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A Comparison of Metal-Loaded DOW3N Ion Exchangers for Removal of Perchlorate from Water

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Abstract: In this work, an alternative class of perchlorate selective ion exchangers (known as polymeric ligand exchangers, PLEs) were prepared by loading six transition metals (Cu(II), Co(II), Zn(II), Ni(II), Fe(II), and Fe(III)) onto a commercially available chelating resin Dowex M4195 (DOW3N). The resultant PLEs (DOW3N-Me, where Me = one of the metals) were tested with respect to their perchlorate selectivity, capacity, kinetics, and regeneration efficiency through a series of batch and column experiments. Within this group of PLEs, DOW3N-Cu(II) showed the highest perchlorate capacity; all four PLEs had similar perchlorate sorption kinetics; and DOW3N-Fe(III) demonstrated better regeneration potential.

Keywords: Anionic ligand, ion exchange, ligand exchange, perchlorate, polymeric ligand exchanger, water treatment

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INTRODUCTION

Perchlorate has been on the United States Environmental Protection Agency's (USEPA's) Contaminate Candidate List since 1998 (1). Consumption of perchlorate poses a health risk to humans because it limits the proper functioning of the thyroid glands by displacing iodine and inhibiting the production of human thyroid hormone (2). Recent data collected through the Unregulated Contaminant Monitoring Rule showed that perchlorate was found in drinking water systems in 26 states throughout the United States (US) (1). These findings were somewhat alarming as they demonstrated that perchlorate contamination in drinking water is widespread in the U.S., and it is expected that the USEPA will regulate this endocrine disrupting contaminant in the next few years.

Because perchlorate is nonvolatile, highly soluble, and kinetically inert, its remediation in contaminated groundwater is inefficient by conventional treatment technologies (3). A variety of technologies including ion exchange, bioremediation, electrodialysis, reverse osmosis filtration, and chemical reduction have been explored as potential perchlorate remediation strategies (2). For drinking water, ion exchange is a dominant perchlorate removal technology (4).

Strong base anion exchangers with quaternary ammonium functional groups, such as Purolite A530E and Purolite A520E, are capable of removing perchlorate selectively (5). Efficient regeneration of these anion exchangers using traditional brines has proven difficult due to the high affinity of perchlorate for these resins (3). An alternative regeneration scheme that is capable of the complete reduction of perchlorate in the regenerate has been developed (3,6); but, its industrial applicability has been questioned due to the corrosive properties of the regenerate and the energy demand for perchlorate destruction (7). In light of the limitations that exist in developing sustainable regeneration schemes for current ion exchange processes, strong base anion exchange technology remains one of the best technologies for separating trace levels of perchlorate from contaminated water. There is a clear need for a more effective ion exchange-based perchlorate treatment technology with high selectivity and an efficient, environmentally sound regeneration scheme.

Metal-loaded chelating resins, termed as polymeric ligand exchangers (PLEs), have been successfully used for removing neutral as well as anionic solutes (8–18). PLEs have shown potential to remove anionic ligands due to their dual binding mechanism which is a combination of electrostatic and Lewis acid/base interactions (13). One example includes an iron-loaded chelating ion exchangers for the separation of thiocyanate and arsenate (8,9). Additionally, Cu(II), Cr(III), and Fe(III) loaded chelating ion exchangers having oligo(ethyleneamine) functional groups (19) can be used to remove carboxylic and amino carboxylic anions from water (13–17). Most recently, a study by Henry et al. has extended the applicability of PLEs to the selective removal of ionizable organic contaminants such as 2,4,6-trichlorophenol (20).

Perchlorate sorption and regeneration with Cu based PLEs have been previously studied by this group (21,22). A Cu loaded PLE prepared with the chelating ion exchange resin DOW3N was found to have practically acceptable perchlorate sorption properties compared to other commercially available ion exchange resins (22). Little is known, however, about perchlorate removal and regeneration properties of PLEs made using transition metals other than copper. The objective of this study has been to compare the perchlorate selectivity, capacity, and regeneration efficiency of six different PLEs; using the same chelating resin (DOW3N) as the backbone for each of the following transition metals: Cu(II), Co(II), Zn(II), Ni(II), Fe(II), and Fe(III). We have compared the performance of each PLE in a series of equilibrium, kinetic, and column experiments.

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METHODS AND MATERIALS

Resin Morphology and Matrix

The role of the matrix in a PLE is to provide support for the functional groups as well as to define the structure of the ion exchanger. Ion exchangers are generally obtained in a gel or porous bead morphology. Typically, ion exchangers with gel morphology have greater capacity than those with a bead morphology; however, porous bead morphology ion exchangers are more durable, more resistant to oxidation, and less susceptible to organic fouling than gel morphology ion exchangers (23,24). Since most of the commercially available resins with desirable functional groups are available as macroporous beads with a polystyrene cross-linked divinyl benzene backbone, this structure has traditionally been used for the preparation of PLEs (8,9,13–18,20,25). Additionally, the increased durability and resistance to fouling provided by bead morphology is desirable. When selecting the resin backbone, the degree of resin cross-linking requires consideration because this controls the strength and flexibility of the resin matrix thus affecting sorption kinetics. Our choice was to use commercially available resins in this study, so we deemed that the degree of cross-linking selected by the resin manufacturer was appropriate.

