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Removal of Perchlorate from Contaminated Water Using a Regenerable Polymeric Ligand Exchanger

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Abstract: A polymeric ligand exchanger (PLE), DOW 3 N-Cu, has been investigated for perchlorate (ClO_4^-) removal from contaminated water. Batch kinetic tests revealed that the perchlorate sorption equilibrium for DOW 3 N-Cu can be reached within 20 hours and perchlorate removal by DOW 3 N-Cu follows standard ion exchange stoichiometry. Fixed-bed column runs showed that 12,388 bed volumes of perchlorate-free water can be obtained when DOW 3 N-Cu was used to treat a simulated contaminated water with an influent perchlorate concentration of 200 μg/L. It was found that the regeneration of spent DOW 3 N-Cu is pH dependent. It was shown that addition of ethanol and a surfactant Tween 80 to a 4% NaCl/2% NaOH regenerant solution

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increased the regeneration efficiency of spent DOW 3 N-Cu by 11 and 5 percent, respectively. Nearly 90% of perchlorate capacity of saturated DOW 3 N-Cu was recovered using 35 bed volumes of a regenerant containing 4% (w/w) NaCl, 2% NaOH, 5% Tween 80, and 5% ethanol.

Keywords: Ion exchange, ligand exchanger, perchlorate, perchlorate removal, regeneration

INTRODUCTION

Perchlorate removal from contaminated surface and ground water has become of higher interest due to its adverse effect on the ability of thyroid gland to produce hormones by inhibiting iodide uptake (1). The high mobility of perchlorate has also proven to be problematic because it has recently been detected in the crops and dairy products originating from regions with perchlorate-contaminated waters. Analysis for the presence of perchlorate in leafy crops from a farm near Redlands, CA in 2002 that were irrigated with perchlorate-contaminated water showed that lettuce retained 4.49 μg perchlorate per gram of fresh vegetable (2). The perchlorate uptake by plants shares the similar mechanism for nitrate and pertechnetate uptake, and accumulation of perchlorate within the plant is expected due to the basic principles of ion transport (2). Two years after the detection of perchlorate in crops of Southern California, perchlorate was detected at levels up to 11 μg/L in several samples of milk taken from across California (3). While perchlorate has been on the Contaminant Candidate List since 1998, the EPA has not yet established a maximum contaminant level (MCL) for perchlorate. The California Office of Environmental Health Assessment has set a public health goal for perchlorate at a concentration of 6 μg/L (2). While the final perchlorate MCL remains under deliberation, it is expected that the MCL will be set between 0 and 20 μg/L.

Perchlorate is a highly soluble monovalent oxyanion with a large ionic volume. Its highly delocalized monovalent anionic charge, large volume, and low charge density result in a high solubility of perchlorate which allows it to readily separate from cations in aqueous systems (1). While molecular thermodynamics predicts that perchlorate should readily oxidize water due to its favorable reduction potential, kinetic limitations, including a high activation energy, prevent this from occurring (1). Perchlorate is generally considered to be non-complexing in the presence of water, but it has been shown to complex with certain chelating agents. In the presence of specific transition metals, namely Cu, Ni, Co, and Sn, as well as specific organic compounds such as CH_3CN, CH_3, or pyridyl nitrogen, the formation of perchlorate complexes has been reported (5).

Application of conventional technologies for perchlorate remediation has been a challenge for the quite unusual physical and chemical properties of perchlorate (6); it is nonvolatile, highly soluble in water, and kinetically inert. Among various technologies reported are bioremediation (4, 7, 8), electrodialysis (4), membrane filtration (4, 9, 10), chemical/electrical reduction (1, 4, 11), and ion-exchange (IX) (4, 6, 12–14), of which ion exchange has shown to be one of the promising technologies for lowering perchlorate level to less than 10 parts per billion (ppb). Ion exchangers are capable of the selective sorption of perchlorate at levels down to a few parts per billion. Some of the advantages associated with IX processes are its easy implementation, low cost, and moderate maintenance requirements (4).

In general, strong base anion exchangers (SBAE) with quaternary ammonium functional groups and polystyrene backbone can offer fairly high sorption capacity for perchlorate removal. In particular, two modified SBA resins, Purolite A-530E and A-520E, have shown unusually high selectivity and sorption capacity for perchlorate (12). However, regeneration of these highly selective resins has been found to be rather difficult. Gu et al. (6) reported an iron tetrachloride regeneration scheme for the Purolite A-530E, which employed a regenerant consisting of 0.35 M $FeCl_3$, 2 M HCl, and 35% ethanol. They also showed that perchlorate in the spent regenerant brine can be degraded at an elevated temperature (up to 200°C) and pressure (up to 20 atm) (13). On the other hand, SBA exchangers with polyacrylic backbone exhibited high regeneration efficiency (96% with 13 bed volumes of 12% NaCl) but limited perchlorate sorption capacity (14). So, it is in great need to find a novel ion exchanger with both high perchlorate sorption capacity and regenerability. In this study, a polymeric ligand exchanger (PLE) is prepared for perchlorate removal. Compared with conventional ion exchangers, PLE utilizes a metal as its functional group, which provides a new perchlorate uptake mechanism and regeneration approach.

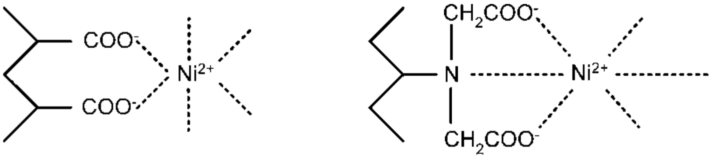
The Concept of Ligand Exchange

A PLE is composed of a chelating ion exchanger with transition metal cations affixed to its uncharged nitrogen-containing functional groups (15). The binding mechanism of PLEs differs from that of SBAEs, which have traditionally been used for perchlorate sorption. While SBAEs bind with anions mainly based on electrostatic interactions, PLEs bind with anionic ligands through concurrent Lewis acid/base and electrostatic interactions. The unique binding mechanism of PLEs allows for the selective sorption of anionic ligands from solution. In addition, unlike SBAEs, the sorption capacity of a PLE can be strongly affected by solution pH (16, 17) because hydroxyl anions are strong ligands and will compete for the sorption sites. This pH dependence offers a PLE the advantage that it can be more easily regenerated at higher solution pH, hence using lower saline solutions to regenerate a saturated PLE. The latter is important in deployment of bioremediation to destroy perchlorate in concentrated spent regenerant solutions (18–20).

