- (~1 mg/L) with the same background ionic composition. The effluent solution was collected at a given time interval and analyzed for ClO_4^- concentration as described.

Additionally, a sample of groundwater contaminated with ClO_4^- was obtained from the CrimSouth well, Redlands, California (sampled by HSI GeoTrans, April 19, 1996), and used for the column flow-through experiment so that the effect of groundwater composition on resin performance could be evaluated. The anionic composition of CrimSouth groundwater and the synthetic test solution are listed in Table 2 for comparison. Because the CrimSouth groundwater contained a low ClO_4^- concentration (~16 ppb), approximately 1 mg/L ClO_4^- (as $NaClO_4$) was added to the groundwater to accelerate the breakthrough of ClO_4^-.

Based on the results of laboratory-batch and column studies, a small-scale field trial of two different batches of the bifunctional resins was performed in parallel with a field trial of one

of the best commercial nitrate selective resins (Purolite® A-520E). The field trial was composed of three pairs of ion-exchange columns with different resins (25 x 115 mm glass columns, Figure 1), and the field test started on August 19, 1998 at a site in Northern California (Figure 2). Each pair of columns was in a lead-and-lag configuration with groundwater passing through one column before it passed through the second.

Table 2. Anion composition of the synthetic test solution and a typical groundwater from CrimSouth well, Redlands, CA.

Anion	Synthetic test solution	CrimSouth groundwater
HCO_3^- (mg/L)	183	~180
F^- (mg/L)	0	0.94
Cl^- (mg/L)	106	19.6
NO_3^- (mg/L)	31	59.4
$SO_4^=$ (mg/L)	49	63.5
ClO_4^- (mg/L)	0.1–100	0.016
pH	8.4	8.1

The first set of columns used a commercial resin (Purolite® A-520E, a monofunctional resin with triethylamine exchange sites), and the second set used a bifunctional resin (D-3696, with trihexylamine and triethylamine exchange sites) made by Purolite to our specifications. The third set of resins were made at the University of Tennessee, Knoxville. The results obtained with the UTK-prepared columns were anomalous in that the performance was inconsistent with previous results. These results will not be discussed because it is believed they are not representative of typical performance. Each of these anion exchange resins was initially in the chloride form. The contaminated groundwater was pumped directly through the resin columns without pre-treatment at an initial flow rate of ~200 mL/min per column set. The inlet pressure ranged from ~20 to 30 psi and varied slightly in each individual column. The flow rate was kept relatively constant (between 150 and 210 mL/min) by adjusting the inlet pressure (or flow rate) periodically. The actual bed volumes of groundwater passing through the columns were calculated on the basis of the flow rate in a given time period and the actual run time measured by the pump timer. Concentrations of ClO_4^- in the influent and the effluents of the lead and lag columns were monitored three times a week and analyzed by means of ion chromatography as described previously. The effluent was then diverted to a collection tank where samples were analyzed prior to disposal.
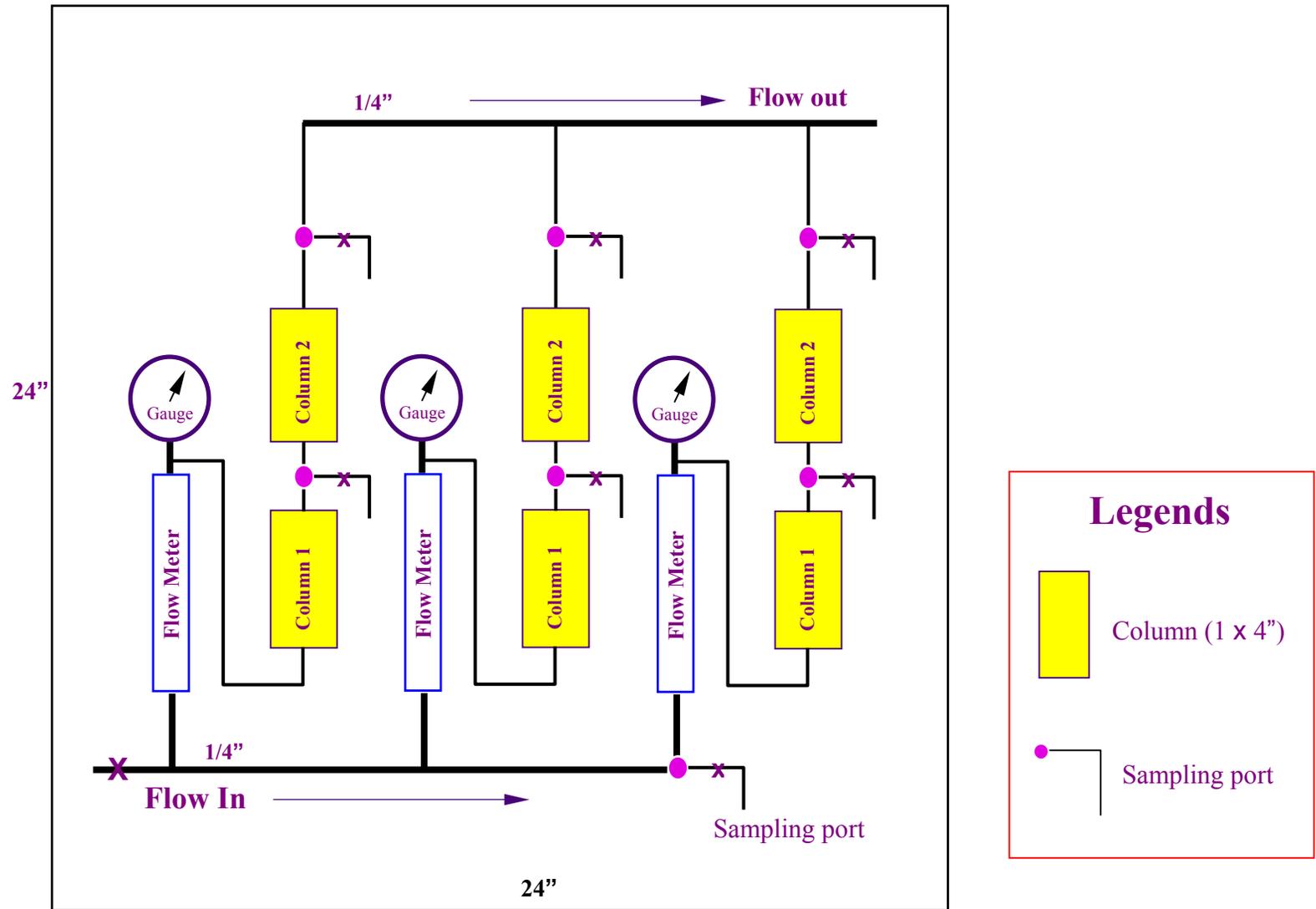
Figure 1. Design of the field experiment for flow-through column testing.

Figure 2. Field experimental site in Northern California.

RESULTS AND DISCUSSION

Sorption Characteristics of ClO_4^- on Synthetic Resins (Kinetics and Isotherms)

Measurement of ClO_4^- distribution coefficients indicated that ClO_4^- is strongly sorbed to the anion exchange sites of all of the resins investigated in this study. More than 98% of the ClO_4^- was removed from the test solution with an initial concentration ranging from 0.1 to 100 mg/L in a 24-h period (Figure 3). The bifunctional resins, RO-02-119 and VP-02-217, were particularly effective in removing ClO_4^- and, at an initial concentration of ~10 mg/L, the equilibrium concentration was near or below the detection limit (~3 μg/L). Sorption isotherms shown in Figures 3 and 4 indicate that sorption of ClO_4^- did not follow a linear partitioning but may be described by the classical Langmuir isotherm (Langmuir, 1918), that is,

$$ q = \frac{K_{lm} q_{max} C}{K_{lm} C + 1} \, , $$

where q is the amount of ClO_4^- sorbed by synthetic resins (mg/g), K_{lm} is the sorption coefficient, and q_{max} is the maximum quantity or capacity of ClO_4^- sorbed.

