Branched Polymeric Media: Perchlorate-Selective Resins from Hyperbranched Polyethyleneimine

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Supporting Information

ABSTRACT: Perchlorate (ClO_4^-) is a persistent contaminant found in drinking groundwater sources in the United States. Ion exchange (IX) with selective and disposable resins based on cross-linked styrene divinylbenzene (STY-DVB) beads is currently the most commonly utilized process for removing low concentrations of ClO_4^- (10–100 ppb) from contaminated drinking water sources. However, due to the low exchange capacity of perchlorate-selective STY-DVB resins (~ 0.5 – 0.8 eq/L), the overall cost becomes prohibitive when treating groundwater with higher concentration of ClO_4^- (e.g., 100–1000 ppb). In this article, we describe a new perchlorate-selective resin with high exchange capacity. This new resin was prepared by alkylation of branched polyethyleneimine (PEI) beads obtained from an inverse suspension polymerization process. Batch and column studies show that our new PEI resin with mixed hexyl/ethyl quaternary ammonium chloride exchange sites can selectively extract trace amounts of ClO_4^- from a makeup groundwater (to below detection limit) in the presence of competing ions. In addition, this resin has a strong-base exchange capacity of 1.4 eq/L, which is 1.75–2.33 times larger than those of commercial perchlorate-selective STY-DVB resins. The overall results of our studies suggest that branched PEI beads provide versatile and promising building blocks for the preparation of perchlorate-selective resins with high exchange capacity.

INTRODUCTION

Perchlorate (ClO_4^-) is a water-soluble anion that has been widely used in the manufacturing of explosives, mines, and solid propellants for pyrotechnic devices, rockets, and missiles.¹ It has emerged as a groundwater and surface water contaminant in 22 U.S. states since the development of a sensitive ion chromatography assay that can detect low levels of perchlorate in water, i.e. $2 \mu\text{g/L}$ (ppb).^{1–3} When ingested at high concentrations, ClO_4^- can inhibit the uptake of iodide by the thyroid gland and may disrupt its ability to produce hormones critical to developing fetuses and infants. Although the United States Environmental Agency (EPA) has yet to formally set a limit for the level of ClO_4^- in potable water, various states have set public health goals (PHG) for drinking water. For example, Massachusetts has established a PHG based on a maximum concentration limit (MCL) of ClO_4^- of 2 ppb. Similarly, the State of California established an MCL of 6 ppb in October 2007 and, in January 2011 and has proposed to reduce the

MCL for ClO_4^- in drinking water from 6 to 1 ppb.⁴ Reverse osmosis, nanofiltration and electrodialysis are not cost-effective for the treatment of drinking groundwater sources contaminated by low-concentrations of ClO_4^- (<100 ppb).⁵ Ion exchange (IX) using selective resins is currently the most widely used process for treating groundwater with low concentration of ClO_4^- , that is, less than 100 ppb.^{6–8} Today, anion-selective resins used to extract ClO_4^- from groundwater are exclusively prepared by functionalization of cross-linked styrene divinylbenzene (STY-DVB) beads.^{9–11} STY-DVB resins such as the commercial A-530E resin from Purolite can selectively and efficiently extract ClO_4^- from groundwater containing low amounts of perchlorate (10–100 ppb) to below

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the detection limit of 2 ppb.^{6–8} However, resins such as the A-530E resin have limited exchange capacities (0.6 eq/L)¹² and cannot be efficiently regenerated by conventional brine elution. Because of this, perchlorate-selective media such as the A530-E resin are discarded after a single use once they become saturated with ClO_4^- and as a result, the overall cost becomes prohibitive when treating groundwater with higher perchlorate concentrations (e.g., 100–1000 ppb). Thus, there is a critical need for new perchlorate-selective resins with high exchange capacity.

Most anion extraction processes by ion exchange in water treatment such as the removal of ClO_4^- from drinking groundwater are carried out in columns or packed beds.^{6–9} In these applications, the strong-base volume exchange capacity (SBEC_v)—defined as the number of exchange sites (eq) per unit volume (L) of fully swollen resin bed—is the critical measure of the resin capacity.⁹ Since the first reported synthesis of STY-DVB anion exchange resins, many attempts have been made to synthesize anion exchange resins with high SBEC_v using polyamines such as branched polyethyleneimine (PEI) as precursors.^{9,13–19} However, none of these previous studies has reported anion exchange resins with SBEC_v exceeding those of the commercial STY-DVB resins. In our efforts to develop high capacity and selective resins for ClO_4^- removal, we report a perchlorate-selective resin with high SBEC_v . This resin was prepared by alkylation of branched polyethyleneimine (PEI) resins obtained from an inverse suspension process. Batch and column studies show that our new PEI resin with mixed hexyl/ethyl quaternary ammonium chloride exchange sites can selectively extract trace amounts of ClO_4^- (to below detection limit) from a makeup groundwater in the presence of competing ions. In addition, our new perchlorate-selective resin has a strong-base exchange capacity of 1.4 eq/L, which is 2.3 times higher than that of the commercial A530-E resin. This perchlorate-selective STY-DVB resin has a SBEC_v of 0.6 eq/L.¹² The overall results of our studies suggest that branched PEI beads provide versatile and promising building blocks for the preparation of perchlorate-selective resins with high exchange capacity.

■ EXPERIMENTAL METHODS AND PROCEDURES

Resin Synthesis. Reagent grade chemicals (>98 wt %) were used to synthesize the PEI resin beads. Deionized (DI) water (minimum resistivity 18M Ω) was obtained from a Milli-Q filtration unit. Anhydrous sodium chloride (NaCl), sodium perchlorate (NaClO_4), sodium bicarbonate (NaHCO_3), sodium nitrate (NaNO_3) and sodium sulfate (Na_2SO_4) were purchased from Alfa Aesar. Concentrated hydrochloric acid (12 N) was purchased from EMD. Branched polyethyleneimine (PEI) [SP-200 with molar mass $M_n = 10,000$ Da and SP-018 with $M_n = 1800$ Da] was purchased from Nippon Shokubai Co., Ltd. Sulfonic 100 (branched dodecyl benzene sulfonic acid, 97%) was purchased from the Stepan Company. Bromoethane, iodomethane, 1-bromopropane, 1-bromo-2-methylpropane, 1-bromobutane, 1-bromo-3-chloropropane (BCP), diisopropylethylamine and epichlorohydrin (ECH) were purchased from Sigma-Aldrich. Methanol (MeOH), ethanol (EtOH), toluene, isopropanol, and sodium hydroxide (NaOH) were purchased from Mallinckrodt Chemicals. All chemicals were used as received. All base PEI resins were synthesized using an inverse suspension of water-in-toluene stabilized by a surfactant as recently described by Diallo and co-workers.²⁰ The PEI resins were subsequently reacted with alkylating reagents to produce

resins with quaternary ammonium chloride (Cl^-) exchange sites and tunable perchlorate-selectivity. Section 1 of the Supporting Information (SI) provides a detailed description of the resin synthesis procedures.