Conventionally, a cation exchange resin is utilized as the support for hosting transition metal cations which proceed to selectively adsorb ligands from solution (21). Both the resin and affixed metal can be varied to modify the sorption characteristics of a given ligand exchanger. For instance, a modification of the resin functionality can change the number of available coordination sites, thus affecting the ligand exchange stoichiometry at the resin surface (see Fig. 1). Unlike for standard SBA resins, the ligand exchanger selectivity and regenerability for the PLE can be manipulated by controlling the interactions between the metal affixed to the resin backbone and the target ligand.

It is also important that in the ligand exchange process the formation of the metal-ligand complex must not cause the detachment of the complex from the hosting resin. Therefore, the hosting resin must be able to offer extremely high affinity to the metals to be loaded, which can be achieved by varying the types of resin functional groups. For example, an aminodiacetate resin provides greater metal-resin stability than a carboxylic-acid resin (Fig. 1), due to the additional coordination site being used for the metal-backbone interaction.

The phenomenon of anionic ligand exchange was studied by SenGupta et al. (22) and by Zhao et al. DOW 3 N (23). SenGupta et al. investigated anionic ligand exchange by comparing the arsenate, selenite, and oxalate sorption properties of a copper-loaded chelating resin DOW 2 N (DOW 2 N-Cu) with a common quaternary ammonium strong base anion exchanger IRC-718 (24). Results of this study show that the anionic ligand exchanger has a higher selectivity for selenite and arsenate than sulfate and chloride while the strong base anion exchanger is selective towards sulfate and chloride (24). They also determined that strong base anion exchangers were less selective to these contaminants than DOW 2 N-Cu (24). Regeneration of oxalate loaded DOW 2 N-Cu was accomplished with 4% Na_2CO_3 or with 4% NaCl/1% NaOH. However, the large number of regenerant bed volumes necessary for an efficient regeneration made these regeneration schemes undesirable (24).



Carboxylic-acid Resin
(4 avaliable Coordination Sites)

Iminodiacetic-acid Resin
(3 available coordination Sites)

Figure 1. Example of the effect of weak acid cation exchanger backbone on the number of available metal coordination sites (21).

Studies completed by Zhao et al. (15, 17, 23) further enhanced the understanding of anionic ligand exchange processes through the study of trace contaminant sorption using tailored chelating ion exchangers, which they defined as polymeric ligand exchangers (PLEs). They observed the ability of DOW 3 N-Cu to selectively adsorb phosphate, selenite, and oxalate in the presence of sulfate, noting the large ligand/sulfate separation factors observed during equilibrium studies (15, 23). They also validated the anion exchange stoichiometry of DOW 3 N-Cu by showing that the overall resin capacity remains constant over a wide range of aqueous-phase phosphate concentrations (23). Zhao and SenGupta determined that the regeneration of phosphate loaded DOW 2 N-Cu can be effectively accomplished with a 6% NaCl solution at a pH of 4.3 (23).

Zhao and SenGupta investigated the effect of pH on the anionic ligand exchange process (15, 17). They have reported that increasing solution pH results in enhanced selenite sorption capacity and selectivity due to the existence of selenite as a divalent, bidentate ligand at a pH above 8.3 (15, 17). With phosphate sorption, on the other hand, a maximum capacity is obtained at a solution pH between 6.5 and 8.5 due to phosphate existing mostly in its divalent, bidentate form (15, 17). Increasing the solution pH above 9 does not result in phosphate changing into its trivalent form, but the increasing hydroxide ion competition for ion exchange sites decreases the resin capacity for phosphate sorption (17). The objectives of this study are to

1. test the feasibility of using DOW 3 N-Cu for removal of perchlorate from water;
2. explore the possibility of regenerating DOW 3 N-Cu using a regenerant with low salt concentration and high pH and compare the regeneration efficiency of DOW 3 N-Cu to three commercial ion exchange resins A-530E, A-520E, and P4VP.

EXPERIMENTAL METHODS AND MATERIALS

Resins

Poly-4-vinylpyridine (P4VP) and DOW 3 N were purchased from Aldrich (Milwaukee, WI) DOW 3 N is composed of a polystyrene cross-linked with divinyl benzene backbone and bis(2-pyridylmethyl)amine functional groups. Copper was loaded onto DOW 3 N to prepared DOW 3 N-Cu by following the procedure reported by Zhao et al. (17). A-530E and A-520E were purchased from Purolite (Bala Cynwyd, PA)

Chemicals

The following chemicals were used as received: Ethanol (denatured, Fisher, Fair Lawn, NJ); Cupric chloride (laboratory grade, Fisher, Fair lawn, NJ); Sodium bicarbonate (Certified A.C.S, Fisher, Fair Lawn, NJ); Sodium chloride (certificted A.C.S. crystal, Fisher, Fair Lawn, NJ); Sodium perchlorate (98 + %, A.C.S. reagent, Aldrich, St. Louis, MO); Sodium sulfate (certificated A.C.S. Anhydrous, Fisher, Fair Lawn, NJ); Tween 80 (Aldrich, St. Louis, MO).

Sorption Stoichiometry Test

To test the Chloride-perchlorate exchange stoichiometry, ~0.3 g DOW 3 N-Cu in chloride form was added to 4 L solution containing 10 mg/L ClO_4^-. The solution was agitated and pH was kept at near neutral. Samples were taken at predetermined time intervals, and perchlorate and chloride were analyzed.

Column Runs

Fixed-bed column runs were carried out for DOW 3 N-Cu to test its breakthrough behavior. The experiment set-up included a Plexiglass column (diameter = 11 mm, length = 300 mm, Omnifit, Cambridge, England), a HPLC pump and a fraction collector (Eldex Laboratories, Napa, CA). The empty bed contact time (EBCT) was 10 minutes and the superficial liquid velocity (SLV) was 0.4 ml/min. A synthesized wastewater solution containing 0.2 mg/L ClO_4^-, 50 mg/L SO_4^{2-}, 35.5 mg/L Cl^- and 30.5 mg/L HCO_3^- at pH 7.2 was used as inflow.