The amount of ClO_4^- sorbed by the synthetic resins was also time-dependent (Figure 4). The sorption process did not appear to reach an equilibrium in 2 weeks. These results are consistent with previous studies of pertechnetate (TcO_4^-) sorption on these resins (Bonnesen et al., 1999) and are explained by the microporous nature of the resin beads so that diffusion of TcO_4^- (or ClO_4^-) into internal sorption sites of resin beads became the rate-limiting step. Note that the sorption curves for of ClO_4^- on the RO-02-119 resin at 24 and 336 h appeared to overlap (Figure 3). This is because only a limited amount of ClO_4^- was added to the initial solution, most of the ClO_4^- was removed quickly irrespective of the equilibrium time (either 24 or 336 h).
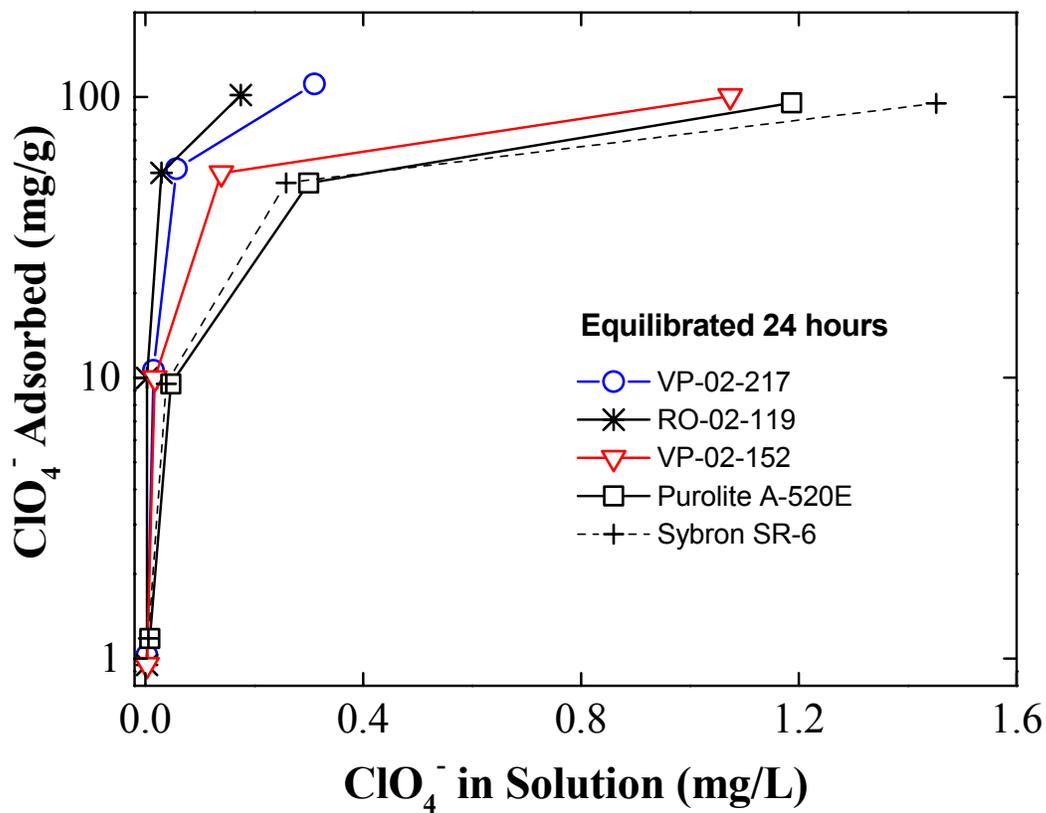
Figure 3. Sorption isotherms of ClO_4^- on synthetic resins.
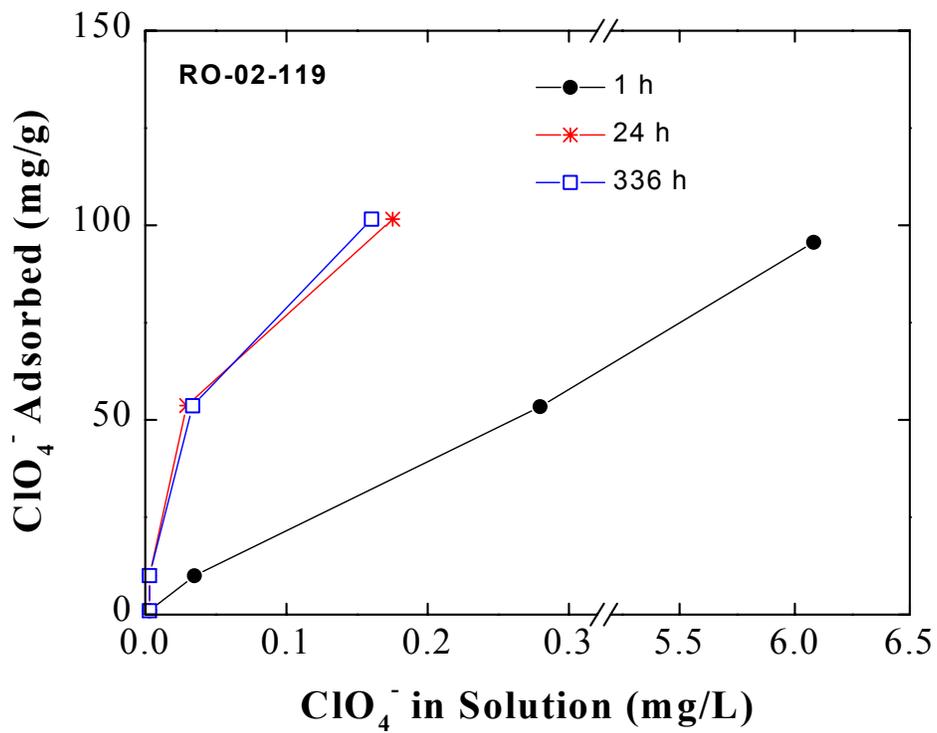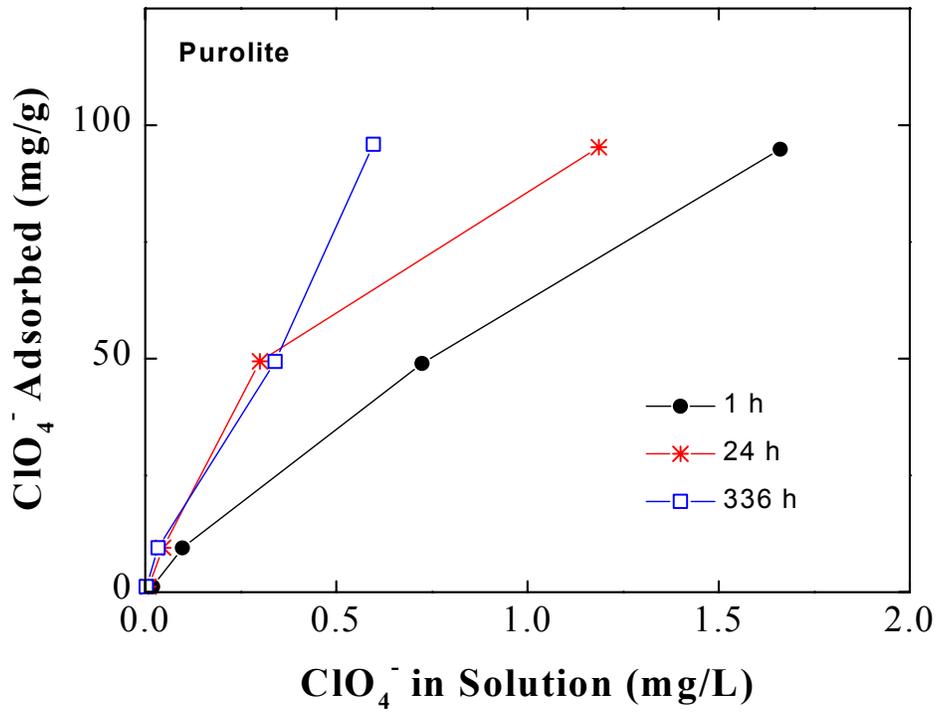
Figure 4. Sorption of ClO_4^- on Purolite® A-520E and synthetic resin RO-02-119 at varying equilibration times.