Commercial Resins. We utilized three commercial resins to benchmark the performance of our new perchlorate-selective resins. Samples of the A-850 and A-530E resins were provided by The Purolite Company (Bala Cynwyd, PA). The commercial DOWEX 1 resin was purchased from The Dow Chemical Company (Midland, MI).

Resin Characterization. The physicochemical properties of the PEI resins were characterized using a broad range of analytical assays/tools including (i) FT-IR spectroscopy, (ii) SEM imaging, (iii) particle size distribution (PSD) analysis, and (iv) water content and exchange capacity measurements. The FT-IR spectra of selected PEI resins were acquired using a Bruker VERTEX 70/70v FT-IR spectrometer with KBR pellets and OPUS software for data processing. All the reported IR spectra represent averages of more than 100 consecutive scans. The SEM images were acquired using a JEOL JEM-2100F microscope. Prior to imaging, each sample was mounted on a stage covered with carbon tape and sputter-coated with platinum. A Malvern Mastersizer 2000 was employed to analyze the PSD of the perchlorate-selective PEI resins.

The water content of each resin was measured by drying 2–3 g of moist resin under reduced pressure until the weight remained constant. Prior to testing, all resins were loaded in a glass column (5.1 cm i.d. $\times$ 20.3 cm in length) and washed successively with methanol (1 L/10 g of resin), deionized (DI) water (1 L/10 g of resin), 5.0 wt % NaCl (1 L/10 g of resin), and again with DI water (1 L/10 g of resin). Following the wash, the resins were partially dried at room temperature. The strong-base volume exchange capacity (SBEC_v) of each resin was measured by Mohr titration using the standard procedure ASTM-D2187 (2009).²¹ In a typical experiment, 4 g of resin was mixed with 10 mL of DI water. The resin slurry was packed in a graduated cylinder and allowed to equilibrate for overnight. The bed volume (BV) of the resin was then measured. Subsequently, the resin slurry was packed in a fritted glass column and saturated with a solution of sodium chloride (NaCl) [5.0 wt %] to obtain its chloride form. The column was then washed with 1 L of DI water to remove excess chloride in the solution. The remaining chloride ions were eluted out with a 1 L solution of sodium nitrate (NaNO_3) [2.0 wt %] and collected in a volumetric flask. Following this, the concentration of chloride in the effluent was measured by titrating an aliquot of 100 mL effluent solution with a solution of silver nitrate (AgNO_3). The strong base capacity (meq/mL) was expressed as follows:

$$\text{SBEC}_v = V \times N \times \text{DR} / \text{BV} \quad (1)$$

where V (mL) and N (meq/mL) are, respectively, the volume and normality of the silver nitrate solution, BV (mL) is the volume of the swollen resin and DR is the dilution ratio, which is equal to 10 in this case.

Batch Equilibrium Sorption Studies. Batch equilibrium sorption studies were carried out to evaluate the performance of the PEI resins against representative commercial resins. The ClO_4^- resin–water distribution coefficient K_d (mL/g) was used as a measure of resin binding affinity for the batch studies. For the screening studies, we performed single point K_d measurements. In this case, perchlorate sorption onto the resins was measured by mixing 50 mg (dry weight equivalent) of media

with 50 mL of a test solution containing 625 ppb of ClO_4^- . For isotherm measurements in the linear sorption range, perchlorate sorption onto the resins was determined by mixing 50 mg (dry weight equivalent) of media with 50 mL of a test solution with ClO_4^- concentration ranging from 0.5 to 10 mg/L. In both cases, the test solution was representative of a contaminated groundwater from Redlands (California) that was employed in a previous study of perchlorate-selective STY-DVB resins conducted by Oak Ridge National Laboratory.⁶ The makeup Redlands groundwater was prepared by dissolving 3 mM of NaHCO_3 , 3 mM of NaCl , 0.5 mM of Na_2SO_4 and 0.5 mM of NaNO_3 in deionized water. The initial and final concentrations of ClO_4^- in solution were measured by ion chromatography (IC) using EPA method 314.0.³ The instrument consisted of a Dionex ICS-2000 ion chromatograph equipped with an electrolytic suppressor (CSRS-300 4 mm), a dual piston pump, a potassium hydroxide eluent generator cartridge (EGCIII), a heated conductivity cell, an AS40 auto sampler, an AS20 analytical column (4×250 mm), and AG20 guard column (4×50 mm). The ClO_4^- resin–water distribution coefficient K_d (mL/g) was expressed as:

$$K_d = \frac{(C_0 - C_f) \times V/m}{C_f} \quad (2)$$

where C_0 and C_f are, respectively, the initial and final (equilibrium) concentrations of ClO_4^- (mg/mL) in solution measured by IC, V (mL) is the volume of the sample solution and m (g) is the mass of resin.

Batch Equilibrium Desorption Studies. We carried out batch studies to investigate the desorption of ClO_4^- from selected PEI and STY-DVB resins. For each resin, 0.1 g of dry media was first equilibrated overnight with a 50 mL solution of Redlands makeup groundwater containing 200 mg/L of ClO_4^- . Following the determination of the amount of ClO_4^- sorbed by each resin using IC with EPA method 314.0,³ the supernatant solutions were decanted. Each resin was subsequently washed twice with a 50 mL aliquot of deionized water to remove residual and unbound ClO_4^- . Following this, each resin was equilibrated with an aqueous solution of NaCl (5.8 wt %) to induce desorption through the exchange of Cl^- ions with the sorbed ClO_4^- ions. The percent of perchlorate desorbed (F_{desorbed}) was expressed as follows:

$$F_{\text{desorbed}} = 100 \times [C_f/C_0] \quad (3)$$

where C_0 and C_f are, respectively, the initial and final concentrations of ClO_4^- (mg/L) in solution measured by IC.