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Chelating Resin Selection

After investigating a variety of commercially available chelating ion exchange resins, DOW3N was selected for use during this study. DOW3N has effectively been used in the preparation of PLEs for other trace sorption processes (8,9,13–15,17), and it offers a suitable base resin for the preparation of PLEs because of its uncharged functional groups which, when complexed with transition metals, allow the sorption of anionic ligands. The functional group specific to the DOW3N, bispicolylamine, is also desirable because it forms stable complexes with a variety of transition metal cations (26). Bispicolylamine contains pyridyl nitrogen that is known to complex with perchlorate in the presence of transition metal cations in dehydrated conditions (27). It should be noted that Lewis acid/base interactions under aqueous conditions may enhance some aspect of perchlorate sorption and/or desorption.

Metal Selection

Six transition metals were selected for their affinity for DOW3N as well as the possibility that they are able to interact with perchlorate when complexed with the resin's bispicolylamine functional group. The affinity of transition metal cations for DOW3N was approximated using the Irving-Williams order. The Irving-Williams order that represents the transition metal cations selected for this study appears as:

$$\mathrm{Fe(II)} < \mathrm{Co(II)} < \mathrm{Fe(III)} < \mathrm{Ni(II)} < \mathrm{Cu(II)} > \mathrm{Zn(II)}$$

Earlier studies have shown that the Irving-Williams order provides a good indication for the overall capacity of the PLEs prepared (13,20). It should be noted, however, that perchlorate removal capacities cannot be predicted from the Irving-Williams order alone because perchlorate's affinity for a complexed metal is independent of the metal's affinity for the bispicolylamine functional group.

PLE Preparation

All PLEs used for this study were prepared using DOW3N. To prepare each PLE, DOW3N was first conditioned to remove any residual organics from the resin and to stabilize the resin performance in the early few swelling cycles (12). To maximize metal loading during the PLE preparation the DOW3N was fully converted to its weak base form (13). Resin conditioning included a sequential washing at a solution to resin volume ratio of 10:1 in the following solutions; 4% (v/v) methanol, 1 N HCl, and 1 N NaOH, respectively. After each wash, the resin was rinsed in deionized water. Following the wash cycle, the conditioned DOW3N was air-dried and stored for later use. Each PLE was prepared by loading a chloride salt of Co(II), Cu(II), Fe(III), Fe(II), Ni(II), or Zn(II) onto DOW3N following the procedure outlined by Henry et al. (20). The metal-loaded chelating ion exchangers is referred to as DOW3N-M(n), where M(n) denotes the loaded transition metal cation.

Experimental Methods

Equilibrium Tests

A known mass, 0.40 g , of each PLE was added to 450 mL of solution containing perchlorate (range of concentrations, 5–35 mg/L) nitrate (150 mg/L) and sulfate (75 mg/L) at a pH of 7.5. The pH of each solution was maintained at a pH of 7.5 ± 0.5 by addition of 0.1 N NaOH or 0.1 N HCl, and the solution temperature was held at $22 + 1$°C. These solutions were agitated daily and allowed to equilibrate for approximately three weeks. Upon equilibration, the solutions were sampled and analyzed for perchlorate, nitrate, and sulfate. A mass balance was then performed to determine the resin capacity and overall perchlorate separation factor for each resin.

Kinetic Tests

Each PLE's perchlorate sorption kinetics was evaluated in an agitated batch reactor. Agitation minimized film diffusion resistance and left the effective diffusivity, a combination of intraparticle diffusion and the ion exchange reaction, as the rate limiting step for sorption process. For each kinetic test, 0.20 g of a PLE was placed in 950 mL of solution at a pH of 7.5 containing 16 mg/L perchlorate. Competing ions were intentionally excluded from the kinetic test to create competition-free conditions. Beginning once the resin was mixed with the perchlorate solution ($t = 0$), perchlorate sorption was followed by intermittently sampling the solution (600 μL) for approximately 3000 min. to ensure that the resin equilibrated with the solution. In all tests, the solution pH was maintained at 7.5 ± 0.3 by addition of 0.1 N NaOH or 0.1 N HCl. A mass balance was performed at each sample interval in order to determine the perchlorate uptake and the fractional attainment of equilibrium as a function of time.

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Column Sorption Studies

In order to evaluate the perchlorate removal performance of each PLE, flow-through column sorption experiments were conducted. Keeping in mind consistency between packing of columns; 2.0 grams (*ca.*3.3 mL) of each PLE was wet packed in an 11 mm diameter glass column on a bed of glass wool. A feed solution containing perchlorate (3 mg/L), nitrate (110 mg/L), and sulfate (100 mg/L) was pumped through the column at a rate of 1.2 mL per minute in order to achieve an empty bed contact time (EBCT) of 2.8 min. The column effluent was sampled regularly and analyzed for perchlorate, nitrate, sulfate, chloride, and pH so that complete breakthrough curves for each of the tested PLE could be constructed. The flow rates for each column were monitored daily to ensure that appropriate flow conditions were maintained.