Selectivity of Resins

The partitioning coefficient (K'_d), which defines the selectivity of the resin to a specific anion, was calculated based on the sorption isotherms shown in Figures 3 and 4. However, because sorption of ClO_4^- on synthetic resins did not follow a linear partitioning, K'_d values listed in Tables 3 and 4 are both concentration- and time-dependent. Nevertheless, results indicated that the ORNL-developed bifunctional resins are much more selective toward ClO_4^- (K'_d values are 2 - 5 times higher) than are the two commercial resins (Purolite[®] A-520E and Sybron Ionac[®] SR-6). At an initial concentration of ~1 mg/L ClO_4^-, the bifunctional resins removed ClO_4^- in solution to below the detection limit (~0.003 mg/L, Table 3) within 1 h. The synthetic monofunctional resin VP-02-152 (tripropylamine resin) reduced the perchlorate to below detection limits within 24 h. On the other hand, the commercial resins Purolite[®] A-520E and Sybron Ionac[®] SR-6 took ~1 week to remove ClO_4^- below the detection limit. The bifunctional resins are therefore particularly effective in removing trace quantities of ClO_4^- in aqueous solution as it is commonly encountered under natural groundwater conditions. To be cost-effective, treatment of trace quantities of ClO_4^- contamination in groundwater (e.g., parts per billion levels) requires a highly selective anion exchange resin.

Table 4 lists the $K'd$ values of a group of synthetic bifunctional resins at an initial ClO_4^- concentration of ~10 mg/L. Included are data for two commercial versions of the bifunctional resins (D-3696 and D-3694) made by Purolite to our specifications which were also tested under the same experimental conditions. The laboratory prepared tripropylamine monofunctional resin (VP-02-152) showed good sorption characteristics as well. Results again indicate that the bifunctional resins have superior selectivity for ClO_4^- sorption compared to the commercial Purolite[®] A-520E resin. Even at an initial ClO_4^- concentration of 10 mg/L, the RO-02-119 and VP-02-217 resins were able to remove ClO_4^- to below its detection limit. The two commercial versions of the bifunctional resins, particularly the D-3696 resin, performed very well in removing ClO_4^-. This resin was later used for the field trial in California.

Results presented in Tables 3 and 4 are also consistent with those observed for pertechnetate (TcO_4^-) removal by the synthetic resins. We have detailed measurements for the sorption of pertechnetate from a solution containing 0.06 M sodium sulfate, 0.06 M sodium chloride, and 0.06 M sodium nitrate as the background (so called Groundwater Test Solution). Values for K'_d after 24 h from this solution were 12,800 mL/g for the Purolite resin and 20,700 mL/gm for the Sybron resin. The synthetic or laboratory-prepared resins VP-02-217, RO-02-119, and VP02-152 had K'_d values from this solution of 48310 mL/g, 38040 mL/g, and 22340 mL/g respectively. We have done a few measurements as a function of the total ionic concentration of the background electrolyte, and the order of magnitude of the K'_d for pertechnetate sorption increases to 10^6 mL/g for the better resins in a dilute simulant that is closer to a true groundwater (Bonnesen et al., 1999).

A systematic study of the K'_d values as a function of the length of the hydrocarbon chain (size of the alkyl groups), and the percentage of divinylbenzene (DVB) added as a crosslinking agent, were also performed for ClO_4^- sorption. Results indicated that the K'_d values (24-h measurement) increased in the series of methyl<ethyl<propyl in the order expected from measurements on the sorption of pertechnetate (Column 8, Table 5). However the value for the

resin with tributylamine functional groups shows a decrease. If these values are corrected for the difference in exchange capacity of the resins, this is still a decrease at the larger size alkyl group. We did not observe this decrease in K'_d with pertechnetate sorption until the size of the alkyl group reached six carbons (trihexylamine). We interpreted that decrease as the result of kinetic effects, and it may be that kinetic inhibition is more significant for perchlorate than for pertechnetate sorption. The same trend seems to be occurring on the influence of cross-linking on the value of K'_d. The values, even when corrected for the differences in exchange capacity, show a sharp drop with increasing cross-linking. Again, this could be interpreted as showing that the influence of cross-linking is to make the resin structure "tighter," inhibiting the diffusion of perchlorate into the inner recess of the resin beads. For perchlorate sorption to the bifunctional resins, the K'_d values indicate that the triethylamine/trihexylamine resin is the most selective. This was not the case for pertechnetate sorption. The bifunctional resin based on the combinations of tripropylamine/trihexylamine and tributylamine/trihexylamine were more selective for 24-h measurements of K'_d. In small column experiments, we found that the triethylamine/trihexylamine combination had superior pertechnetate sorption performance due to kinetic effects. A conclusion is that the kinetics of sorption of perchlorate to these resins is inhibited relative to that of pertechnetate, and a different combination of amines might be more appropriate for the application to perchlorate-contaminated groundwater.

Table 3. Distribution coefficients (K'_d) of ClO_4^- on synthetic bifunctional resins (VP-02-217, RO-02-119, and RO-04-012), a synthetic monofunctional resin (VP-02-152), and two commercial resins (Purolite® A-520E and Sybron Ionac® SR-6) [1].

Resin	1 h K'_d (mL/g)	24 h K'_d (mL/g)	168 h K'_d (mL/g)
RO-02-119	>316,000 [2]	>316,000 [2]	>316,000 [2]
VP-02-217	>342,00 [2]	>394,000 [2]	>394,000 [2]
RO-04-012	>325,000 [2]	>325,000 [2]	>325,000 [2]
VP-02-152	96,800	>316,000 [2]	>316,000 [2]
Purolite® A-520E	59,500	143,000	>394,000 [2]
Sybron Ionac® SR-6	47,500	222,000	>394,000 [2]

[1] All K'_d values have a ±5% uncertainty. Experiments were performed with 100 mL test solution and 0.1g dry resin. The initial ClO_4^- concentration was ~1 mg/L, and the equilibrium concentration ranged from 0.0 to 0.03 mg/L.

[2] Equilibrium concentration is below the detection limit (~3 μg/L). The K'_d values should be considered as a minimum because the final concentration (3 μg/L) was used in the calculation of K'_d values.

Table 4. Distribution coefficients (K'_d) of ClO_4^- on synthetic and commercial resins) [1].

Resin	1 h K'_d (mL/g)	24 h K'_d (mL/g)	168 h K'_d (mL/g)
RO-02-119	285,000	>3,330,000 [2]	>3,330,000 [2]
VP-02-217	408,500	714,000	>3,500,000 [2]
RO-04-012	514,000	1,659,000	1,216,000
RO-04-075	224,000	855,000	1,009,000
Purolite® D-3696	164,800	1,877,000	1,842,000
Purolite® D-3694	232,000	749,000	794,000
VP-02-152	144,000	588,000	771,000
Purolite® A-520E	97,000	203,000	217,000
Sybron Ionac® SR-6	65,400	250,000	282,000

[1] All K'_d values have a ±5% uncertainty. Experiments were performed with 100 mL test solution and 0.1g dry resin. The initial ClO_4^- concentration was ~10 mg/L, and the equilibrium concentration ranged from 0.0 to 0.2 mg/L.

[2] Equilibrium concentration is below the detection limit (~3 µg/L). The K'_d values should be considered as a minimum because the final concentration (3 µg/L) was used in the calculation of K'_d values.

Table 5. Comparison of K'_d values for some selected synthetic resins[1].

Resin	Amine	%DVB	Mesh Size	TAEC [2] (meq/g)	24 h $K'd$ (mL/g)	96 h $K'd$ (mL/g)	Tc-24 h $K'd$ (mL/g)
Effect of amine chain length							
VP-01-165	(Methyl)$_3$N	10	40 – 60	3.77	86,800	73,500	6,400
VP-01-168	(Ethyl)$_3$N	10	40 – 60	2.84	166,000	162,000	16,200
VP-02-152	(Propyl)$_3$N	10	40 – 60	2.33	588,000	ND [3]	22,300
VP-02-083	(Butyl)$_3$N	10	40 – 60	1.66	319,000	351,000	31,800
Effect of cross-linking							
VP-02-152	(Propyl)$_3$N	10	40 – 60	2.33	588,000	ND [3]	22,300
VP-02-138	(Propyl)$_3$N	15	40 – 60	1.58	169,000	191,000	20,400
VP-02-072	(Propyl)$_3$N	25	40 – 60	1.32	155,000	154,000	17,300
Amberlite® IRA-900	(Methyl)$_3$N	5	16 – 50	3.56	40,100	46,600	2,500
Purolite® A-520E	(Ethyl)$_3$N	5	16 – 50	2.80	203,000	217,000	12,800
Sybron Ionac® SR-6	(Butyl)$_3$N	5	16 – 50	1.80	250,000	282,000	20,700
Effect of chain length of small amine							
VP-02-092	Me$_3$N/Hex$_3$N	5	40 – 60	3.20	138,000	137,000	13,200
RO-02-74	Et$_3$N/Hex$_3$N	5	40 – 60	3.04	527,000	993,000	40,100
RO-02-119	Et$_3$N/Hex$_3$N	5	40 – 60	2.53	>3,300,000 [4]	ND [3]	38,000
RO-02-61	Pr$_3$N/Hex$_3$N	5	40 – 60	2.15	523,000	>3,300,000 [4]	38,200
VP-02-217	Pr$_3$N/Hex$_3$N	5	60 – 200	2.06	714,000	>3,500,000 [4]	48,300

1. All K'_d values have a ±5% uncertainty. All resins are prepared from a poly(vinylbenzyl chloride) backbone, crosslinked with divinylbenzene (DVB). Initial ClO_4^- concentration was 10 mg/L.
2. TAEC = Total anion exchange capacity.
3. ND = Not determined.
4. K'$_d$ values were estimated as the equilibrium concentration approached zero (with a detection limit of ~3 μg/L).