Separation Factor Measurements. Batch studies were conducted to benchmark the selectivity of our most perchlorate-selective PEI resin against that of the A530-E STY-DVB resin. For this purpose, we used the binary separation factor as measure of selectivity. Following Clifford et al.,²³ the binary separation factor α_{ij} can be expressed as follows:

$$\alpha_{i/j} = \frac{q_i/C_i}{q_j/C_j} \quad (4)$$

where q_i (meq/mL) and q_j (meq/mL) are, respectively, the concentrations of ions i and j in the resin phase and C_i (meq/mL) and C_j (meq/mL) are, respectively, the concentrations of ions i and j in the aqueous phase. Because chloride (Cl^-) is the preferred exchange site for commercial perchlorate-selective

resins, we measured three binary separation factors (SF): perchlorate-chloride SF ($\alpha_{\text{ClO}_4^-/\text{Cl}^-}$), nitrate-chloride SF ($\alpha_{\text{NO}_3^-/\text{Cl}^-}$) and sulfate-chloride SF ($\alpha_{\text{SO}_4^{2-}/\text{Cl}^-}$). We used the procedure of Clifford et al.²³ to measure the binary separation factors. For this purpose, 50 mL aliquots of binary mixtures of $\text{ClO}_4^-/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{Cl}^-$, and $\text{NO}_3^-/\text{Cl}^-$ were, respectively, mixed and equilibrated for 24 h in a rotary shaker with 0.025, 0.050, 0.075, 0.100, and 0.150 g (dry weight equivalent) of resins in polypropylene vials to achieve target concentrations of (i) 2–20 ppb for perchlorate and (ii) 10–50 ppm for nitrate and sulfate. In all cases, the total ion concentration in each vial was equal to ~ 5.0 meq/L.²³ Following equilibration, the concentrations of ClO_4^- , NO_3^- , SO_4^{2-} , and Cl^- in the initial and supernatant solutions were measured by ion chromatography as previously described in the experimental section. The measured concentrations of ClO_4^- , NO_3^- , SO_4^{2-} , and Cl^- were subsequently used to estimate the corresponding binary SF using eq 4. Each reported SF is the average of five measurements.

Column Studies. Column studies were conducted to benchmark the performance of our most perchlorate-selective PEI resin against that of the A-530E STY-DVB resin. To compare the operational capacity of these perchlorate-selective resins while reducing the length of the column experiments, we carried out accelerated breakthrough experiments using a Redlands makeup groundwater sample containing an initial ClO_4^- concentration of 10 mg/L. Following Tripp and Clifford,⁷ the ion exchange mini-column consisted of 3 mL of resins (Cl^- form) that were packed in glass columns (0.7 cm ID) with a bed depth of 8 cm. Test solutions were pumped through the mini-columns with a flow rate of 3.0 mL/min using a peristaltic pump (model EP-1 Econo Pump from Bio-Rad Laboratories). The system had an empty bed contact time of 1 min and a superficial linear velocity of 8 cm/min (1.0 BV/min). The concentrations of ClO_4^- in the column effluents were analyzed by IC using EPA method 314.0.³ The volume of water treated (m^3) per volume of media (m^3) at 50% breakthrough of perchlorate (i.e., $C/C_0 = 0.5$) was used as measure of resin operational capacity (OC). In all cases, the OC was determined by linear interpolation using the two closest measured throughput values.

RESULTS AND DISCUSSION

Synthesis of Base PEI Beads by Suspension Polymerization. Perchlorate-selective resins (PSRs) such as the commercial A-530 resin are prepared by functionalization of cross-linked STY-DVB beads using a two-step process.^{9–11} In the first step, chloromethyl groups are attached to the STY-DVB beads via a *Friedel–Crafts* reaction involving the aromatic rings of the resin and an alkyl halide such as chloromethoxy-methane in the presence of a Lewis acid catalyst. In the second step, the chloromethyl groups are reacted with a trihexyl amine followed by reaction with a triethyl amine to produce a bifunctional resin with trihexyl/triethyl ammonium chloride (Cl^-) exchange sites. While the amination of chloromethylated STY-DVB beads is a facile reaction, which takes place in high yield, several side-reactions including the secondary cross-linking of the bead aromatic rings via “methylene bridging” occur during chloromethylation. This reduces the number of functional sites available for amination.^{9–11} and as a result of this, the maximum reported SBEC_v for anion-exchange STY-DVB resins with methyl ammonium chloride (Cl^-) exchange sites is 1.4

eq/L.^{10,23} For perchlorate-selective STY-DVB resins, reported SBEC_v values range from 0.5 to 0.8 eq/L.^{12,23} In our efforts to develop PSRs with higher exchange capacity than those of commercial STY-DVB resins, we selected branched polyethyleneimine (PEI) as precursor both for its high content of reactive primary/secondary amine groups and availability from commercial sources.^{24,25} Due to the solubility of PEI macromolecules in water, we employed a surfactant-stabilized inverse suspension of water-in-toluene²⁰ to prepare the base PEI beads possessing high density of amine groups as described in Section 1 of the SI. Note that the size of commercial STY-DVB resin beads range from 300 to 1200 μm with a mean diameter of 700 μm .¹⁰ Consequently, we first optimized the reaction conditions to prepare PEI beads with an average diameter comparable to those of commercial STY-DVB resins. During suspension polymerization, the size of the droplets in the dispersed phase controls the size of the polymeric beads.²⁶ In the case of water-in-oil suspensions, the size of water droplets depends on several variables including stirring speed, surfactant concentration, and the viscosities of the oil and water phases.²⁶ Figure 1 illustrates the effects of suspension stirring

Figure 1. Synthesis of PEI beads with cross-linked epichlorohydrin (ECH) matrices: Effects of suspension stirring rate (A) and PEI molecular weight (B) on particle size. In these experiments, the NCR was kept constant and equal to 33 wt %.

rate and PEI molar mass on the size of beads prepared by cross-linking hyperbranched PEI with epichlorohydrin (ECH) in suspensions of water-in-toluene as described in reaction Scheme 1S of the SI. In these experiments, we kept the nominal cross-linking ratio (NCR) constant and equal to 33 wt %. For convenience, the NCR was used as a surrogate for the actual degree of cross-linking. Following Sherrington,¹¹ the NCR was taken as the wt% of cross-linker (ECH) used to prepare the base PEI resin beads. Figure 1 shows that we were

able to prepare base PEI beads with average diameter of 694 μm by optimizing the stirring rate and using a precursor PEI macromolecule of molar mass M_n equal to 10000 Da.