Batch Perchlorate Loading

Air-dried, conditioned samples of A-530E, A-520E, P4VP, and DOW 3 N-Cu were batch loaded with perchlorate for later regeneration uses. Approximately 10 mL of each resin was weighed and placed in a loading solution ($V \approx 4L$) containing a calculated perchlorate concentration (added as sodium perchlorate) and 100 ppm sulfate (added as sodium sulfate) at an initial pH of approximately 8.3. The amount of perchlorate placed in each loading solution was calculated based on the sorption isotherm of each resin. The loading solutions were agitated daily, and solution pH was monitored and adjusted using 0.1 N HCl and/or 0.1 N NaOH as necessary so that a neutral equilibrating pH was obtained. Once the loading solutions had equilibrated (running about one week), each resin was extracted and stored in approximately 30 mL of its equilibrating solution. Samples from the initial and final solution were analyzed for perchlorate concentration and a mass balance was performed to determine the amount of perchlorate loaded onto each resin. The perchlorate capacity per gram of dry resin in the chloride form and the perchlorate capacity per milliliter of resin after loading were then calculated. The initial perchlorate loaded was (in mg/g based on air-dried resin weight): 66 for DOW 3 N-Cu, 136 for A-520E, 71 for A-530E, and 68 for P4VP.

Batch Regenerations

Prior to regeneration, approximately ten grams of DOW 3 N-Cu were batch loaded with perchlorate at a neutral equilibrating pH. The resin was divided into twenty-four 0.5 ML portions which are equivalent to approximately 0.30 g of dried resin and stored in its loading solution. For each of the regenerant solutions to be studied, six 200 mL portions of the desired regenerant were prepared at pH ranging from approximately seven to thirteen. The pH, perchlorate concentration, and copper concentration in each regenerant solution were then measured. One of the previously separated portions of perchlorate loaded DOW 3 N-Cu was then added to each regenerant after rinsing with five bed volumes of deionized water to remove any residual perchlorate from the resin. Solutions containing perchlorate-loaded DOW 3 N-Cu were then placed on a shaker table to insure complete mixing. After 24 hours the regenerate solution was analyzed for pH, perchlorate concentration, and copper concentration. The resin was then separated from solution, rinsed with several bed volumes of deionized water, dried, and weighed. The recovered resin mass was used as the amount of resin in each batch regeneration experiment. The amount of perchlorate and copper desorbed were calculated by mass balance. These values were then used to calculate the regeneration efficiency and the percentage copper desorbed from the resin.

Column Regenerations

A sample of perchlorate loaded resin was wet packed into an ACE #11 column on top of a glass wool plug for regeneration. The resins were wet packed into the column to avoid air bubbles in the resin bed and were washed with 5 to 10 bed volumes of distilled water to remove any residual perchlorate from the loading solution. The regenerant solution was pumped through the column at a predetermined flow rate by an Accuflow Series III Pump (Fisher Scientific). The regenerant solutions for the commercial strong base ion exchangers (A-530E, A-520E, P4VP) were traditional 6% or 12% NaCl brines.

For regeneration of DOW 3 N-Cu, 1% or 2% of the salt in brine was replaced by sodium hydroxide. This difference in regenerate was made because the perchlorate capacity of DOW 3 N-Cu was found to decrease rapidly at a pH above 10. An additional study was conducted for the regeneration of DOW 3 N-Cu with a 4% NaCl and 2% NaOH brine by varying the brine solvent with the addition of ethanol and or nonionic surfactant, Tween 80 to further enhance regeneration efficiency.

The flow rate for each regeneration was selected based on bed volume to achieve and empty bed contact time (EBCT) of approximately 20 minutes. The regenerant solution was collected one bed volume at a time by means of an Eldex Fraction collector (Eldex), and selected fractions were then analyzed for perchlorate concentration after proper dilution. The concentration data from each bed volume sampled was used to construct a perchlorate elution and regeneration efficiency curve as a function of bed volumes of regenerant. The regeneration efficiency at each bed volume was determined with a mass balance over the resin bed during the regeneration and the total amount of perchlorate loaded onto the resin.

Chemical Analysis

All analysis of perchlorate was performed on a Dionex DX120 Ion Chromatograph (Dionex) with an AS16 column and a 0.05 N sodium hydroxide eluent prepared with certified 50% w/w NaOH solution. Cl^- and SO_4^{2-} were analyzed by Dionex DX120 Ion Chromatograph (Dionex) using an AS14 column. A 3.5 mM sodium carbonate and 1.0 mM sodium bicarbonate solution was used as the eluent. Bicarbonate was analyzed as Inorganic Carbon (IC) using a TOC Analyzer (Phoenix 8000, TEKMAR DOHRMANN). Copper was analysized by a Varian SpectrAA 220 FS.

RESULTS AND DISCUSSION

Perchlorate Sorption Stoichiometry and Distribution Coefficient

Batch kinetic tests were conducted to investigate the perchlorate sorption rate and to determine whether the uptake of perchlorate follows the standard ion-exchange stoichiometry, i.e., sorption of an anion onto the solid phase must be accompanied by desorption of an equivalent amount of other anions. Figure 2 shows that perchlorate sorption equilibrium of DOW 3 N-Cu can be reached within 20 hours. Further, Fig. 2 reveals that the perchlorate (q_P) and chloride (q_C) uptake by DOW 3 N-Cu followed the standard ion exchange stoichiometry, i.e. sorption of one equivalent perchlorate is always coupled with desorption of the same equivalent amount of chloride at different times. Note that DOW 3 N-Cu was initially in chloride form. The ClO_4^- and Cl^- were considered to be the predominant counter ions in determining the equivalent concentrations. The perchlorate uptake increased at the expense of the decreasing of chloride loading, while the total capacity Q_T, in milliequivalents per gram of resin ($Q_T = q_P + q_C$), remained constant for the perchlorate-chloride system over a period of 50 hours.