Column Breakthrough of ClO$_4^-$

Laboratory column results of ClO$_4^-$ breakthrough on the two bifunctional resins (RO-02-119 or RO-04-012) and two commercial resins (Purolite$^®$ A-520E and Sybron Ionac$^®$ SR-6) are presented in Figure 5. The x-axis shows the bed volumes of test solution 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$_0$). When the effluent concentration is equal to the influent, the column is exhausted and it is said to have reached complete "breakthrough." The influent concentration and flow rate were kept constant at 1.1 mg/L ClO$_4^-$ (or 1100 ppb ClO$_4^-$) and 30 mL/min, respectively. The initial ClO$_4^-$ concentration was relatively high in comparison with the ClO$_4^-$ concentration that we expect to be treating in drinking water or groundwater that are known to be contaminated with ClO$_4^-$ (data from HSI GeoTrans, California). Such a relatively high concentration of ClO$_4^-$ was used to accelerate the breakthrough of ClO$_4^-$ in the laboratory experiments. The results indicated that all of these resins exhibited a substantial removal of ClO$_4^-$; less than 8% breakthrough of ClO$_4^-$ was observed after ~5000 bed volumes of test solution were passed through the columns. However, the synthetic resin, RO-02-119, performed the best as predicted from the previous batch studies. No ClO$_4^-$ breakthrough was observed within the instrument detection limit (~3 µg/L) after ~2000 bed volumes of test solution had been treated with this resin column; and less than ~0.5% breakthrough of ClO$_4^-$ was observed after ~5000 bed volumes. On the other hand, the two commercial resins (i.e., Purolite$^®$ 520E and Sybron Ionac$^®$ SR-6) showed an early breakthrough of ClO$_4^-$. Approximately 2% breakthrough of ClO$_4^-$ was observed following treatment of <100 bed volumes of the test solution, and about 8% breakthrough of ClO$_4^-$ was observed after ~5000 bed volumes of test solution passed through these two columns. The RO-04-012 resin performed nearly as well as the RO-02-119 resin, although it showed a slightly higher initial breakthrough (~1%) which remained relatively constant throughout the experiment. Less than 1.5% breakthrough of ClO$_4^-$ was observed after treatment of ~5000 bed volumes of the test solution on this column.

Note that C/C$_0$ increased with time (or with the number of bed volumes) but to a much lesser extent with the two synthetic resins than with the two commercial resins. This property is of particular importance and is attributed to a high selectivity of the two bifunctional resins for ClO$_4^-$ (Tables 3 and 4) since the concentration of ClO$_4^-$ in solution was about 3 to 4 orders of magnitude lower than the background anion concentration (composed of Cl$^-$, HCO$_3^-$, NO$_3^-$, and SO$_4^{-2}$). The high selectivity of the resins for sorption of large, poorly hydrated anions is expected to be the most significant factor for treating groundwater contaminated with only trace quantities of ClO$_4^-$ (e.g., < 0.1 mg/L). As illustrated in Figure 5, an early breakthrough (~2%) of ClO$_4^-$ on the Purolite and Sybron can be attributed to their lower selectivity (Tables 3 and 4) compared with that of RO-02-119. It is also anticipated that a lower initial influent concentration may result in a higher initial fractional breakthrough of ClO$_4^-$ on these two commercial resins, although it will take more bed volumes for complete breakthrough to be achieved. On the other hand, the performance of the synthetic resins would be superior under such circumstances. As the initial influent concentration increases, however, the differences between commercial monofunctional resins and the bifunctional resins may become smaller with respect to ClO$_4^-$ removal within a given time period as the column capacity is being approached.

Figure 5 also shows that an intermittent flow through the resin may enhance the performance of resins to remove ClO_4^-. A lower ClO_4^- breakthrough (<0.5%) was observed when the flow through the RO-02-119 resin column stopped and then was re-started (after 5 days of storage) for an additional 3000 bed volumes. This observation may be attributed to a slow diffusion and redistribution of adsorbed ClO_4^- anions within the macroporous and microporous structures of the resin beads. Therefore, a treatment protocol in which intermittent flow of solution is employed may actually enhance the treatment efficiency and longevity of resins in the removal of ClO_4^- from contaminated groundwater.

Additional experiments were performed to further evaluate the performance of synthetic resins in ClO_4^- removal from actual groundwater obtained from the CrimSouth well, Redlands, California. Both the commercial resin (Purolite[®] A-520E) and the synthetic resin (RO-02-119) were evaluated, and results are presented in Figure 6. Note that the initial groundwater contained ~16 ppb ClO_4^- and was spiked with approximately 1.15 mg/L (or ~1150 ppb) ClO_4^- in order to accelerate the breakthrough in this experiment. Results (Figure 6) were almost identical to those observed previously (Figure 5) for Purolite and RO-02-119 resins and suggest that the chemical composition of our synthetic test solution and the actual groundwater did not significantly influence the breakthrough of ClO_4^-. The bifunctional resin (RO-02-119) again performed much better than the commercial resin (Purolite[®] A-520E) with respect to ClO_4^- removal. Less than 0.5% ClO_4^- breakthrough was observed after ~5000 bed volumes of groundwater was passed through this column.

Results of these column studies are also summarized in Table 6 and have demonstrated that the performance of our synthetic resins was superior to that of the best commercial nitrate resins (Purolite[®] A-520E). The synthetic bifunctional resins exhibited a much better selectivity as indicated in the previous section, and results are also consistent with our early studies using the bifunctional resins to selectively remove pertechnetate (TcO_4^-) from the contaminated groundwater at the U.S. DOE Paducah Gaseous Diffusion Plant site (Gu and Dowlen, 1996; Gu et al., 1998). The Paducah study used a 25 x 110 mm column that was packed with RO-02-119 resin. After treatment of ~700,000 bed volumes of groundwater, less than 4% TcO_4^- breakthrough was observed. The bifunctional resin also exhibited better hydraulic flow characteristics in comparison with the Purolite[®] A-520E resin.