Synthesis of Perchlorate-Selective Resins by Functionalization of Base PEI Beads. The synthesis of our new PSRs was carried out by alkylation of base PEI beads to afford quaternized PEI beads with ammonium chloride (Cl^-) exchange sites. It is well-known that the affinity of STY-DVB resins for monovalent anions increase with anion size and hydrophobicity.^{6,7} Table 1S of the SI shows that ClO_4^- has a larger ionic radius and hydration free energy, which is much less favorable than those of anions such as Cl^- , NO_3^- , HCO_3^- , and SO_4^{2-} . This suggests that anion-exchange STY-DVB resins tend to exhibit a higher affinity for large and poorly hydrated anions such as ClO_4^- . However, the performance of perchlorate-selective STY-DVB is strongly affected by anions such as sulfate (SO_4^{2-}) and nitrate (NO_3^-) as their concentrations in most contaminated groundwater are 1–3 orders of magnitude greater than that of ClO_4^- . Both SO_4^{2-} and NO_3^- compete for the exchange sites (Cl^-) of perchlorate-selective STY-DVB resins.^{6,7} Based on our earlier studies of ClO_4^- binding to a fifth generation (G5- NH_2) poly(propyleneimine) [PPI] dendrimer and a fourth generation G4- NH_2 poly(amidoamine) [PAMAM] dendrimer,²⁷ we expected that branched PEI resins with hydrophobic cavities containing quaternary amine chloride groups would exhibit higher affinity for ClO_4^- over competing anions in aqueous solutions. Previous studies from Oak Ridge National Laboratory have also shown that a bifunctional STY-DVB resin with trihexyl and triethyl ammonium chloride groups can selectively remove trace amounts of large and poorly hydrated anions such as ClO_4^- and TcO_4^- (Table 1S of the SI) in contaminated groundwater in the presence of competing anions.^{6,22} Therefore, we employed a multipronged approach to synthesize new PSRs with high exchange capacity. First, we evaluated the effects of resin degree of cross-linking and water content on ClO_4^- binding affinity to PEI resins with hexyl ammonium chloride groups. For this purpose, we prepared a series of ECH-cross-linked PEI beads (Table 2S of the SI) with varying NCR. These resins were subsequently reacted with bromohexane to afford PEI resins with hexyl ammonium chloride (Cl^-) exchange sites as described in reaction Scheme 5S of the SI. Figure 2 illustrates the effect of cross-linking on resin water content and perchlorate resin–water distribution coefficient. Following Gu and Brown,⁶ we utilized the perchlorate resin–water K_d as a measure of a resin “efficiency for sorbing ClO_4^- from the solution phase”. Figure 2 illustrates the effect of the NCR on both the water contents and K_d of ECH-cross-linked PEI beads with hexyl ammonium chloride (Cl^-) exchange sites. The K_d values were taken as the slopes of the linear sorption isotherms given in Figure 4S of the SI. Note that as the NCR of the PEI resins increases, their water contents decrease and then level off followed by a slight increase. In contrast, their K_d values increase to a maximum followed by a decrease and a slight increase as the NCR increases. A maximum K_d value (13922 mL/g) is reached when the NCR and water contents of the ECH-cross-linked PEI beads with hexyl ammonium chloride groups are, respectively, equal to 33 wt % and 58 wt %. At the present time, we have no definitive explanation for this behavior. We speculate that the K_d trend shown in Figure 2 could be attributed to a decrease in resin moisture content and accessibility due to both matrix cross-linking and functionalization.

Figure 2. Synthesis of PEI resins with cross-linked epichlorohydrin (ECH) matrices and hexyl quaternary ammonium chloride (Cl^-) exchange groups: Effect of cross-linking degree on resin water content (A) and ClO_4^- distribution coefficients (K_d) in redlands makeup groundwater (B). The nominal cross-link ratio (NCR) was used a surrogate for the resin degree of cross-linking. The K_d values were derived from batch equilibrium sorption studies (Figure 4S of the SI). In these experiments, 0.025, 0.050, and 0.10 g of media (dry-weight) were contacted with 625 ppb ClO_4^- in Redlands makeup water for 24 h.

We also evaluated the effects of cross-linker chemistry on perchlorate binding. For this purpose, we first prepared a base PEI bead using a mixture ECH and 1-bromo-3-chloropropane (BCP) to cross-link a precursor PEI with molar mass $M_n = 10000$ Da as described in reaction Scheme 2S of the SI. This ECH/BCP cross-linked PEI resin has an nominal cross-link ratio of 41 wt % with a BCP:ECH molar ratio of $\sim 1.3:1$. We subsequently reacted this base PEI resin with bromohexane (Scheme 5S of the SI) to afford a quaternized PEI resin with a cross-linked ECH/BCP matrix and hexyl ammonium chloride exchange sites. Not surprisingly, Figure 3 shows that the ECH/BCP cross-linked PEI resin with hexyl ammonium chloride groups has a ClO_4^- resin–water distribution coefficient ($K_d = 29768$ mL/g) that is larger than that of the corresponding ECH-cross-linked resin ($K_d = 13922$ mL/g). We attribute the higher K_d value of the PEI resin with ECH/BCP cross-linkers to a more hydrophobic matrix with a lower water content (35 wt %) as shown in Table 3S of the SI.

Batch Sorption and Desorption Studies. Building upon the results of the previous investigations, we prepared a series of quaternized PEI resins with ammonium chloride exchange sites (Table 2) containing alkyl groups of varying chain lengths including methyl (QPEI-1), butyl (QPEI-2), hexyl (QPEI-3), hexyl/ethyl (QPEI-4), and isobutyl/propyl (QPEI-5). All these resins were synthesized by alkylation of a base PEI bead (PEI-

Figure 3. Synthesis of PEI Resins with Hexyl Quaternary Ammonium Chloride (Cl^-) Exchange Groups: Effect of Cross-linker Chemistry on ClO_4^- Distribution Coefficients (K_d) in Redlands Makeup Groundwater. For the ECH cross-linker, the nominal cross-link ratio (NCR) was 33 wt %. For the mixture of ECH/BCP cross-linkers, the total NCR was equal to 41 wt % with a BCP:ECH molar ratio of $\sim 1.3:1$. The K_d values were derived from batch equilibrium sorption studies (Figure 4S of the SI). In these experiments, 0.025, 0.050, and 0.10 g of media (dry-weight) were contacted with 625 ppb ClO_4^- in Redlands makeup groundwater (Table 1) for 24 h.