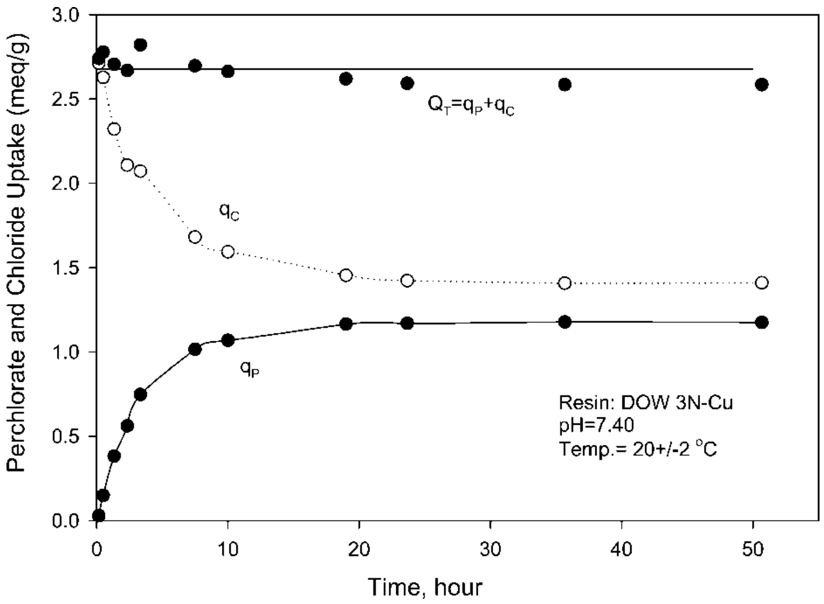


Figure 2. Validation of ion-exchange stoichiometry with DOW3 N-Cu in perchlorate-chloride system.

Distribution coefficient (K_d, mL/g) was calculated by using the same sorption data. K_d is an indication of adsorption selectivity of a given anion onto an adsorbent and it is defined as the ratio of the amount of ClO_4^- sorbed (as mg/g dry resin) divided by the concentration of ClO_4^- remaining in the equilibrium solution (as mg/mL):(12)

$$K_d = \frac{ClO_4^- \text{sorbed on resin (mg/g)}}{ClO_4^- \text{in solution (mg/mL)}} \tag{1}$$

In this test, 0.3 g DOW 3 N-Cu was used to treat 4 L simulated water containing an initial 10.64 mg/L ClO_4^-. The remaining ClO_4^- concentration was 2.11 mg/L at 24 hours. So the K_d at 24 hours was calculated to be 53,902 mL/g, which suggests that DOW 3 N-Cu has moderate perchlorate selectivity.

Fixed Bed Column Runs

Figure 3 shows the multi-component breakthrough histories from a fixed-bed column run with DOW 3 N-Cu and with an influent containing a trace concentration of perchlorate (0.2 mg/L) and much higher concentrations of competing bicarbonate (30.5 mg/L), sulfate (50 mg/L), and chloride (35.5 mg/L). A superficial liquid velocity (SLV) = 0.1 Bed Volume

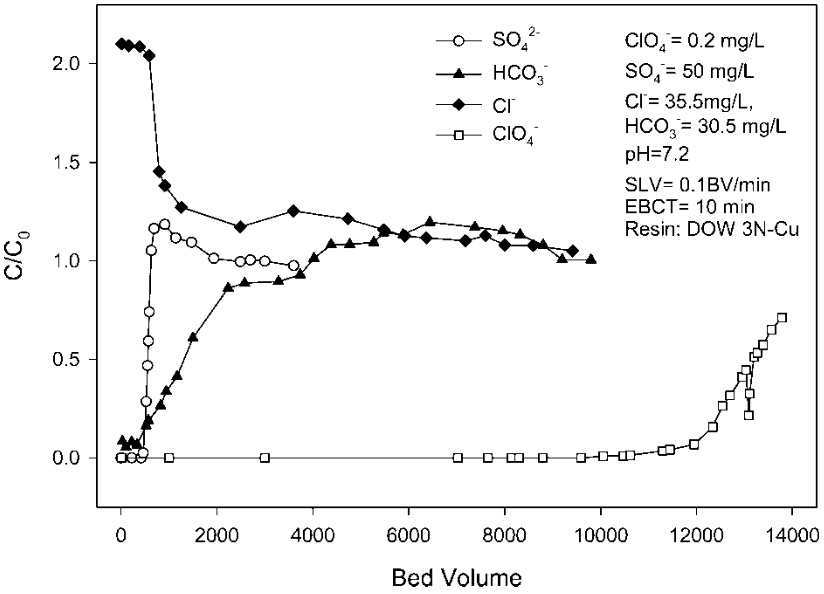


Figure 3. Fixed-bed column runs' breakthrough history curves of a multi-component system using DOW 3 N-Cu.

(BV)/min and an empty bed contact time (EBCT) = 10 minutes were used in this test. It is noteworthy that complete sulfate breakthrough happened at 633 BVs and complete bicarbonate breakthrough happened at 4,026 BVs, while 10% perchlorate (20 μg/L) breakthrough took place at 12,338 BVs. Also, chromatographic elution was observed for sulfate and bicarbonate, i.e., effluent sulfate and bicarbonate concentration, immediately after breakthrough, became greater than their influent concentrations. Considering chloride is the initial form of DOW 3 N-Cu, the following affinity sequence can be inferred for DOW 3 N-Cu: $ClO_4^- > HCO_3^- > SO_4^{2-} > Cl^-$.

Other column tests on commercial resins have been reported with similar breakthroughs (12, 14). The lagged perchlorate breakthrough in comparison to other anions suggests the preference of monovalent perchlorate over divalent sulfate toward commercial resins. The breakthrough histories demonstrated that some mechanism, such as Lewis acid-base interaction, beyond electrostatic interaction between ion-exchange resins and ClO_4^- is operative.