Column Regenerations

A known mass of perchlorate-loaded resin (~1.8 g) was regenerated with a 4% NaCl solution at a pH of 12.4 and an EBCT of 30 ± 2 min, which corresponded to a regenerant flow rate of *ca.* 0.11 mL/min. The regenerant solution was collected by a fraction collector and then analyzed for perchlorate. A mass balance was performed on the samples to determine regeneration efficiency as a function of the bed volumes of the regenerant. A plot of regeneration efficiency versus bed volumes of regenerant was used to compare the relative regeneration efficiency of each PLE.

Brine solutions of different ionic strengths are typically employed as anion exchange resin regenerants. Additionally, for PLEs, regenerants at high pH can take advantage of strong hydroxide ion competition for occupied sites thus effectively increasing regeneration efficiency. The affect of regenerating PLEs with solutions of elevated pH has previously been explored, and based on those studies regenerations were followed with an acidic rinse to restore the resin to its original form (8).

Analytical Methods

Perchlorate was analyzed by ion chromatography (Dionex DX-120) equipped with auto sampler (Dionex AS-50) and a Dionex Ion-Pac AS-16 column. A 35 mM NaOH solution (Fisher Scientific) was used as eluent at a flow rate of 1.00 mL/min. For perchlorate concentrations ranging from 0.03 mg/L to 2.00 mg/L a 750 μL sample loop was used. A 25 μL sample loop was used if the perchlorate concentration was between 10 mg/L and 100 mg/L. Four-point linear calibrations were used for both sample loops. Nitrate, sulfate, and chloride were also analyzed by the ion chromatography with a 25 μL sample loop and a Dionex Ion-Pac AS-12A column. Based on the manufacturer's recommendations, the eluent was a 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ solution. The system operated at a flow rate of 1.50 mL per minute.

Reagents

Certified standards were used for the calibration of analytical instruments for the analysis of chloride, nitrate, and sulfate (Dionex). Perchlorate standards were prepared from two separate sources. One of the sources was used for standards preparation (Sigma Aldrich) while the other source was used for experimental procedures (Fisher Scientific). Concentrations of these standards were verified against each other for consistency.

PLEs used in this study were prepared using DOW3N (Dow Chemicals, Dowex M4195), a chelating ion exchange resin consisting of a polystyrene cross-linked with divinyl benzene backbone and bis(2-pyridylmethyl)amine functional groups. DOW3N was obtained in spherical bead form with sizes ranging from 20 to 50 mesh (0.30–0.84 mm) from Dow Chemical Company. Care was taken to ensure that samples of DOW3N used for PLE preparation and all subsequent experiments had a particle size distribution representative of the bulk sample. Deionized water with a resistance of at least 18.2 MΩ was used for all experiments. Degassed, organics-free deionized water was used for the preparation of all eluents used for ion analysis.

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RESULTS AND DISCUSSION

Equilibrium Study

In order to provide competitive sorption conditions, equilibrium studies were performed on each of the PLEs in the presence of the nitrate and sulfate. Equilibrium data are reported for all of the PLEs studied except for DOW3N-Fe(II) because analysis of the post-equilibrium samples for DOW3N-Fe(II) showed a large degree of scatter due to metal-salt precipitation during the DOW3N-Fe(II) equilibrium tests. This phenomenon was not observed in any of the other equilibrium studies. We suspect that the precipitation observed with the DOW3N-Fe(II) is due to the lower affinity of Fe(II) ions for DOW3N compared to the other metals in this study. This observation indicates that DOW3N-Fe(II) is unstable and thus not a feasible PLE for perchlorate removal.

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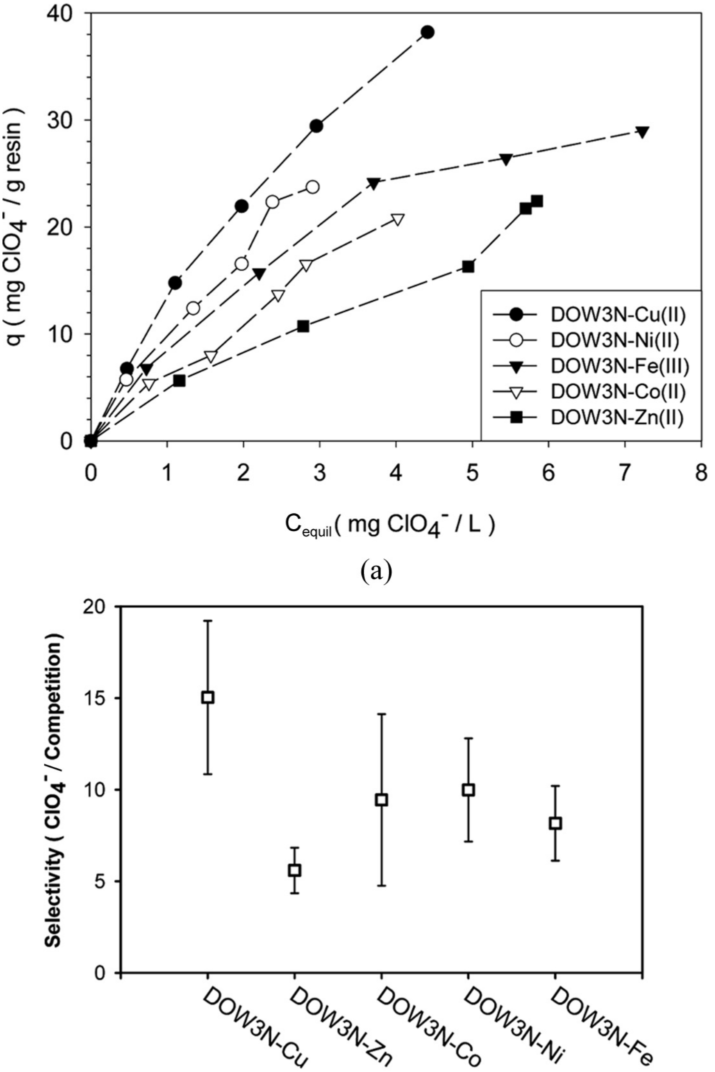