6) with mixed ECH/BCP cross-linker, nominal cross-link ratio of 51 wt % and water content of 58.6 wt % (Table 2S of the SI). The SI provides a detailed description of the reaction schemes (Schemes 4S–8S) and synthetic procedures used to prepare the quaternized PEI (QPEI) resins listed in Table 2. Batch sorption studies were carried out to screen the performance of the QPEI resins listed in Table 2 against representative STY-DVB resins in a Redlands makeup groundwater solution (Table 1). Table 2

Table 1. Concentration of Competing Anions in the Redlands Makeup Ground Water^a

anion	concentration	unit
Cl^-	106	mg/L
NO_3^-	31	mg/L
HCO_3^-	183	mg/L
SO_4^{2-}	49	mg/L

^aThe test solution was a simulation of a typical contaminated groundwater found in Redlands (CA, USA). It was utilized in a previous study of perchlorate-selective resins conducted by Oak Ridge National Laboratory as described in the report by Gu et al. (See ref 22). The makeup Redlands groundwater was prepared by dissolving 3 mM of NaHCO_3 , 3 mM of NaCl , 0.5 mM of Na_2SO_4 , and 0.5 mM of NaNO_3 in deionized water.

lists the estimated K_d values for the QPEI resins and STY-DVB resins. Each reported K_d value is the average of three replicate measurements (with a standard deviation of 5%) after 24 h of equilibration time. The magnitudes of the K_d values for the QPEI 1–3 resins clearly indicate that their affinity for ClO_4^- increase with resin hydrophobicity (Table 2). This trend is consistent with the results of our previous studies showing that a G5- NH_2 PPI dendrimer provides a more favorable environment for the partitioning of ClO_4^- anions than the more hydrophilic G4- NH_2 PAMAM dendrimer in aqueous solutions and model electrolyte solutions.²⁷ This observation is also consistent with the higher affinity of ClO_4^- for the DOWEX-1 STY-DVB resin ($K_d = 97398$ mL/g) when compared to the

Table 2. Perchlorate Resin–Water Distribution Coefficients (K_d) for Selected Commercial and QPEI Resins in a Redlands Makeup Groundwater Solution^a

resin	f SBEC _v (eq/L)	water content (%)	gK_d (mL/g)	matrix	ammonium chloride group
^b A-850E	1.25	48	3617	ACR-DVB	trimethyl
^c DOWEX-1	1.40	45	97 398	STY-DVB	trimethyl
^d A-530E	0.60	53	195 422	STY-DVB	triethyl and triethyl
^e QPEI-1	2.70	42	7359	PEI	methyl
^e QPEI-2	1.80	44	48 906	PEI	butyl
^e QPEI-3	0.70	24	233 318	PEI	hexyl
^e QPEI-4	1.40	25	295 490	PEI	hexyl + ethyl
^e QPEI-5	1.23	38	123 098	PEI	isobutyl + propyl

^aDuring these experiments, perchlorate sorption onto the resins was measured by mixing 50 mg (dry weight equivalent) of media with 50 mL of a test solution containing 625 ppb of ClO_4^- . ^bPurolite A-850E: Acrylic-divinylbenzene (ACR-DVB) resin (Gel). ^cDOWEX-1: Styrene-divinylbenzene (STY-DVB) resin (Gel). ^dPurolite A-530E: Bifunctional perchlorate-selective STY-DVB resin (Macroporous). ^eQPEI: Quaternized polyethyleneimine (PEI) resins. These resins were synthesized using the procedures described in the SI. ^fSBEC_v: Strong-base exchange capacity. The SBEC_v of each resin was measured by Mohr titration using the procedures described in the section “Experimental Methods and Procedures”. ^g K_d : Perchlorate resin–water distribution coefficient. Each K_d value reported in Table 2 is the average of three replicate measurements (with a standard deviation of 5%) after 24 h of equilibration time.

more hydrophilic acrylic-DVB resin Purolite A-850E ($K_d = 3617 \text{ mL/g}$) (See Table 2).

Table 2 also shows that the QPEI-3 resin with hexyl quaternary ammonium groups has a K_d value that is larger than that of the A-530E resin with triethyl and triethyl quaternary ammonium groups. We were able to increase the SBEC_v of the QPEI-3 resin to 1.4 eq/L while maintaining its high affinity for ClO_4^- ($K_d = 295490 \text{ mL/g}$) via a secondary alkylation with bromoethane (QPEI-4) as described in reaction Scheme 7S of the SI. Note that a key limitation of K_d as a measure of sorption affinity is its dependence on several factors including the initial concentration of the target anions and the resin exchange capacity.⁶ Consequently, we also measured ClO_4^- sorption onto the QPEI-4 and A-530 E resins as a function of concentration. Figure 4 shows that the sorption isotherms of the QPEI-3 and A-530 E resins are linear when the initial ClO_4^- concentration ranges from 0.5 mg/L to 10 mg/L. In this case, the ClO_4^- resin–water partition coefficients (K_d) are equal to the slopes of the linear sorption isotherms of the resins. Table 2 and Figure 4 show that the single point K_d value

Figure 4. Perchlorate resin–water distribution coefficients (K_d) for the QPEI-4 and A-530E resins in redlands makeup groundwater. The K_d values were derived from batch equilibrium sorption studies. In these experiments, perchlorate sorption onto the resins (24 h) was measured by mixing 50 mg (dry weight equivalent) of media (for 24 h) with 50 mL of Redlands makeup groundwater with ClO_4^- concentration ranging from 0.5 to 10 mg/L.

of the A-530E resin (195422 mL/g) (Table 2) is 2.66 times larger than its K_d value (73247 mL/g) from the linear sorption isotherms (Figure 4). In contrast, the K_d value of the QPEI-4 resin (254890 mL/g) in the linear sorption range is comparable (Figure 4) to its single point K_d value (295490 mL/g) reported in Table 2. We primarily attribute this difference between the two resins to the higher strong-base exchange capacity of the QPEI-4 resin (Table 2).

Although the resin–water distribution coefficient (K_d) can provide valuable insight into the affinity of a sorbent for a given ion, the regeneration efficiency of a resin is a critical measure of its selectivity.²⁸ A low regeneration efficiency of resin can be ascribed to strong interactions between counterions (e.g., ClO_4^-) and resin exchange sites (e.g., hexyl quaternary ammonium chloride groups).²⁸ We carried out batch studies to measure the desorption of ClO_4^- from selected QPEI and commercial resins in 1.0 M NaCl (5.8 wt %) solution as a function of equilibration time. Figure 5 shows that the resins

Figure 5. Perchlorate desorption from selected PEI and STY-DVB resins in 1.0 M sodium chloride (NaCl) solution (5.8 wt %). For the desorption experiments, 0.1 g of dry media was first equilibrated overnight with a 50 mL solution of Redlands makeup groundwater containing 200 mg/L of ClO_4^- . Following this, each resin was equilibrated with an aqueous solution of NaCl (5.8 wt %) to induce desorption through the exchange of Cl^- ions with the sorbed ClO_4^- ions.