Batch Regenerations

DOW 3 N-Cu pre-loaded with perchlorate was investigated for the effect of pH on regeneration efficiency and copper loss through a series of batch regenerations. In this paper, regeneration efficiency refers to the percentage of

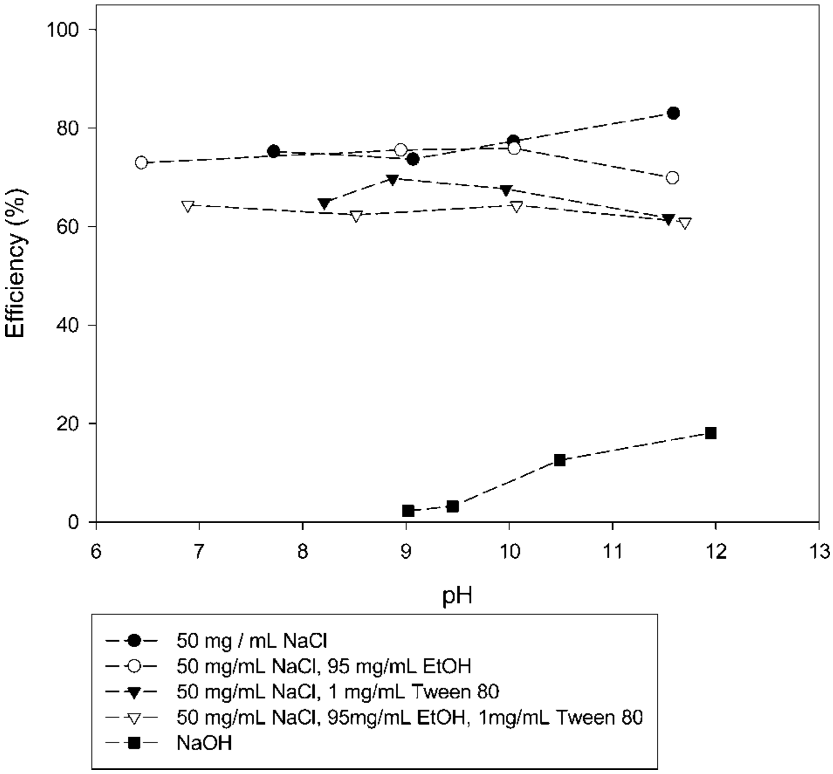


Figure 4. Plot of regeneration efficiency versus pH grouped by regenerant.

perchlorate that is washed off from the used resin. Figure 4 is a scatter plot of the regeneration efficiency for all batch regeneration as a function of pH. It was calculated by dividing the perchlorate mass recovered in the regenerant solution by the total perchlorate mass loaded onto fresh resins. For NaCl and NaOH, the regeneration efficiency showed an increasing trend with pH, which is expected due to competition of hydroxide ions for positions on the ion exchange resin since OH^- is a strong ligand replacing perchlorate. However, the competitive effect of OH^- was not significant for other three regenerants that contained ethanol and/or surfactant.

Figure 4 reveals that the regeneration with pure brine solution performed the best in this batch study. The regeneration results for the NaCl/EtOH (ethanol) regenerant were similar to those of the NaCl except between the pH range of 11 to 13 where the NaCl regeneration performed significantly ($\sim$10%) better. It was not expected to see the regenerant containing just salt perform the best over this range of pH because our results in flow analysis reported earlier showed that the regenerants containing ethanol and surfactant in addition to the salt performed more efficiently over a period of 35 bed volumes. In this batch study the addition of Tween 80 to the regenerant decreased the regeneration efficiency by approximately seven percent except in the pH range from 11 to 13 where the difference was about 20%. When the combination of ethanol and Tween 80 were used with the salt the regeneration efficiency was similar to that of ethanol.

It should be noted that this test does not give a full kinetic analysis of each system hence, it does not allow the determination of which regenerant works best over a small scale. Based on the results of the column regenerations it is expected that modification of the regenerate solvent will decrease the equilibrium regeneration efficiency, but it will increase initial regeneration kinetics.

As shown in Figure 5, for all regenerants tested in this study nearly zero copper loss was observed at a regenerant pH up to 9. Above pH of 10, copper was detected in regenerant solutions. Due to the complex mixture of the regenerant solutions, quantifying the amount of copper in each regenerant at pH >12 turned out to be difficult, and thus not presented. However, the experimental results show a positive correlation between regeneration pH and copper loss above a pH of 10. Among all components added to the brine solution, it was observed that the presence of ethanol generally tends to increase the amount of copper loss at pH greater than 9.

Visually examining the resin allows one to see a change in resin color as its pH increases (see Fig. 6). Up to a pH of 10 the resin retains its blue color. Beyond pH of 10 its color gradually turns to yellow and then dark brown or

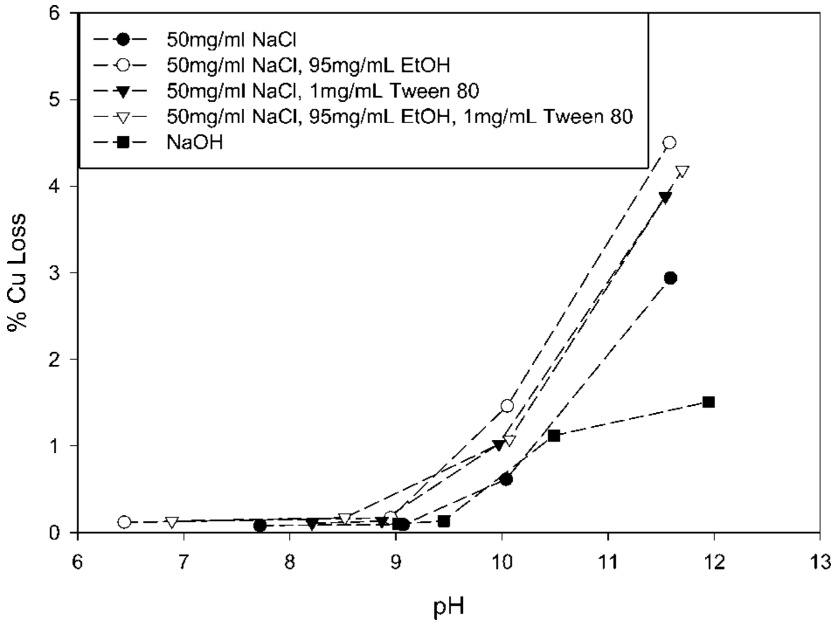


Figure 5. Plot of percent Cu loss versus pH for different regenerants.