(a)

(b)

Figure 1. (a) Perchlorate sorption isotherms with various PLEs. For each system, pH = 7.5 ± 0.1 $[NO_3^-] = 96$ mg/L, $[SO_4^{2-}] = 65$ mg/L, $[Cl^-] = 58$ mg/L. The initial perchlorate concentration for all equilibrium tests ranged from 5 – 36 mg/L.; L.; (b) Mean PLE separation factors based on the equilibrium study. Error bars represent the standard deviation of the mean separation factor of the PLE perchlorate sorption isotherms. For each system the solution conditions were maintained as: pH = 7.5 ± 0.1, $[NO_3^-] = 96$ mg/L, $[SO_4^{2-}] = 65$ mg/L, $[Cl^-] = 58$ mg/L.

Figure 1a shows the perchlorate sorption isotherms for the five PLEs investigated in this study. The perchlorate sorption capacity follows the sequence: DOW3N-Cu(II) > DOW3N-Ni(II) > DOW3N-Fe(III) > DOW3N-Co(II) > DOW3N-Zn(II). It is noteworthy that the sequence of the PLEs' perchlorate capacity differs from the order of overall metal capacity as predicted by the Irving-Williams order. Although the Irving-Williams order can be used to infer the relative overall capacity of a series of PLEs (13,20), it will not accurately predict the relative sorption capacity of a given component if the PLEs do not have comparable sorption selectivity's for that component. Thus, the obtained result suggests that DOW3N-Zn(II) has a lower perchlorate sorption selectivity than the other PLEs

In order to quantitatively compare the selectivity of each PLE with the others, the average overall perchlorate separation factor ($\alpha_{ClO_4^-/comp}$) for each PLE was calculated (Fig. 1b). This is defined as the ratio of the perchlorate distribution coefficient to the competition distribution coefficient between the resin and aqueous phase:

$$\alpha_{\mathrm{ClO_4^-/Comp}} = \frac{\mathrm{q}_{\mathrm{ClO_4^-}} / \mathrm{C}_{\mathrm{e,ClO_4^-}}}{\sum_{i=1}^{\mathrm{n}} \mathrm{q_i} / \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{C_{e,i}}} \tag{1}$$

where q is the capacity (meq/g-resin), C_e is the equilibrium solution concentration (meq/L), and n is the number of competing ions.

After performing a two sample t-tests on the mean overall perchlorate separation factors for each PLE, we show that at 95% confidence there is a statistically significant difference between the perchlorate separation factor of DOW3N-Cu(II) and DOW3N-Co(II). However, no significant difference in mean perchlorate separation factors can be observed for other PLEs. While the selectivity of DOW3N-Zn(II) is not statistically less than the other PLEs (except DOW3N-Cu(II)), in the presence of competing anions it exhibited a lower than expected capacity. When compared to the other resins, this suggests that DOW3N-Zn(II) is not a suitable choice for trace perchlorate sorption processes.

In order to gain insight into perchlorate sorption characteristics of the PLEs, a mass balance was performed on each kinetic test to determine the competition-free perchlorate sorption capacity of each PLE. The relative overall perchlorate capacity results were consistent with the Irving-Williams order in that DOW3N-Cu(II) (72 mg/g) > DOW3N-Ni(II) (69 mg/g) > DOW3N-Zn(II) (68 mg/g) > DOW3N-Fe(III) (65 mg/g) > DOW3N-Co (II) (47 mg/g). The combination of its relatively moderate perchlorate capacity in the absence of competitor anions with its low perchlorate capacity in the presence of competition confirmed that the DOW3N-Zn(II) has the lowest perchlorate selectivity of the examined PLEs.

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Kinetic Study

Batch kinetic studies were performed to determine the PLE with the greatest perchlorate removal rate. Based on prior studies (13,15), intraparticle diffusion is considered to be the rate limiting step for polymeric ligand exchangers. Figure 2a shows the transient change in solution perchlorate concentration as a function of time for each of the PLEs. Visual analysis of the concentration versus time data presented in Figure 2a does not allow for a simple determination of the relative kinetic performance of the PLEs.