with the lowest K_d values (A-850 and QPEI-1) have the largest extent of ClO_4^- desorption, that is, greater than 80% in all cases. In contrast, the resin with the largest (QPEI-4) value exhibits the lowest extent of ClO_4^- desorption, that is, less than 25% in all cases. A deeper insight into the selectivity of a resin for specific ions can also be gleaned by comparing their relative separation factors. Table 3 indicates that the perchlorate-

Table 3. Relative Separation Factors for QPEI-4 and A-530E Resins^a

resin	^a $\alpha_{\text{ClO}_4^-/\text{Cl}^-}$	^b $\alpha_{\text{SO}_4^{2-}/\text{Cl}^-}$	^c $\alpha_{\text{NO}_3^-/\text{Cl}^-}$
^d QPEI-4	523 ± 29.5	28.6 ± 0.04	4.79 ± 0.07
^e A-530E	597 ± 2.16	14.7 ± 0.40	4.66 ± 0.01

^aThese experiments were carried using the procedures developed by Clifford et al.²³. ^a $\alpha_{\text{ClO}_4^-/\text{Cl}^-}$: Perchlorate-chloride separation factor ^b $\alpha_{\text{SO}_4^{2-}/\text{Cl}^-}$: Sulfate-chloride separation factor ^c $\alpha_{\text{NO}_3^-/\text{Cl}^-}$: Sulfate-chloride separation factor ^dQPEI-4: Perchlorate-selective PEI resin (Table 2). ^eA-530E: Perchlorate-selective STY-DVB resin (Table 2).

chloride separation factor (SF) of the QPEI-4 resin (523 ± 29.5) is comparable to that of the A-530E resin (597 ± 2.16). Similarly, the nitrate-chloride SF of the QPEI-4 resin (4.79 ± 0.07) is equal to that of the A-530E resin (4.66 ± 0.01). These results suggest that the QPEI-4 and A-530E resins have comparable selectivity for perchlorate and nitrate. Not surprisingly, the QPEI-4 resin exhibits a higher affinity for sulfate. Table 4 shows that the sulfate-chloride SF of the QPEI-

Table 4. Estimated ClO_4^- Operational Capacities for QPEI-4 and A-530E Resins in Redland Makeup Groundwater^a

resin	^b SBEC _v (eq/L)	water content (%)	^c particle size (μm)	^d OC (BV)	^e OC ratio	^f SBEC _v ratio
^g QPEI-4	1.4	25	694	7558	2.36	2.33
^h A-530E	0.6	53	634	3200	1.0	1.0

^aWe used a Redlands makeup groundwater solution (Table 1) containing an initial ClO_4^- concentration of 10 mg/L to reduce the duration of the experiments by accelerating the breakthrough of ClO_4^- through the columns (Figure 6). ^bSBEC_v: Strong-base exchange capacity. ^cParticle Size: Median particle diameter (D_{50}) determined by particle size analysis using a Malvern Mastersizer (Figure 3S of the SI). ^dOC: Operational capacity. Taken as the volume of water of effluent water (BV) at 50% breakthrough (Figure 6). ^eOC Ratio: Ratio of the operational capacity of the QPEI-4 resin to that of the A-530E resin. ^fSBEC Ratio: Equal to the ratio of the strong-base exchange capacity of a PEI resin to that of the Purolite A-530E resin. ^gQPEI-4: Perchlorate-selective PEI resin (Table 2). ^hA-530E: Perchlorate-selective STY-DVB resin (Table 2).

4 resin (28.6 ± 0.04) is approximately twice that of the A-530E resin (14.7 ± 0.40). These results are consistent with those reported by Weber and Clifford.²⁹ During their investigations of the binding of monovalent and divalent ions to anion-exchange resins with quaternary ammonium chloride (Cl^-) exchange sites, they found that resins with “closely-spaced N-containing (amine) functional groups” are more selective for divalent anions (e.g., SO_4^{2-}).²⁹ Because the QPEI-4 resin contains more “closely-spaced” amine groups than the STY-DVB A-530E, it is not surprising that it also exhibits a higher sulfate-chloride SF. Given that QPEI-4 resin has a higher perchlorate K_d value than the A-530E resin with comparable perchlorate-chloride and nitrate-chloride separation factors, the

performance advantage of the QPEI-4 resin can be attributed for the most part to its higher exchange capacity (Table 2).

Column Studies. The overall results of the characterization studies showed that the QPEI-4 resin [with mixed ECH/BCH cross-linker and hexyl/ethyl ammonium chloride exchange sites] has a strong-base exchange capacity (SBEC_v) of 1.4 eq/L (Table 2), which is 2.33 times larger than of the A-530E resin. In addition, both the A530-E and QPEI-4 resins have comparable perchlorate selectivity and particle size distribution with mean particle diameters that are, respectively, equal to 635 and 694 μm (Figure 2S of SI). The sorption and desorption studies (Figures 4 and 5) also suggest that the ClO_4^- affinity of the QPEI-4 resin (i.e., K_d value) is larger than of the A-530E resin in the Redlands makeup groundwater with initial perchlorate concentrations of 0.5–10 mg/L (Figure 4). To further benchmark the performance of the QPEI-4 resin against that of the A-530E STY-DVB resin, we carried out column studies of ClO_4^- extraction from a Redlands makeup groundwater sample (Table 1). We utilized a Redlands makeup groundwater solution containing an initial ClO_4^- concentration of 10 mg/L to reduce the duration of the experiments by accelerating the breakthrough of perchlorate through the columns. Figure 6 shows the ClO_4^- breakthrough curves of

Figure 6. Perchlorate breakthrough curves for QPEI-4 and A-530E resins in redlands makeup groundwater. We utilized a Redlands makeup groundwater solution (Table 1) containing an initial ClO_4^- concentration of 10 mg/L to reduce the duration of the experiments by accelerating the breakthrough of perchlorate through the columns. The volume of effluent water (BV) at 50% breakthrough (i.e., $C_t/C_0 = 0.5$) was employed as a measure of the operational capacity (OC) for perchlorate extraction from Redlands makeup groundwater.

the QPEI-4 and A-530E resins. Table 4 lists the operational capacity of the two resins in the Redlands makeup groundwater. Figure 6 and Table 4 shows that the QPEI-4 outperforms the commercial A-530E resin by a factor of 2.33 in OC for perchlorate extraction from Redlands makeup groundwater containing an effluent ClO_4^- concentration of 10 mg/L. Not surprisingly, the OC advantage of the QPEI-4 resin (OC ratio = 2.36) over the A-530E resin matches the corresponding exchange capacity advantage (SBEC_v ratio = 2.33) listed in Table 4.