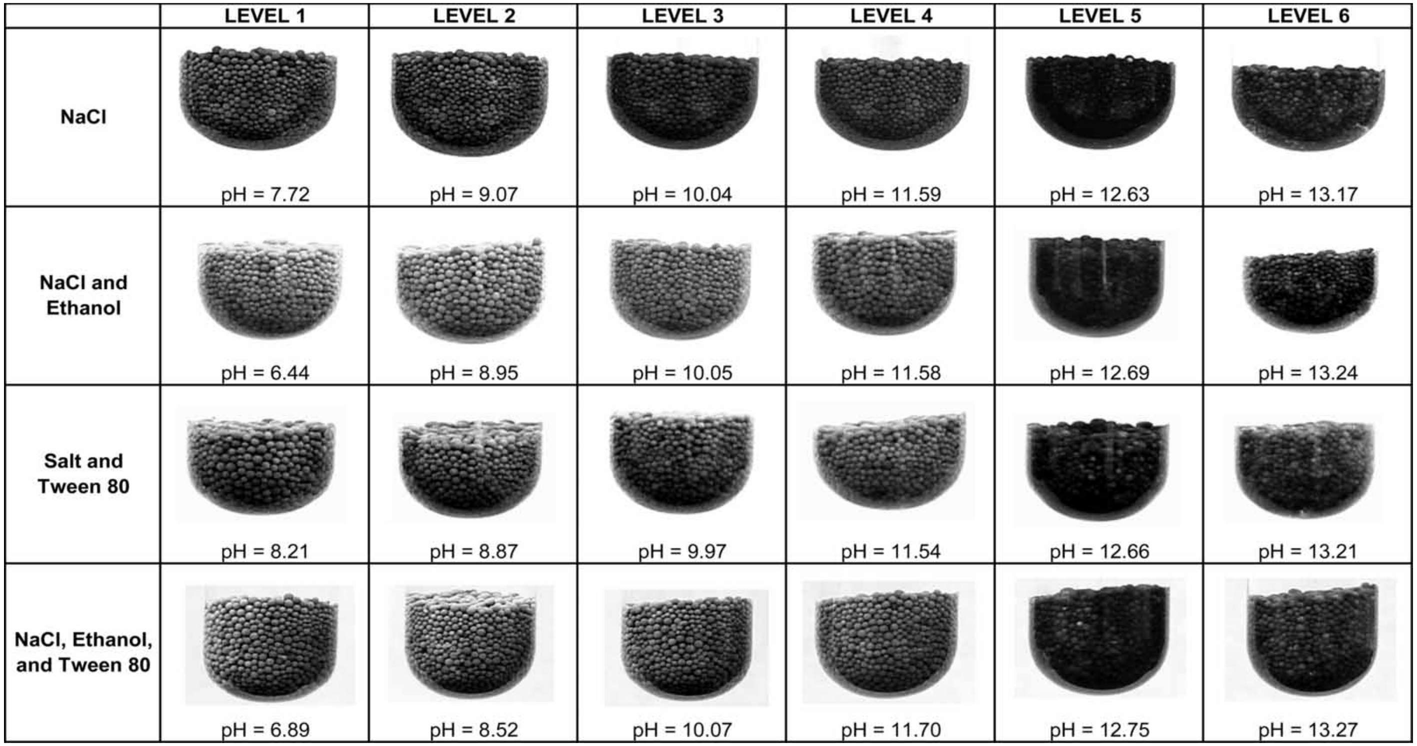


Figure 6. Visual summary of in resin color change with pH for different regenerants. The color of resins turn to dark brown or gray about pH = 12.6 for all of the regenerant formulas used.

gray. As demonstrated in Figure 6, this trend was consistent for all of the regenerant formulas used in this study.

In summary, the results of this batch test indicate that the regeneration efficiency increases with pH. Increase in pH, on the other hand, accelerates the removal of copper from the resin. Thus, in order to determine which regeneration procedure suits best for a given application, an economic analysis would have to be performed to determine whether it is more beneficial to design the process to get higher efficiency or to replace or reload the resin with copper. It is expected that minimal copper leaching is the most beneficial situation for the regeneration, so a resin with a pH of 9 or below would most likely be the best scenario in terms of minimizing copper loss.

Column Regenerations

Column regenerations of the commercial resins A-530E, A-520E, and P4VP were conducted using a 12% NaCl brine with an EBCT of 21 ± 1 minutes. After 35 bed volumes of regenerate were passed through, the resin regeneration efficiencies of A-530E, A-520E, and P4VP were found to be 49%, 69%, and 53%, respectively. The perchlorate elution curves for these regenerations are presented in Fig. 7 and the efficiency curves are listed in Fig. 8. The

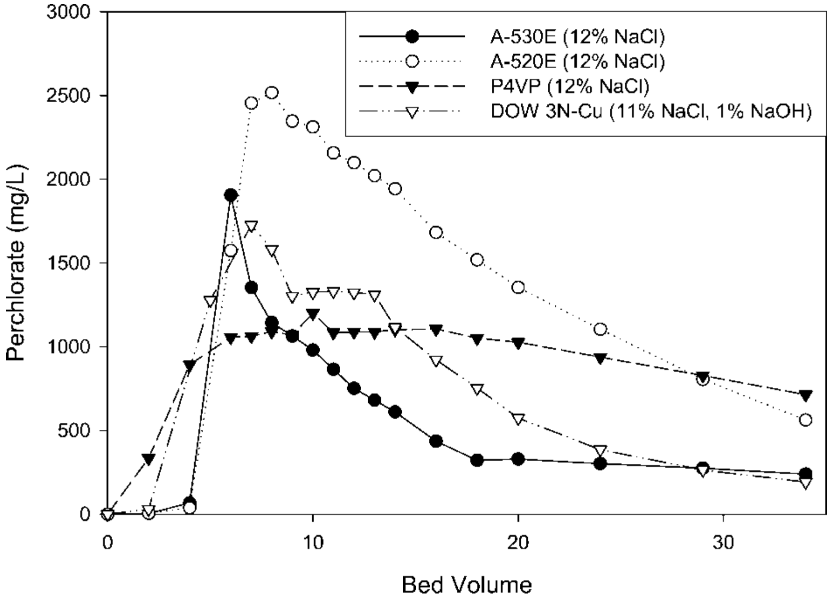


Figure 7. Perchlorate elution curves for the regeneration of DOW 3 N-Cu, A-530E, A-520E, and P4VP with 12% brines or 11% NaCl/1% NaOH at an EBCT of 21 ± 1 minutes.