In order to asses the relative kinetic performance of the examined PLEs, we evaluated the fractional attainment of equilibrium as a function of time and modeled the kinetic data in this form using Infinite solution volume model, which allowed an effective diffusivity for perchlorate sorption to be obtained (Fig. 2b and Table 1). The fractional attainment of equilibrium (U(t)) can be calculated by dividing the time dependent perchlorate capacity of the resin (q(t)) by the resin perchlorate capacity at equilibrium ($q(\infty)$). In order to quantify the effective diffusivity of the PLEs, we chose a solid phase diffusion model with an infinite solution volume boundary condition. Using the appropriate initial and boundary conditions, our solution to the differential equation describing the combination of the flux of a component through the resin bead yielded the following form for the fractional attainment of equilibrium as a function of time (12):

$$U(t) = \frac{q(t)}{q(\infty)} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_e t\pi^2 n^2}{r_o^2}\right) \tag{2}$$

Here, D_e is the effective diffusivity, t is time, r_o is the bead radius, and n is the index of summation. Vermuelen's approximation of the model solution was fit to the data in order to estimate the mean D_e for each PLE (12).

$$U(t) \cong \left[1 - \exp\left(-\frac{D_e t\pi^2}{r_o^2}\right)\right]^{1/2} \tag{3}$$

Comparison of the D_e obtained from the application of the kinetic model with a non-linear least squared analysis (Table 1) indicates that the order of D_e for this series of PLEs is DOW3N-Co(II) > DOW3N-Ni(II) > DOW3N-Cu(II) > DOW3N-Fe(III) > DOW 3N-Zn(II).

The results of non-linear least squares analysis yielded good fits to the theoretical model ($r^2 \geq 0.90$) for all PLEs. Based on the given D_e, the selected model describes the data reasonably well. These values are

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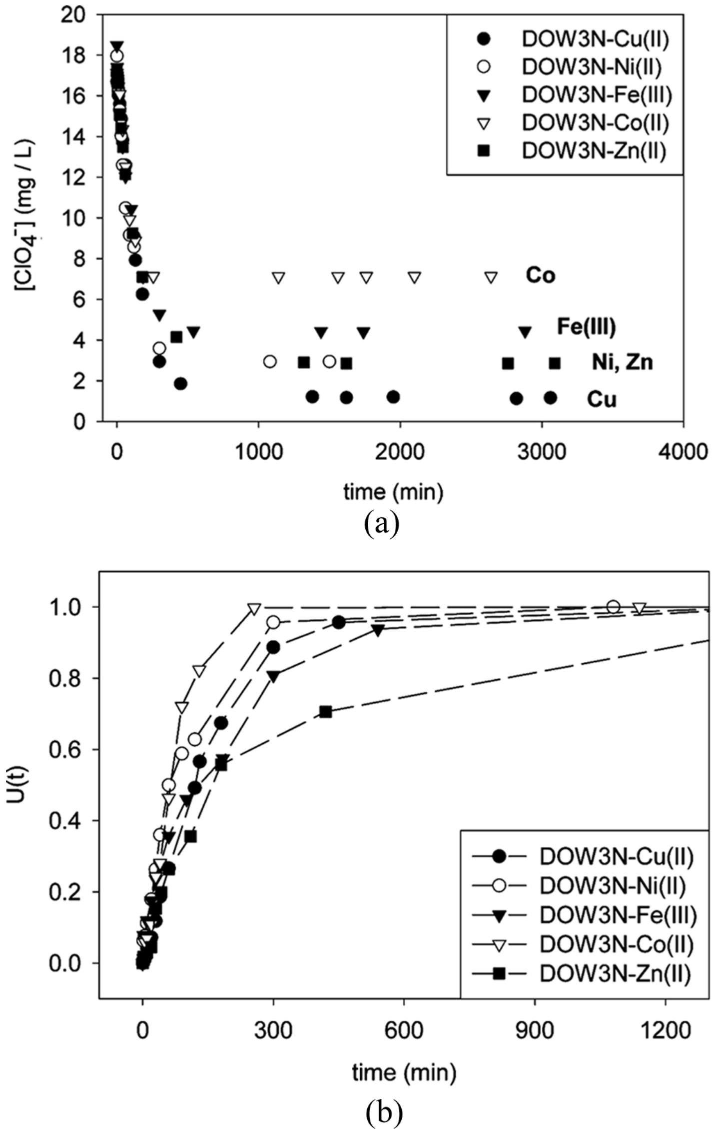

Figure 2. (a) DOW3N-Me Raw Kinetic Data from batch experiments.. For each experiment: the mass of resin = 0.0990 g – 0.1010 g, initial $[ClO_4^-] = 17$–$19\,mg/L$, pH = 7.5 ± 0.3, and solution volume = 950 mL.; (b) Fractional attainment of equilibrium vs. time for each studied PLE. For each experiment: the mass of resin *ca.* 0.10 g, initial $[ClO_4^-] = 17$–$19\,mg/L$, final $[ClO_4^-] = 1$–$7\,mg/L$, pH = 7.5 ± 0.3, and solution volume = 950 mL.