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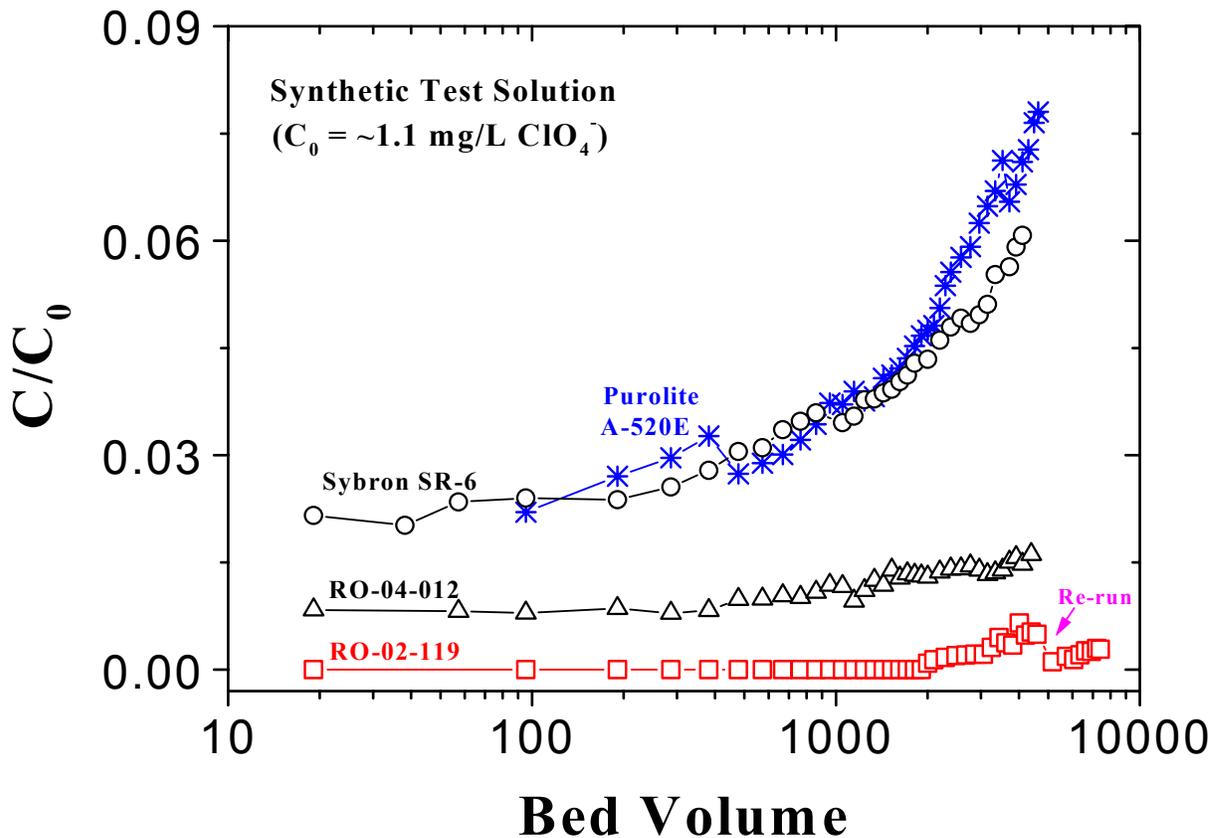
Figure 5. Breakthrough of ClO_4^- on synthetic resins in a background solution of 3 mM $NaHCO_3$, 1 mM $CaCl_2$, 0.5 mM $MgCl_2$, 0.5 mM Na_2SO_4, and 0.5 mM KNO_3.
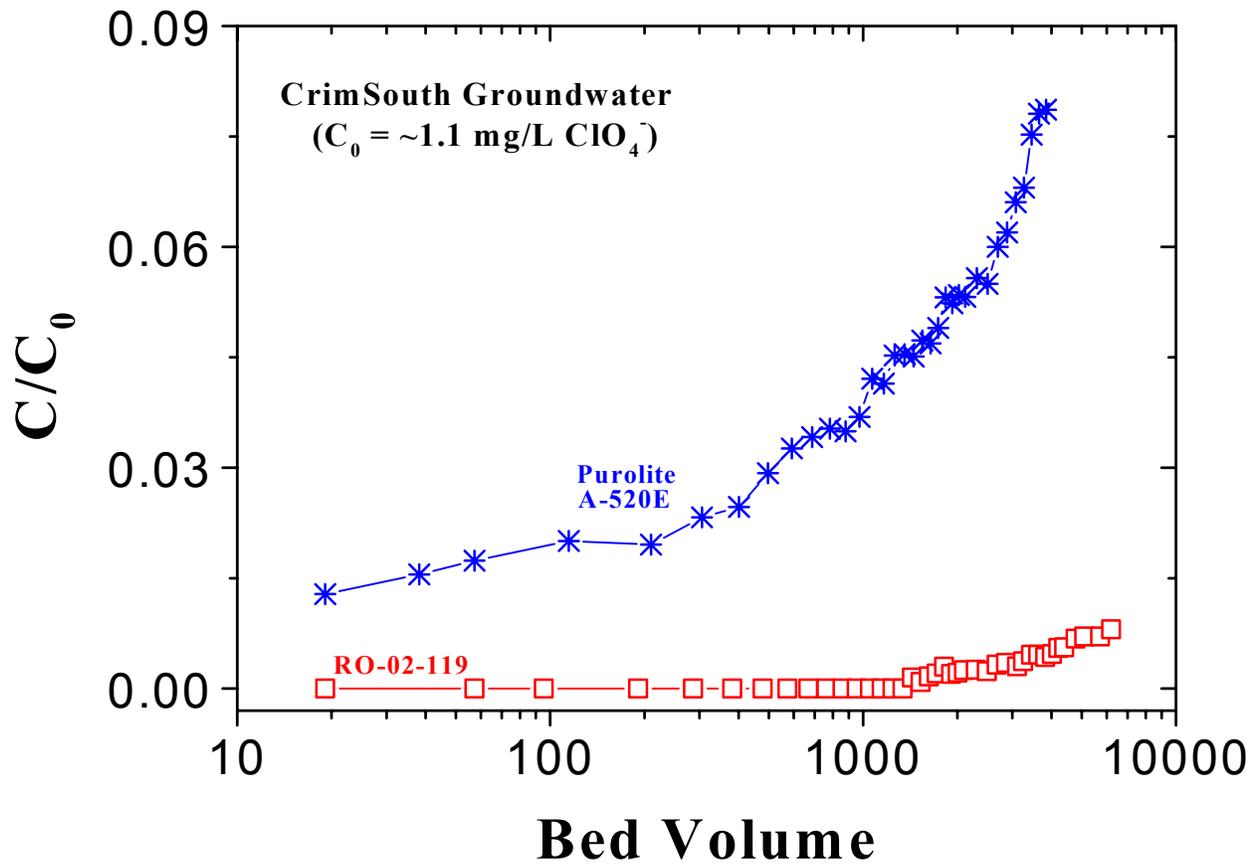
Figure 6. Breakthrough of ClO_4^- on RO-02-119 and Purolite® A-520E resin columns in CrimSouth groundwater.

Table 6. Perchlorate (TcO$_4^-$) removal in column flow-through systems and experimental conditions. Columns (10 x 40 mm) were run at a constant flow rate of 30 mL/min or a linear velocity of ~76 cm/min by assuming an effective porosity of 50% of the bed volume (BV).

Property	Purolite® A-520E		Sybron Ionac®	RO-02-119		RO-04-012
Resin BV (mL)	3.1		3.1	3.1		3.1
Resin AEC[1] (meq/g)	2.8		1.8	2.5		2.6
Mesh size	-16/+50		-16/+50	-40/+60		-40/+60
Background[2]	Test solution	Groundwater	Test solution	Test solution	Groundwater	Test solution
BV at 1% breakthrough	<20	<20	<20	>6000	>6000	600
% breakthrough at 100 BV	2.2	2.0	2.4	0	0	0.8
% breakthrough at 4000 BV	7.0	8.0	6.0	0.5	0.5	1.5

1. AEC = anion exchange capacity.
2. Synthetic test solution is composed of 3mM NaHCO$_3$, 1 mM CaCl$_2$, 0.5 mM MgCl$_2$, 0.5 mM Na$_2$SO$_4$, and 0.5 mM KNO$_3$. The groundwater was from CrimSouth well, Redlands, California (June 9, 1998).

Field Trial

A small-scale field flow-through experiment was conducted between August 19 and November 6, 1998 to evaluate the performance of the bifunctional resins in comparison with Purolite® A-520E under site-specific conditions. Three pairs of ion-exchange columns were used, and each set contained different resins. Each pair of columns is in a lead-and-lag configuration with water passing through one column before it passes through the second. The flow rate was nominally held at 200 mL/min although it fluctuated between ~150 and 210 mL/min. The groundwater is contaminated with ClO_4^- at ~50 µg/L and trace quantities of N-nitrosodimethylamine (N-NDMA) and trichloroethylene. The general chemical properties of the groundwater are given in Table 7. The total anion concentration (except bicarbonate) is ~1.5 mM and approximately 3 orders of magnitude higher than that of the ClO_4^- concentration.

Table 7. Major contaminants and chemical properties of groundwater at the experimental site.

Property	Site groundwater
Cl^- (mg/L)	7.0
NO_3^- (mg/L)	61.2
$SO_4^=$ (mg/L)	14.9
Ca^{2+} (mg/L)[1]	21.7
Alkalinity (mg/L)[1]	98.6
ClO_4^- (mg/L)	0.05
N-NDMA (mg/L)[1]	0.15
Trichloroethylene (mg/L)[1]	0.3
pH	6.9

[1] Analyzed by Radian International, Inc.