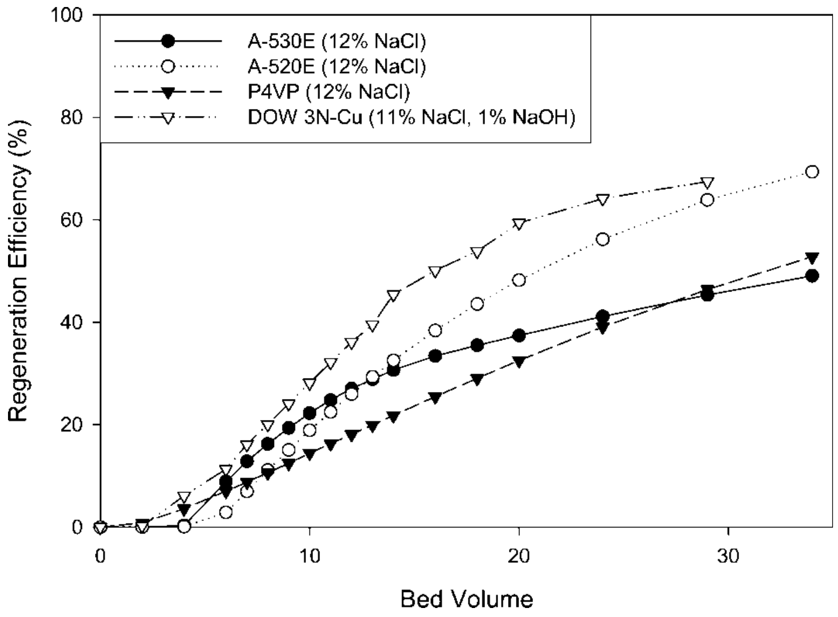


Figure 8. Regeneration efficiency curves for DOW 3 N-Cu, A-530E, A-520E, and P4VP with 12% brines and an EBCT of 21 ± 1 minutes.

low peaks and long tails on the elution curves for these resins shown in Fig. 7 could be indicative of their poor regeneration kinetics.

Of all the commercial resins tested Purolite A-520E is regenerated the most efficiently with the 12% brine solution; 69% efficiency at 35 bed volumes. Purolite A-530E shows better regenerative properties than P4VP until about 27 bed volumes of regenerant had passed through the resin. Although P4VP is more efficient at high bed volumes of regenerant, P4VP shows the worst regenerative properties of all the commercial resins tested. This is evident by its flat elution curve and shallow linear efficiency curve. Although Purolite A-520E shows better regenerative properties with 12% brine solution in the long run, Purolite A-530E is more efficient for up to 14 bed volumes.

When comparing the commercial resin regenerations with 12% brines solution to DOW 3 N-Cu regenerated with 11% NaCl-1% NaOH, DOW3 N-Cu shows better regenerative properties with the high concentration brine solution than all other resins except Purolite A-520E above 30 bed volumes. DOW 3 N-Cu had a regeneration efficiency of 68 percent after 35 bed volumes.

Since the capacity of DOW 3 N-Cu is pH dependent, the effect of replacing a fraction of sodium chloride by sodium hydroxide in the brine regenerant was examined. In this study one to two percent of the sodium chloride was replaced by sodium hydroxide in regenerant brines containing a total of 6% or 12% salt. Efficiency and elution curves for this set of regenerations are shown in Fig. 9. Regeneration with the 4% NaCl, 2% NaOH brine

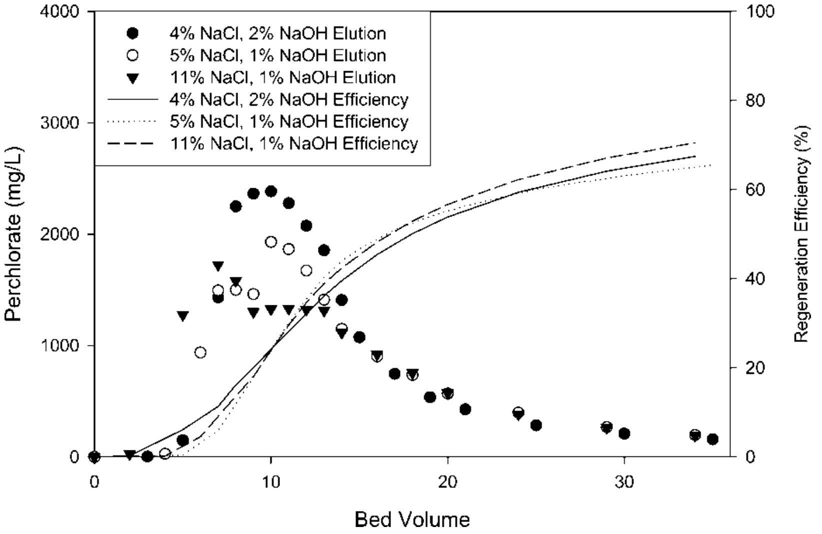


Figure 9. DOW 3 N-Cu regeneration breakthrough and efficiency curves varying salt brine composition regenerated at an EBCT of 20.4 ± 0.4 minutes.

produced an efficiency of 66%. When the regenerant was modified to contain 5% NaCl and 1% NaOH the regeneration efficiency increased to 71% suggesting the existence of an optimal sodium hydroxide concentration. A more detailed study of this effect is warranted to determine this optimum.