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Table 1. PLE intraparticle diffusivities determined from the kinetic test utilizing Vermuelen's Approximation with a non-linear least square analysis. %CV is defined as the standard error of the fitted diffusivity divided by the diffusivity

Resin	$D_e(\text{cm}^2/\text{min}) \times 10^7$	R^2	%CV
DOW3N-Zn(II)	1.6	0.90	26
DOW3N-Fe(III)	3.1	0.96	13
DOW3N-Cu(II)	3.4	0.92	21
DOW3N-Ni(II)	4.5	0.98	28
DOW3N-Co(II)	5.4	0.97	12

in good agreement with values previously obtained for other ion exchangers and PLEs (13). Figure 3 shows one example of the best model fit to the experimental data for DOW3N-Fe(III). Similar results were observed for other PLEs. In all cases, the model fits the experimental data better at early times than at the later. This can be partially due to the less frequent sampling beyond 200 min. Additionally, some assumptions inherent in

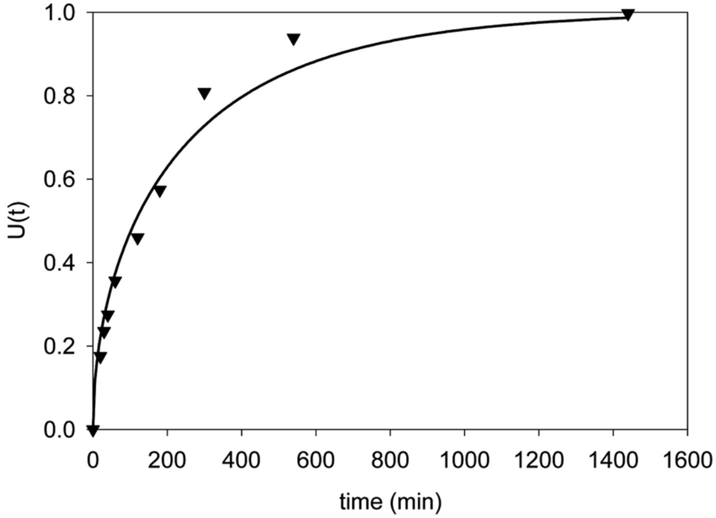

Figure 3. Comparison of fractional attainment of equilibrium vs. time for the DOW3N-Fe(III). For this experiment: solution volume = 950 mL, the mass of resin = 0.201 g, and average radius, r = 0.035 cm. An intra-particle diffusivity, D, of $3.1 \times 10^{-7}\,\text{cm}^2/\text{s}$ was calculated from non-linear least squares fitting to the infinite solution volume model described in the text. ($r^2 =$ 0.96 and the %CV = 13%).

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the model were not consistent with experimental conditions. For example, the kinetic model assumes that the concentration of originally loaded ions, chloride in our case, is negligible in the bulk solution; however, at later times, chloride concentrations no longer satisfy this condition due to desorption of chloride from the resin phase (13,14). Also, changes in perchlorate concentrations over the course of the runs were larger than desired which may result in a portion of our experiments being conducted outside of the linear portion of the isotherm. Although the deviations from the model's assumptions occurred during the experiments, the model's fit quality was acceptable for the goal of intercomparing these PLEs. Since the effective diffusivity of macroporous ion exchangers is known to have a positive correlation with ionic strength (23,24), we feel the finite solution volume model in a representative ionic strength solution was most appropriate for determining the D_e for system design purposes.

The different sorption rates for the PLEs suggest that the sorption kinetics are affected by both the intraparticle diffusion and the surface reaction rate. The intraparticle diffusivity is controlled by the pore structure of the PLE and the ions diffusing through the pores (12). Because each PLE was prepared using the same backbone with similarly sized transition metal cations complexed with the resin functional group, the pore structure of the ion exchangers should be similar. Thus, the differences in PLE sorption kinetics can be attributed to the exchange of ions at the functional groups. Since all PLEs examined in this study had a D_e within the same order of magnitude, it can reasonably be assumed that the observed differences in D_e can be overcome in the process design phase. This conclusion is further supported by the difficulty associated with determining which PLE had the best sorption kinetics based on a visual analysis of the concentration versus time data presented in Fig. 2a.

Column Sorption Studies

Based on the equilibrium and kinetic studies, four PLEs that demonstrated the most promise for a potential perchlorate removal are DOW3N-Fe(III), DOW3N-Co(II), DOW3N-Cu(II), and DOW3N-Ni(II). These PLEs were further tested in column sorption studies in the presence of competing nitrate and sulfate.

Breakthrough histories for all competing anions were comparable to those reported by Zhao (data not shown) (13). In our experiments, we observed chromatographic elution of all competing anions, but we did not find the same for perchlorate which confirms that all PLEs in this series were perchlorate selective. The order of chromatographic

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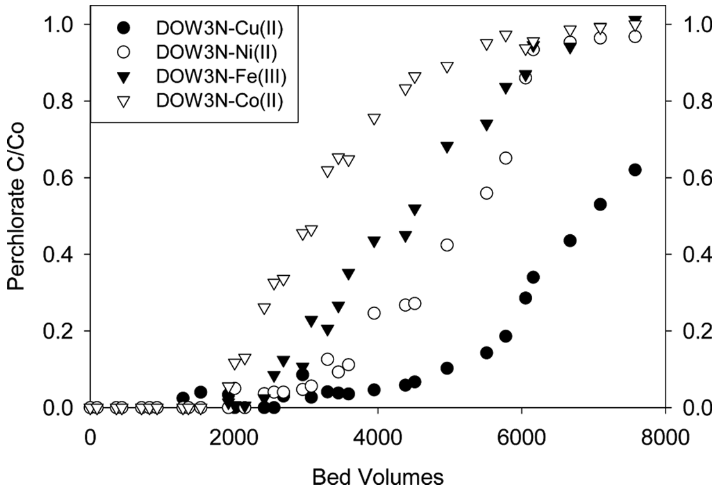