Environmental Implications. As stated in the Introduction, IX with selective and disposable resins is the most widely used process for treating drinking groundwater sources with influent ClO_4^- concentration <100 ppb. Gu et al.³⁰ showed that

selective media such as the A-530E STY-DVB resin was able to treat more than 100 000 bed volumes (BV) of contaminated groundwater with an influent ClO_4^- of 50 ppb before significant breakthrough of perchlorate occurred. In contrast, the A-530E resin could only treat 37 000 BV of contaminated groundwater with an influent ClO_4^- of 860 ppb (Figure S5 of SI) at a field site located in Rancho Cordova (CA) before significant breakthrough.³¹ Note that the concentrations of SO_4^{2-} (15 mg/L) and NO_3^- (10 mg/L) in the groundwater at the Rancho Cordova field site are significantly lower than those in the Redlands makeup groundwater (Table 1). Thus, we attribute the decrease in the OC of the A-530E resin at the Rancho Cordova site to its limited strong-base exchange capacity, which is equal to 0.6 eq/L (Table 2). A recent report by United States Government Accountability Office lists a large number of untreated groundwater sites with ClO_4^- concentrations ranging from 100 to 1000 ppb.³² Thus, perchlorate-selective resins with high exchange capacity could expand the applicability of IX to the treatment of groundwater with influent ClO_4^- concentration higher than 500 ppb. Table 5

Table 5. Extrapolated Operational Capacities for the QPEI-4 and A-530E Resins in Redland Makeup Groundwater With Effluent ClO_4^- Concentrations of 860 ppb^a

resin	$^b\text{OC}_{\text{measured}} (C_0^{\text{perc}} = 10 \text{ mg/L})$	$^c\text{OC}_{\text{extrapolated}} (C_0^{\text{perc}} = 860 \text{ ppb})$	$\text{OC}_{\text{measured}} (C_0^{\text{perc}} = 860 \text{ ppb})$
QPEI-4	7558	87 884	^d NA
A-530E	3200	37 209	^e 37000

^aThe concentration range for linear perchlorate sorption onto the QPEI-4 and A-530E Resins extends from 0.5 ppm to 10 ppm (Figure 4). ^b $\text{OC}_{\text{measured}}$: Measured operational capacity from column experiments (Figure 6). To reduce the duration of the column experiments, the initial concentration of perchlorate (C_0^{perc}) was set at 10 ppm. ^c $\text{OC}_{\text{extrapolated}}$: Extrapolated operational capacity for an initial concentration of perchlorate (C_0^{perc}) of 860 ppb. ^dNA, not available. ^e $\text{OC}_{\text{measured}}$: Estimated operational capacity from a field demonstration of perchlorate extraction conducted at an Aerojet field site located in Rancho Cordova (CA) (Figure S5 of the SI and ref 31). The concentration of sulfate [SO_4^{2-}] (15 mg/L) in the groundwater field site is much lower than that in the Redlands makeup groundwater, which is equal to 49 mg/L (Table 1). Similarly, the concentration of nitrate [NO_3^-] (10 mg/L) is also significantly lower to that in the Redlands makeup groundwater, which is equal to 31 mg/L (Table 1).

shows the extrapolated operational capacity (OC) for the QPEI-4 and A-530E resins in Redland makeup groundwater with initial ClO_4^- concentration of 860 ppb. Note that both resins exhibit linear sorption isotherms in Redlands makeup groundwater with initial ClO_4^- concentrations ranging from 0.5 to 10 mg/L (Figure 4). Because the K_d values of the QPEI-4 and A-530E resins are constant in this concentration range (Figure 4), we assume that their column operational capacities for ClO_4^- are controlled by their exchange capacities (Table 2). Based on this assumption, we express the operational capacity ($[\text{OC}]_{X\text{ppm}}^{\text{ClO}_4}$) of a QPEI-4/A-530E resin in Redlands makeup groundwater with an effluent ClO_4^- concentration equal to X (ppm) [with $0.5 \text{ ppm} \leq X \leq 10 \text{ ppm}$] as follows:

$$[\text{OC}]_{X\text{ppm}}^{\text{ClO}_4} = \left(\frac{10}{X}\right)[\text{OC}]_{10\text{ppm}}^{\text{ClO}_4} \quad (5)$$

where $[\text{OC}]_{10\text{ppm}}^{\text{ClO}_4}$ is the resin operational capacity in Redlands makeup groundwater with an effluent ClO_4^- concentration equal to 10 ppm (Table 4 and Figure 6). To validate our

extrapolation methodology, we subsequently used eq 5 to estimate the OC of the A-530E resin in Redlands groundwater with an effluent ClO_4^- concentration of 860 ppb. Table 5 shows the estimated OC for the A-530E resin (37209 BV) in Redlands groundwater is very close to its measured OC (37 000 BV) in the groundwater from the Rancho Cordova site.³¹ Recall that the groundwater at the Rancho Cordova site has an influent ClO_4^- concentration of 860 ppb with low concentrations of concentrations of sulfate (15 mg/L) and nitrate (10 mg/L).³¹ Table 5 shows that the estimated OC for the QPEI-4 resin (75580 BV) is 2.36 times larger than that of the A-530E resin (37209 BV) in the Redlands makeup groundwater with influent ClO_4^- concentrations of 860 ppb. Thus, the overall results of our initial studies suggest that branched PEI beads provide versatile and promising building blocks for the preparation of perchlorate-selective resins (PSRs) with high exchange and operational capacities. Additional investigations are being conducted to optimize the physical properties (e.g., mechanical strength) and performance (e.g., selectivity and capacity) of our new PSRs for the treatment of drinking groundwater sources contaminated by higher concentrations of perchlorate³² (e.g., 500–1000 ppb).

■ ASSOCIATED CONTENT

● Supporting Information

Supporting information contains additional material as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare the following competing financial interest(s): Prof. Mamadou S. Diallo is the co-founder of a start-up company (AquaNano, LLC). This company is scaling up and commercializing a new generation of high performance media using branched macromolecules as building blocks.

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■ REFERENCES

- (1) Hogue, C. Rocket-fueled river. *Chem. & Eng. News*. **2003**, *81*, 37–46.
- (2) Pontius, F. W.; Damian, P. Eaton, A. D. Regulating perchlorate in drinking water. In *Perchlorate in the Environment*; Urbansky, T. E., Ed.; Kluwer Academic: New York, 2000.
- (3) Mosier-Boss, P. A. Recent developments in perchlorate detection. In *Perchlorate Environmental Occurrence, Interactions and Treatment*; Gu, B. Coates, J. D., Eds.; Springer: New York, 2006.