Results (Figures 7 and 8) indicated that the bifunctional synthetic resin (D-3696) prepared for us by Purolite performed ~5 times better than the best commercial nitrate-selective resin (Purolite® A-520E). Breakthrough of ClO_4^- on the Purolite® A-520E lead column (Figure 7) occurred after ~8,500 bed volumes of groundwater had passed through the column. On the other hand, ClO_4^- breakthrough occurred at ~40,000 bed volumes in the D-3696 resin column. In the second column (lag column, Figure 8), ~3% breakthrough of ClO_4^- occurred at ~22,000 bed volumes in the Purolite® A-520E column but this breakthrough level required ~104,000 bed volumes in the D-3696 column. At a 10% breakthrough (presumably the remediation target), the bifunctional D-3696 resin can treat up to ~112,000 bed volumes of groundwater containing ~50 µg/L ClO_4^- and running at ~2 bed volumes per minute (or at a residence contact time of <20 s). The best commercial resin (Purolite® A-520E, the nitrate selective resin) can treat up to ~24,000

bed volumes of the groundwater under the same experimental conditions. The breakthrough curves shown in Figures 7 and 8 also indicate that the breakthrough curves in D-3696 column is relatively diffuse (slow increase in C/C_0) in comparison with that of the Purolite® A-520E column (relatively sharp increase in C/C_0). These observations suggest that the bifunctional resin, D-3696, can also adsorb more ClO_4^- than Purolite® A-520E after the breakthrough occurs. In other words, the bifunctional resin columns may be configured with a relatively long pass length to enhance its treatment efficiency and longevity.

It should be pointed out that the groundwater was pumped directly through the resin columns without any pretreatment. This resulted in a retention of some dissolved organic matter (DOM) present in the natural groundwater. These organic materials in groundwater are generally negatively charged (Gu et al., 1994), so that they can also be strongly adsorbed by the anion exchange resins and may compete with the adsorption of ClO_4^- on the resin beads. The Purolite® A-520E appeared to have retained the least amount of DOM by visual comparison of the columns. However, the retention of the DOM did not appear to significantly reduce the performance of the Purolite bifunctional resin to remove ClO_4^- (Figures 8 and 9), which may be again attributed to the high selectivity of the bifunctional resins to poorly hydrated oxyanions such as ClO_4^-. These observations suggest that additional cost-savings could be gained by using highly selective synthetic resins in groundwater ClO_4^- treatment. Unlike the conventional groundwater treatment which normally requires a pretreatment stage to remove or filter DOM and other competing anions (such as SO_4^{2-}) that would otherwise reduce or interfere with the retention and removal of ClO_4^-, the use of highly selective bifunctional resins requires no pretreatment.

The resin beads before and after treatment with groundwater were analyzed by both scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. As reported previously (Gu et al., 1998), resin beads (both Purolite® A-520E and D-3696) appeared to be spherical (~0.6 to 0.8 mm in diameter) and smooth on the surface (Figure 10). Small quantities of mineral deposits were observed on resin beads after treatment with ~180,000 bed volumes of groundwater (Figure 10b).   Although SEM images of Purolite® A-520E resin beads were not shown they were similar to those of the D-3696 resin beads. No significant pressure drop was observed and the inlet pressure remained at ~20 and ~24 psi on both Purolite® A-520E and D-3696 resin columns during three months of the field operation

The EDX analysis (Figure 11) of the mineral deposits on resin beads (Figure 10b) suggests that these mineral deposits were composed of Al, Si, and small quantities of S, Fe, and Cu. Note that the Cl peaks in both treated and untreated resin beads were a result of the exchangeable Cl^- anions (as prepared initially). These mineral deposits are likely the aluminosilicate particles present in the groundwater and possibly coprecipitated with iron oxyhydroxides. Interestingly, a small amount of Cu appeared on resin beads which may be adsorbed as a complex with the dissolved organic materials in the groundwater. However, detailed studies and discussion in these aspects are beyond the scope of this work.
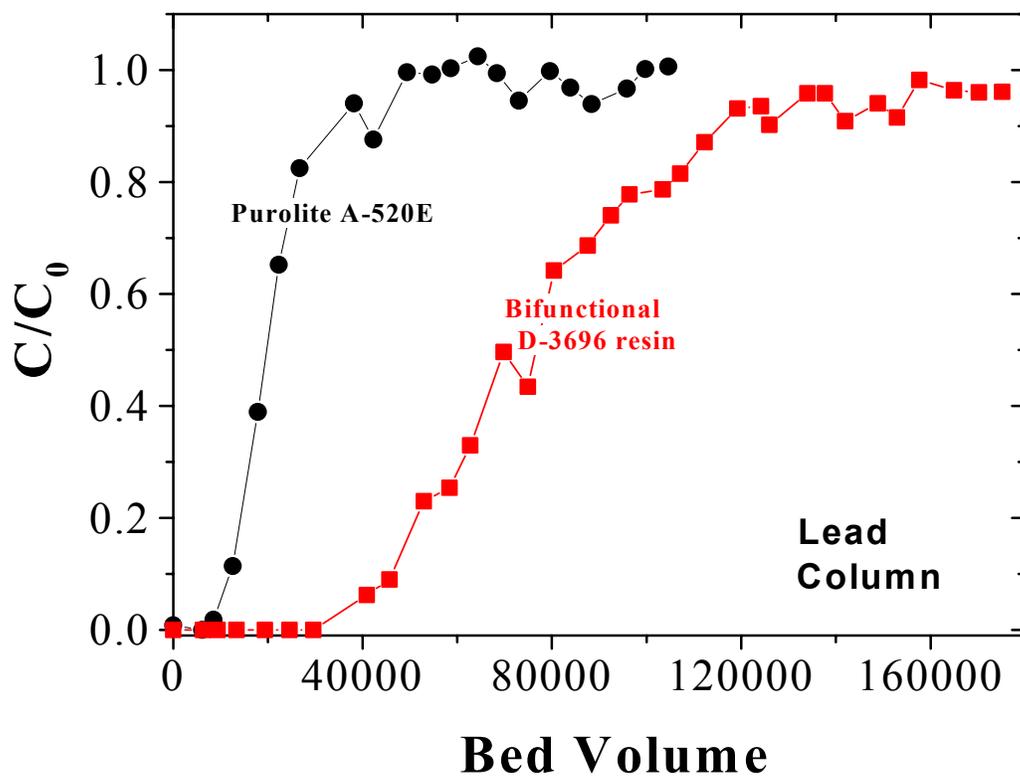
Figure 7. Breakthrough of ClO_4^- on the lead columns of the bifunctional resin (D-3696) in comparison with the best commercial nitrate-selective resin (Purolite[®] A-520E).
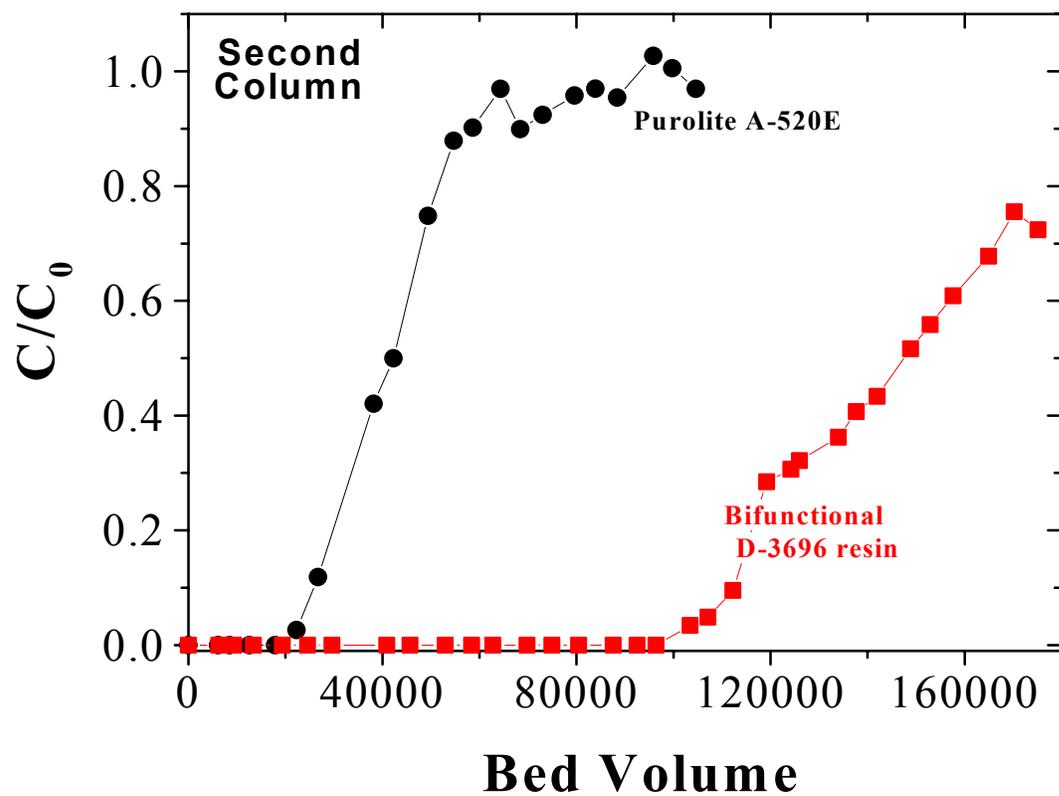
Figure 8. Breakthrough of ClO_4^- on the second (lag) columns of the bifunctional resin (D-3696) in comparison with the best commercial nitrate-selective resin (Purolite® A-520E).