Figure 4. Perchlorate breakthrough for DOW3N-Cu(II), DOW3N-Ni(II), DOW3N-Fe(III) and DOW3N-Co(II).

elution observed suggests the following order of anionic selectivity $ClO_4^- > SO_4^{2-} > NO_3^- > Cl^-$. Figure 4 compares the perchlorate breakthrough profile for each of the PLEs in this study. These results indicate the following order of perchlorate capacity: DOW3N-Cu(II) > DOW3N-Ni(II) > DOW3N-Fe(III) > DOW3N-Co(II). It is noteworthy that the results of column sorption studies indicate the same order of perchlorate capacity for four resins that was determined through the equilibrium studies. While each of these resins has a different perchlorate capacity, initial detection of perchlorate (100 μg/L) in the column effluent occurred after 1200 bed volumes.

Regeneration Study

Because PLEs can be easily regenerated for reuse, perchlorate capacity is not the only factor that should be used to determine the most appropriate PLE for a process. In light of this, we compared the regeneration efficiency to evaluate the relative regeneration potential of each PLE. Although DOW3N-Zn(II) has been ruled out as an effective candidate for trace perchlorate sorption, results from its regeneration have been included since they were different than expected. A portion of each batch perchlorate-loaded PLE was regenerated with a 4% (w/w) sodium chloride solution at a pH of 12.4. An empty bed contact time of 30 min

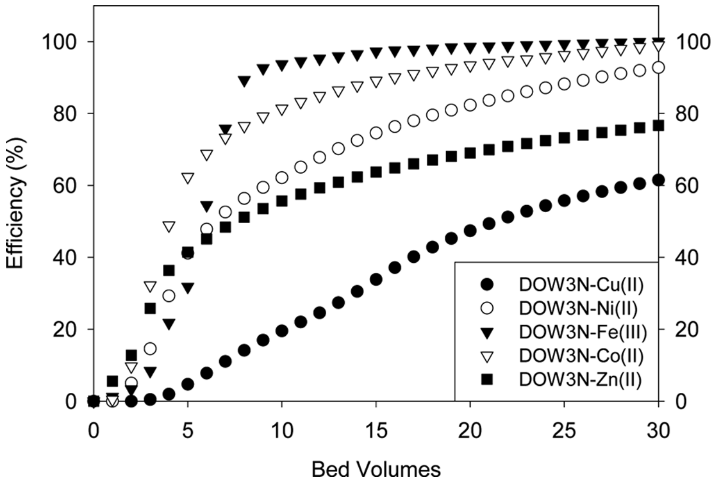

Figure 5. Regeneration efficiency as a function of the number of bed volumes of regenerant solution for each PLE. The mass of resin used was ca. 2.0 g. The regenerant solution was maintained at a pH = 12.4 and 4% NaCl. The empty bed contact time was 30 min.

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was used. The column effluent was collected fractionally and analyzed for perchlorate so that the comparison between perchlorate elution (data not shown) and regeneration efficiency (Fig. 5) could be made. Comparison of the regeneration efficiencies of each PLEs at 15 bed volumes of regenerate suggests the following order of regeneration potentials: DOW3N-Fe(III) (96%) > DOW3N-Co(II) (88%) > DOW3N-Ni(II) (72%) > DOW3N-Zn(II) (62%) > DOW3N-Cu(II) (31%). Because of to the low selectivity of DOW3N-Zn(II), it should have one of the best regeneration efficiencies, but it had the second worst regeneration efficiency. Visually examining the data associated regeneration efficiency as a function of bed volumes presented in Fig. 5 shows that during the first four bed volumes of regenerate DOW3N-Zn(II) had the second highest regeneration efficiency only to DOW3N-Fe(III) then the rate of perchlorate elution slows to a point where by 6 bed volumes of regenerant it has the second worst regeneration efficiency. This change in performance is most likely related to the mechanism, equilibrium kinetics, and thermodynamics associated with the chloride-perchlorate and hydroxide-perchlorate exchange reactions. The poor regeneration potential of DOW3N-Zn(II) under these conditions does imply that nitrate and sulfate are better competitors than chloride and hydroxide for perchlorate sorption on this resin.

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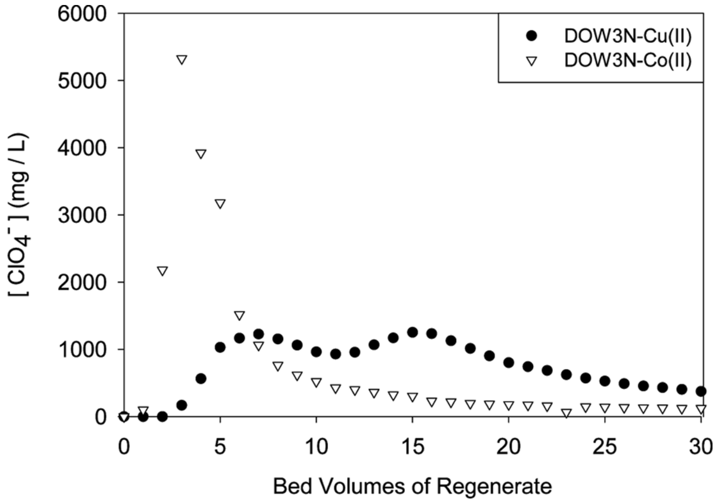

Figure 6. Perchlorate elution comparison for the regeneration of DOW3N-Cu(II) and DOW3N-Co(II). Regenerant solutions were made from a 4% NaCl solution and maintained at a pH of 12.4. The empty-bed contact time was 30 min. The mass of resin was ca. 2.0 g.