When the regeneration of DOW 3 N-Cu was performed using 11% NaCl-1% NaOH, a regeneration efficiency of 68% was obtained. This suggests that a lower sodium chloride concentration than 11% is necessary to achieve optimal regeneration. Though the regeneration conducted with a 10% NaCl, 2% NaOH solution was inconclusive due to an equipment malfunction, from the 13 bed volumes of regenerate collected, it appears that this regeneration follows the same pattern as the one with 2% NaOH and produces lower efficiency in the long run. This is expected because the sodium hydroxide concentration appears to influence the amount of curvature in the efficiency curve. Notice, from Fig. 8, that both regenerations with 1% NaOH have similar curve shapes which are flatter in the beginning and steeper at the end when compared to the regeneration with 2% NaOH. Thus, it is expected that the completion of the regeneration with 10% NaCl and 2% NaOH would yield a lower efficiency due to the expected shape of its efficiency curve. It is important to note that because of the low number of regenerations run and the similarity of the results, no statistically significant difference between each of these regenerations could be found.

Since solvent modifications are commonly used to increase regeneration efficiency, the regeneration of DOW 3 N-Cu with the 4% NaCl/2% NaOH solution was explored by varying the solvent to contain ethanol and/or

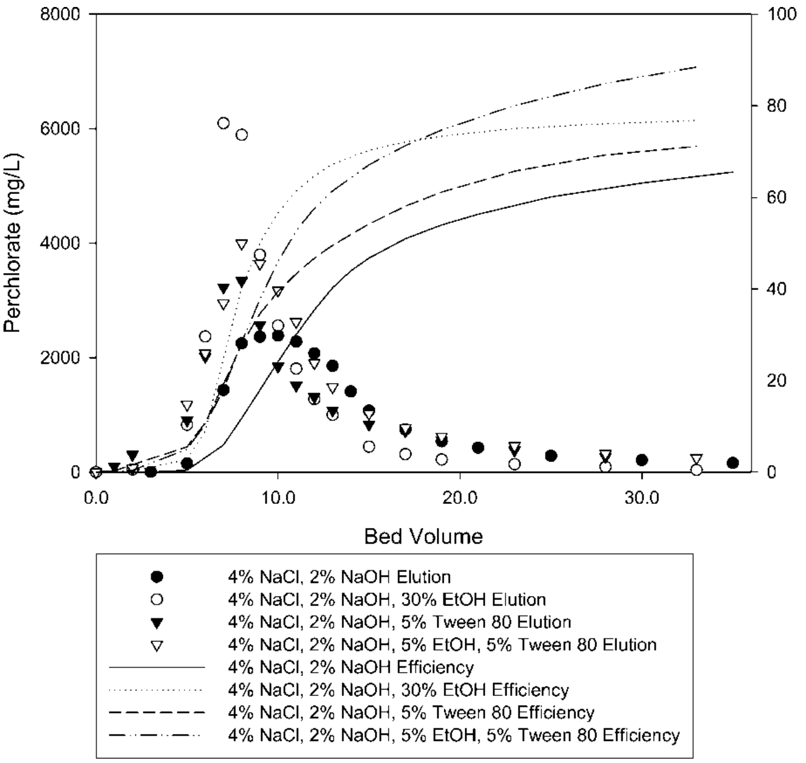


Figure 10. Perchlorate elution and regeneration efficiency curves for DOW 3 N-Cu with regenerate solutions composed of 4% NaCl, 2% NaOH and solvents containing a combination of water, Tween 80, and ethanol regenerated at an EBCT of 20.4 ± 0.4 minutes.

Tween 80, a nonionic surfactant. Figure 10 shows the breakthrough and efficiency curves for each of these regenerations. Regenerating DOW 3 N-Cu without any solvent modifications resulted in a regeneration efficiency of 66% at 35 bed volumes. When the solvent was modified to contain 30% ethanol the regeneration efficiency increased to 77%. This regeneration appears to show improved kinetics as seen from its high peak and short tail in addition to a clearly sigmoidal efficiency curve. These beneficial effects on regeneration efficiency and kinetics can be attributed to the decreased dielectric constant of the regenerant solution when ethanol and/or surfactant were included, which makes the adsorbed perchlorate to be easily washed off. This regeneration reached 67% efficiency after only 15 volumes of brine regenerant. The concentration of ethanol in this regenerant is higher than what would be desired for a commercial regeneration process so a study will have to be conducted to determine an optimal ethanol concentration once the most effective salt composition is obtained.

Performing the regeneration of DOW 3 N-Cu with 5% Tween 80 in the solvent increased the regeneration efficiency from 66% to 71% at 35 bed volumes. Comparison of the efficiency curves shows the regenerations with and without Tween 80 are comparable for approximately 10 bed volumes. At this point the efficiency curve for the regeneration including Tween 80 begins to diverge from that of the one without it. When the regeneration was performed with 5% Tween 80 and 5% ethanol in the brine regenerant the effect of the ethanol and surfactant compounded to produce the most efficient regeneration, 88% at 35 bed volumes. The regeneration using 30% ethanol was actually more efficient than the 5% EtOh 5% Tween80 regeneration until about 17 bed volumes. Both regenerations show good kinetics through sigmoidal efficiency curves and peaked breakthrough curves. It is important to notice that the addition of Tween 80 to the brine regenerant increased the efficiency at later bed volumes that can be seen by the higher slope of the efficiency curve at later bed volumes.

CONCLUSIONS

Perchlorate sorption capacity and regeneration efficiency of the polymeric ligand exchanger DOW3 N-Cu were compared to a number of commercial ion exchange resins including A-530E, A-520E, and P4VP. DOW 3 N-Cu showed a better regenerative property than all other commercial resins except Purolite A-520E when 12% brine solution was used as regenerant solution. Batch kinetic tests revealed that the perchlorate sorption equilibrium for DOW 3 N-Cu can be reached within 20 hours and perchlorate removal by DOW 3 N-Cu follows standard ion exchange stoichiometry. It was found that the regeneration of spent DOW 3 N-Cu is pH dependent; so was the copper loss from the resin. It was shown that addition of ethanol and Tween 80 to a 4% NaCl/2% NaOH regenerant solution increased the regeneration efficiency of spent DOW 3 N-Cu by 11 and 5 percent, respectively. Further investigation is warranted to optimize the levels of ethanol and sodium hydroxide addition to the regenerant.

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