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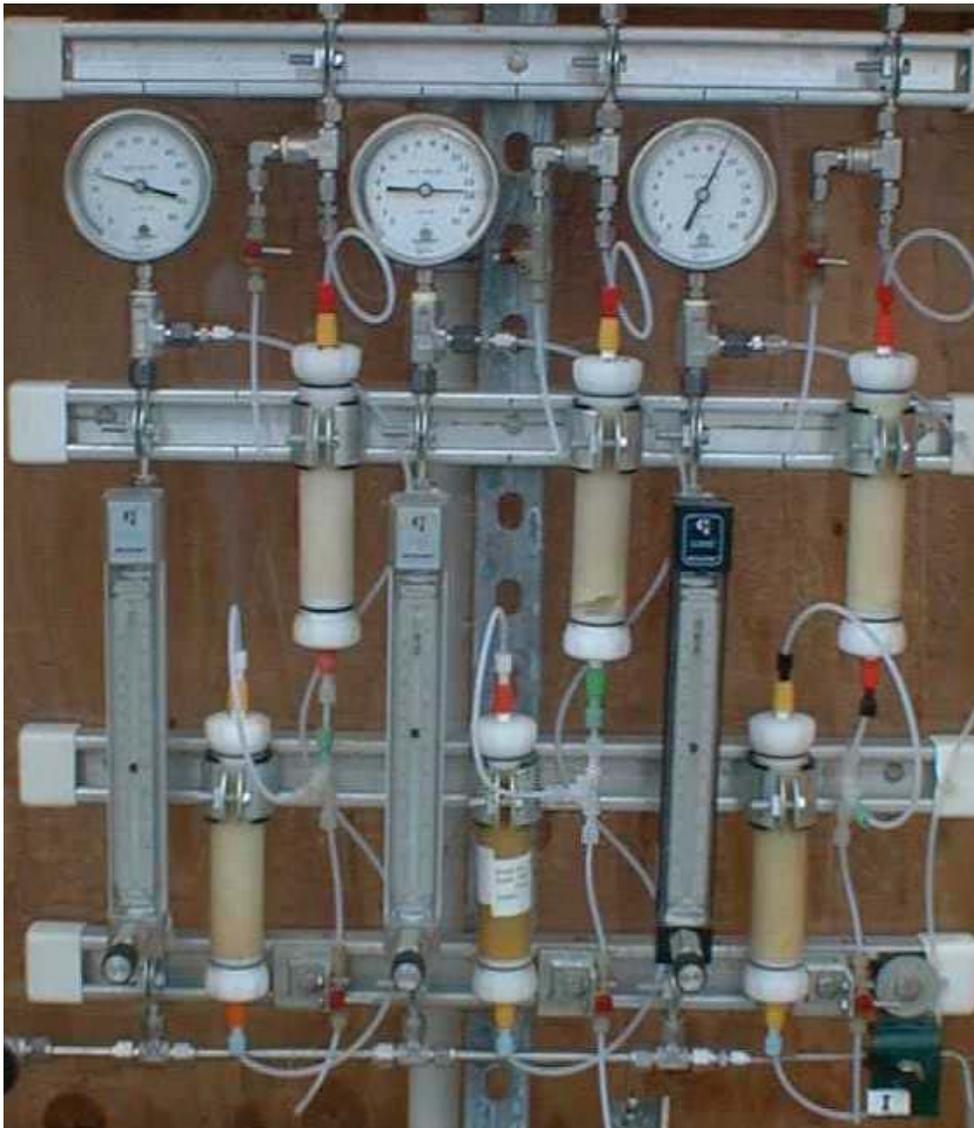
Figure 9. Resin columns after treatment of ~180,000 bed volumes of groundwater in the field.
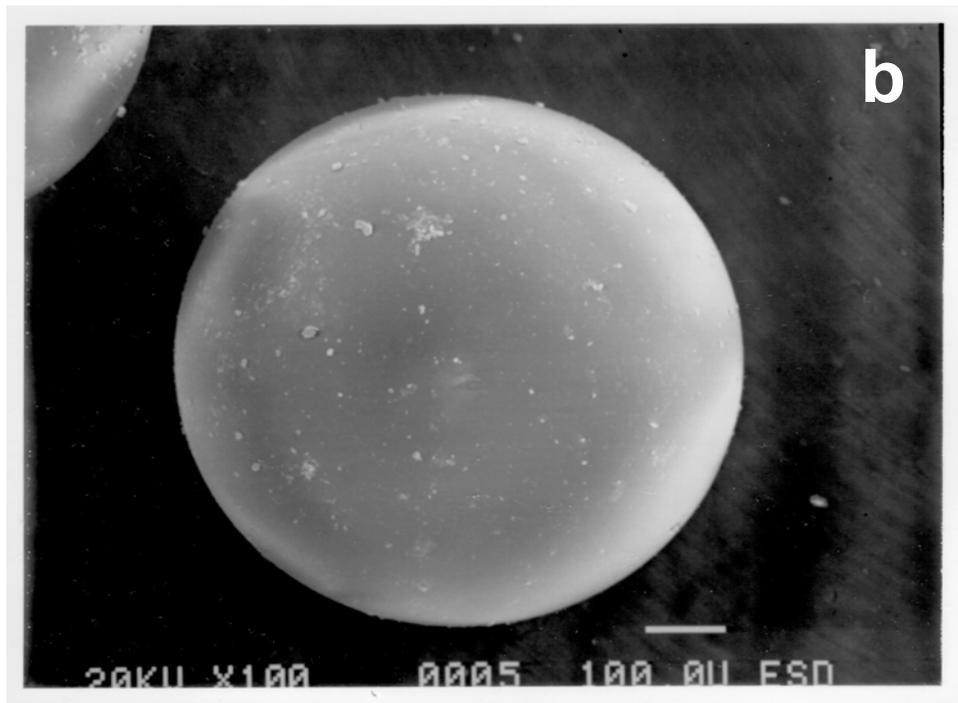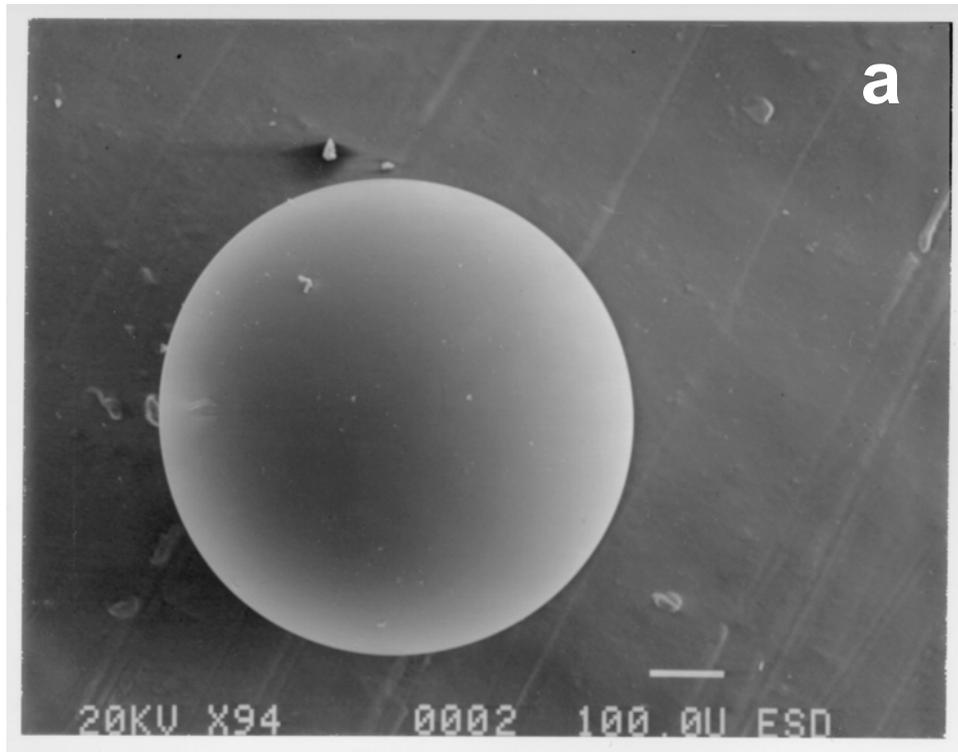
Figure 10. Scanning electron microscopic images of D-3696 resin beads (a) before and (b) after treatment with ~180,000 bed volumes of the ClO_4^- contaminated groundwater.
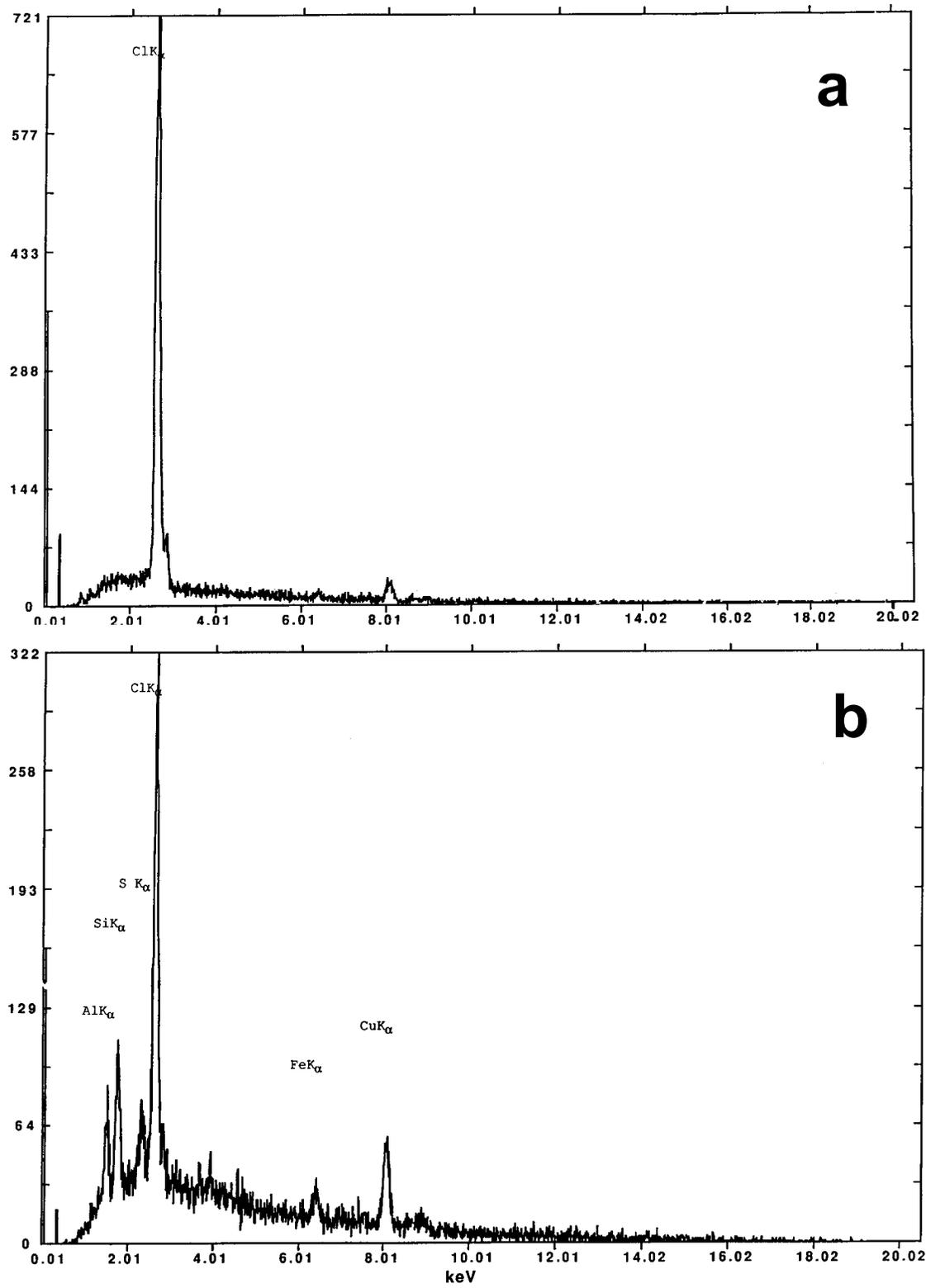
Figure 11. Energy dispersive x-ray analysis of D-3696 resin beads (a) before and (b) after treatment with ClO_4^--contaminated groundwater.