The perchlorate elution curve observed during the regeneration of DOW3N-Cu(II) has a different appearance than any of the other PLEs that we examined. Two distinct perchlorate peaks were observed in the perchlorate elution curve for DOW3N-Cu(II) as opposed to a single sharp peak, similar to one for the regeneration of DOW3N-Co(II), as shown in Fig. 6. One possible explanation for the anomalous perchlorate elution curve of DOW3N-Cu(II) is that the high pH of the regenerant solution caused a small amount of Cu(II) ions to leach from the resin and precipitate in the pores as metal hydroxides that restricted the elution of perchlorate from the resin. Through reloading perchlorate onto the resin following regeneration, we determined that the regeneration scheme did not have a significant impact on the perchlorate sorption capacity. The overall perchlorate sorption capacity of the regenerated resin differed by 2% for all examined resins. While DOW3N-Cu(II) appeared to be one of the best PLEs in terms of capacity and selectivity, its poor regeneration potential may be the limiting factors in its applicability.

In addition to the uncharacteristic perchlorate elution curve produced by DOW3N-Cu(II), a distinct color change was observed after regeneration; from blue to a deep brown color. In fact a closer examination of all the PLEs following regeneration showed occurrence of a color change, but none was as drastic as that observed for DOW3N-Cu(II)

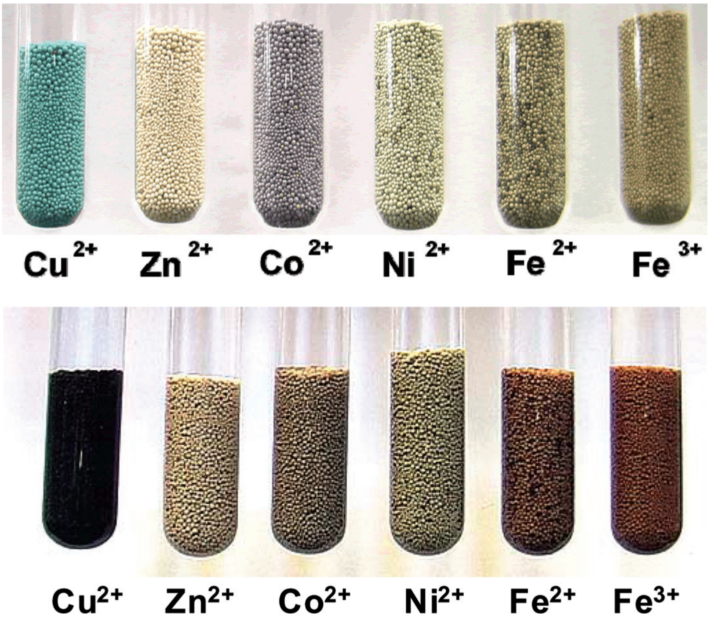

***Figure* 7.** Color of DOW3N-based PLEs following preparation (top) and regeneration (bottom).

(Fig. 7). We suspect that the darkened color of the PLEs resulted from the transition metal cation/hydroxide ion complex formation or the possibility of metal hydroxide precipitation within the resin. Additional laboratory studies demonstrated that this color change can be reversed with acid rinse.

In this work, we investigated one of many possible regeneration schemes for the PLEs. Additional laboratory experiments have shown that the regeneration of DOW3N-Cu(II) is possible across a range of regenerant solution chemistries (21). In order to make PLEs a viable perchlorate removal strategy it is necessary to develop a regeneration scheme which allows the ultimate destruction of perchlorate.

CONCLUSIONS

Six polymeric ligand exchangers, DOW3N-Ni(II), DOW3N-Cu(II), DOW3N-Fe(III), DOW3N-Fe(II), DOW3N-Zn(II) and DOW3N-Co(II), have been systematically studied and compared for capacity, kinetics, and regeneration potential to determine their relative viability for the trace removal of perchlorate. Results demonstrated that

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DOW3N-Zn(II) and DOW3N-Fe(II) PLEs are less desirable for perchlorate removal; either due to poor selectivity (DOW3N-Zn(II)) and/or low stability (DOW3N-Fe(II)). On the other hand, capabilities of Cu(II), Ni(II), Fe(III), and Co(II) PLEs to selectively adsorb perchlorate in the presence of competitors, nitrate and sulfate, were profound. The latter four resins each possess desirable properties as well as limitations. Within this group, DOW3N-Cu(II) showed the highest perchlorate capacity; all four PLEs had similar perchlorate sorption kinetics; and DOW3N-Fe(III), demonstrated better regeneration potential of all four resins examined. These four resins have shown favorable properties that could be utilized in the development of a perchlorate remediation scheme that utilizes on of the PLEs for perchlorate removal and allows perchlorate to be destroyed in the regenerate, possibly through bioremediation.

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