- (4) California Office of Environmental Health Hazard Assessment. <http://www.oehha.ca.gov/water/phg/010711perchlorate.html> (accessed) 7 January 2011).
- (5) Zhou, P.; Brown, G. M.; Gu, B. Membranes and other treatment technologies-pros and cons. In *Perchlorate Environmental Occurrence, Interactions and Treatment*; Gu, B., Coates, J. D., Eds.; Springer: New York, 2006.
- (6) Gu, B. H.; Brown, G. M. Recent advances in ion exchange for perchlorate, treatment, recovery and destruction. In *Perchlorate Environmental Occurrence, Interactions and Treatment*; Gu, B. Coates, J. D., Eds.; Springer: New York, 2006.
- (7) Tripp, A. R.; Clifford, D. A. Ion exchange for the remediation of perchlorate-contaminated drinking water. *J. Am. Water Works Assoc.* **2006**, 98, 105–114.
- (8) Lehman, S. G.; Badruzzaman, M.; Adham, S.; Roberts, D. J.; Clifford, D. A. Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment. *Water. Res.* **2008**, 42, 969–976.
- (9) Helfferich, F. *Ion Exchange*; McGraw-Hill Series in Advanced Chemistry: New York, 1962.
- (10) Harland, C. E. *Ion Exchange: Theory and Practice*; The Royal Society of Chemistry: Cambridge, 1994.
- (11) Sherrington, D. C. Preparation, structure and morphology of polymer supports. *Chem. Commun.* **1998**, 2275–2286.
- (12) Purolite A530E Macroporous strong base anion exchange resin. <http://www.purolite.com/default.aspx?RelID=606288&ProductID=333> (accessed).
- (13) Hagge, W.; Naumann, G.; Leverkusen, O.; S. Polyethylene Imine Anion-Exchange Resins of Sponge-like Structure. US Patent 3,210,299. Patented October 5, 1965.
- (14) Rivas, B. L.; Maturana, H. A.; Catalán, R. E.; Perich, I. M. Branched and linear polyethyleneimine supports for resins with retention properties for copper and uranium. VII. *J. Appl. Polym. Sci.* **1989**, 38 (5), 801–807.
- (15) Rivas, B. L.; Geckeler, K. E. Synthesis and metal complexation of poly(ethyleneimine) and derivatives. In *Polymer Synthesis Oxidation Processes*; Springer: Berlin/Heidelberg, 1992; Vol. 102.
- (16) Shepherd, E. J.; Kitchener, J. A. 15. Studies of a cross-linked poly(ethyleneimine) ion-exchange resin. *J. Chem. Soc.* **1957**, 86–92.
- (17) Rademann, J.; Barth, M. ULTRA Loaded resins based on the cross-linking of linear Poly(ethyleneimine). Improving the atom economy of polymer-supported chemistry. *Angew. Chem., Int. Ed.* **2002**, 41, 2975–2978.
- (18) Barth, M.; Fischer, R.; Brock, R.; Rademann, J. Reversible cross-linking of hyperbranched polymers: A strategy for the combinatorial decoration of multivalent scaffolds. *Angew. Chem., Int. Ed.* **2005**, 44, 1560–1563.
- (19) Roise, M.; Christensen, S. F.; Meldal, M. ULTRAMINE: a high-capacity Polyethylene–Imine-based polymer and its application as a scavenger resin. *Chem.-Eur. J.* **2004**, 10, 4407–4415.
- (20) Mishra, H.; Yu, C.; Chen, D. P.; Dalleska, N. F.; Hoffmann, M. R.; Goddard, W. A., III; Diallo, M. S. Branched polymeric media: boron-chelating resins from hyperbranched polyethyleneimine. *Environ. Sci. Technol.* **2012**, 46, 8998–9004.
- (21) ASTM D2187 - 94(2009): Standard Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins, 2009. <http://www.madcad.com/store/subscription/ASTM-D2187-94-Reapproved2009/> (accessed).
- (22) Gu, B. H.; Brown, G. M.; Alexandratos, S. D.; Ober, R. Patel, V. Selective anion exchange resins for the removal of perchlorate (ClO_4^-) from groundwater. Oak Ridge National Laboratory Report ORNL/TM-13753, 1999.
- (23) Clifford, D.; Sorg, T. J.; and Ghurye, G. L. Ion Exchange and Adsorption of Inorganic Contaminants. In *Water Quality and Treatment: A Handbook on Drinking Water*; Edzwald, J. K., Ed.; American Water Works Association: Denver, 2011.
- (24) Frechet, J. M. J.; Boz, E.; Chi, Y.; Diallo, M. S. Extraction of anions from solutions and mixtures using hyperbranched macro-molecules. U.S. Patent Application. Pub No. US 2009/0181257 A1. Publication Date: July 22, 2010.
- (25) Diallo, M. S.; Yu, C. J. Soluble anion exchangers from hyperbranched macromolecules. U.S. Patent Application. Pub No. US 2011/0315636 A1. Publication Date: December 29, 2011.
- (26) Arshady, R. Suspension, emulsion and dispersion polymerization: a methodological survey. *Colloid Polym. Sci.* **1992**, 270, 717–732.
- (27) Diallo, M. S.; Falconer, K.; Johnson, J. H. Dendritic anion hosts: Perchlorate uptake by GS-NH₂ Poly(propyleneimine) dendrimer in water and model electrolyte solutions. *Environ. Sci. Technol.* **2007**, 41, 6521–6527.
- (28) Xiong, D.; Zhao; Harper, W. F. Sorption and desorption of perchlorate with various classes of ion exchangers: A comparative study. *Ind. Eng. Chem. Res.* **2007**, 46, 9213–9222.
- (29) Clifford, D.; Weber, W. J., Jr The Determinants of divalent/monovalent selectivity in anion exchangers. *React. Polym.* **1983**, 1, 77–89.
- (30) Gu.; B. Brown, G. Efficient treatment of perchlorate (ClO_4^-)-contaminated groundwater by bifunctional anion exchange resins. In *Perchlorate in the Environment*; Urbansky, T. E., Ed.; Kluwer Academic: New York, 2000; pp 165–176.
- (31) Gu, B.; Brown, G.; Chiang, C.-C. Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies. *Environ. Sci. Technol.* **2007**, 41, 6277–6282.
- (32) United States Government Accountability Office. *Perchlorate: Occurrence Is Widespread but at Varying Levels; Federal Agencies Have Taken Some Actions to Respond to and Lessen Releases*; United States Government Accountability Office: Washington, DC, 2010