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Summary, Engineering Analysis for Field Applications, and Further Research Needs

Ion exchange technology is well-established and has been used for drinking water treatment for decades. It is probably one of the most efficient and cost-effective technologies for treating groundwater at a flow rate of a few thousand gallons per minute (or with a residence time of only a few seconds or minutes). However, the effectiveness of the ion exchange process is highly dependent on a number of factors, one of which is the microenvironment of the resin which can influence the selectivity. The microenvironment of the bifunctional resin has been optimized to remove trace quantities of ClO_4^- (at ppb levels) from competing anions that are present at concentrations of 4 to 5 orders of magnitude higher than the ClO_4^- concentration in groundwater.

ORNL and University of Tennessee researchers have developed a novel bifunctional anion exchange resin (nicknamed BiQuat), and Purolite International adapted the process to a commercially viable resin. Both laboratory and field experiments demonstrated that its performance in the remediation of groundwater contaminated with ClO_4^- ions surpasses that of commercially available materials by a factor of ~5. The new technology involves building into the exchange sites of the resin those features that are known to enhance the selectivity of large poorly hydrated anions, such as ClO_4^- and TcO_4^-, over other anions, while maintaining favorable exchange kinetics and good capacity. The bifunctional resins are particularly effective in removing trace quantities of ClO_4^- in groundwater to below the detection limit (~3 µg/L). No pretreatment is necessary to remove either dissolved organic matter or other competing anions (such as SO_4^{2-} or NO_3^-) in the groundwater, and the treatment process does not alter the water quality by removing or adding secondary byproducts. The results indicate that the new bifunctional resin could provide an efficient and cost-effective solution to the removal of ClO_4^- from groundwater because of reduced costs in operation (e.g., pretreatment and construction), maintenance and waste disposal.

Based on both laboratory and field experimental results, the design criterion for a scale-up treatment unit for field application is summarized. A useful scale is a single unit with a flow rate of 1000 gallon per minute (gpm). We have demonstrated that Purolite manufactured bifunctional resin (D-3696) could be operated at a flow rate of ~2 bed volumes per min (or a contact time of <20 s) in a column with an 8-in bed depth (and 1-in diameter). Less than 10% breakthrough of ClO_4^- occurred after an operation of nearly 40 days with an initial input ClO_4^- concentration of ~50 µg/L. Equating these two expressions for the flow rate of 2 BV/min and 1000 gpm leads to the use of a 500-gal BV (~67 cu ft). To be conservative, a treatment unit of 100 cu ft should be employed. We learned from the field experiment that we could process ~1.1 x 10^5 BV of groundwater per BV of resin, and this works out to a processing time of ~57 days for a 100 ft^3 bed. We round this high to a period of 2 months with a bed depth of 4 to 5 ft. The conservative design of a 1000-gpm system will be a pair of 100 ft^3 columns (lead and polishing) run in series. An additional column will be held in reserve to switch in when the lead columns reach 10% breakthrough. This requires a total of three 100 ft^3 treatment units. Based on the above design criterion, one 100 ft^3 column will have to be replaced every 2 months (six times a year) for each 10000-gpm stream. The mass transfer bed zone is quite narrow at this flow rate, and in actual practice a four-foot bed depth column may last four or more months. If this is the case the resin will need to be changed only three times a year. It may be possible to run at an even higher flow rate and field trials at 3 and 4 BV/min flow rate are planned. The ability to

regenerate the resin should make the use of the bifunctional resin an economically viable option, and research on regeneration of the resin is in progress.

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