Short communication

Utilization of iodide as a perchlorate-laden resin regenerating solution and isolation of perchlorate from simulated ground water samples

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Abstract

The selective ion exchange of perchlorate from simulated groundwater samples using the bifunctional Purolite A-530E resin was performed. Regeneration of the resin is difficult due to the relatively hydrophobic nature and high selectivity of perchlorate over the most common ions. Use of the tetrachloroiron(III) complex in 2 M or higher hydrochloric acid solutions as a regenerant and displacer of perchlorate can be problematic if one wishes to recover the perchlorate and/or use stainless steel columns, fittings, and HPLC-type pumps. 0.1 M sodium iodide was investigated as an alternative to $FeCl_4^-$ to circumvent these problems. Regeneration efficiencies in between those of $FeCl_4^-$ and Cl^- were observed. During elution a peak fraction of 0.068 M $NaClO_4$ in 0.1 M NaI was obtained. Pure $KClO_4$ was then precipitated by addition of KCl and methanol to this fraction.
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1. Introduction

The perchlorate (ClO_4^-) anion is a water contaminant that originates from salts such as ammonium and sodium perchlorate, which are used in rocket fuel, fireworks, air bags, and some fertilizers. These salts are very soluble in water and their improper disposal has lead to the contamination of aquifers in many communities [1]. Perchlorate is a rather inert ion, and most people are exposed through the consumption of contaminated water supplies or food grown with such water. Once in the human body perchlorate targets the thyroid gland. The thyroid gland gathers large amounts of iodine, which is used for the production of two hormones, triiodothyronine (T_3) and thyroxine (T_4), that facilitate several biochemical and metabolic processes [2]. Perchlorate acts as a competitive inhibitor of the sodium/iodide symporter in the thyroid follicular cell through an ion-exchange mechanism from the blood to the thyroid. The intoxication with perchlorate can therefore lead to the blockage of all the functions carried out by T_3 and T_4 by preventing their production. This may be a significant health concern for fetuses and breast-feeding babies of mothers with iodine deficiencies or thyroid problems.

Many water supplies throughout the country, especially in southern California, have exceeded the concentration of perchlorate that can be of risk to human health. The California Department of Public Health currently uses a notification level of 6 ppb [3], which has caused the closure of numerous wells. A recent National Research Council study recommended a safe dose that translates to 24 ppb [4]; however, many states and communities have adapted much lower action levels of 2 ppb.
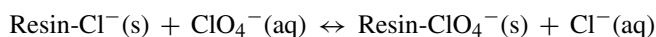
Thermodynamically the perchlorate anion is considered to be a strong oxidizing agent, but there is large activation energy for redox reactions, and complexation interactions are generally weak [5]. In fact, the perchlorate ion has been shown to not accept electrons directly from any reductants, not even from strong reductants or solvated electrons, either in water or any other polar solvents. They are considered "hydrophobic" as far as ions are concerned because the single charge is dispersed uniformly over a rather large tetrahedral molecule. These chemical and physical properties make the elimination of perchlorate anion a challenging task.

Anion exchange has been implemented at some of the affected water wells to remove perchlorate from ground waters to very low concentration levels. In anion-exchange strong and

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weak base resins pre-loaded with anions, usually chloride, are used to extract ClO_4^- from water:

$$Resin\text{-}Cl^-(s) + ClO_4^-(aq) \leftrightarrow Resin\text{-}ClO_4^-(s) + Cl^-(aq)$$

In the resin the chloride anion is substituted with the perchlorate anion, until saturation occurs.

Anion exchange, however, presents problems that make this method economically inefficient. After the resins are saturated, they need to be regenerated, discarded, or incinerated. Regeneration of perchlorate-laden resins has been proven to be difficult since virtually all resins exhibit a greater selectivity for perchlorate than for other common ions. In previous studies, it was found that several dozen bed volumes (BV) of 12% sodium chloride are needed to remove only a fraction of the loaded perchlorate from styrenic-type strong-base resins [6]. Styrenic-type resins are generally more selective than other resins such as acrylics because they are more hydrophobic as is the perchlorate ion, and they are relatively cheaper than others.

The disposal of regenerant brines containing high concentrations of perchlorate is also an issue. A potential solution of this problem is biodegradation of the perchlorate by a perchlorate-reducing bacteria. Different facultative anaerobic microorganisms are able to reduce perchlorate to chloride; numerous studies on perchlorate biodegradation have found many species capable of reducing perchlorate [7,8]. Indeed this approach is also commonly being used to remove and destroy the perchlorate directly at the well head or *in situ*.

In this study, anion-exchange properties of perchlorate from simulated groundwater samples, displacement and isolation of the perchlorate ion from the resin bed, and its precipitation from this solution were investigated. Purolite A-530E was chosen due to its advertisement as a perchlorate-selective resin; this selectivity is due to dual functionality incorporating hexyl groups to increase its hydrophobicity [9–12].

In another aspect of our project, the recovery of a pure perchlorate salt for further isotope ratio mass spectrometric (IRMS) analysis was required. Having the ability to use anion-exchange chromatography to isolate perchlorate from ground waters, and obtaining the isotope ratios of chlorine and oxygen in the perchlorate samples, is a possible forensic method of determining the origin of the perchlorate [13,14]. The ratio signature allows environmental agencies to determine whether the perchlorate is anthropogenic or naturally occurring.

Regenerant/displacer solutes that have chlorine or oxygen atoms, with subsequent evaporation, therefore could not be used. The tetrachloroferrate ($FeCl_4^-$) regenerant solution was previously found to give a nearly 100% recovery of ion-exchange sites with only 6 bed volumes of solution [15]. However, this method requires neutralization of the $FeCl_4^-$/HCl solution and removal of the iron as $Fe(OH)_3$. Upon addition of KCl, a slow crystallization of $KClO_4$ is obtained in low yield. We utilized iodide as the regenerant/displacer solution, due to its similar size and hydrophobicity to perchlorate. Furthermore, we designed a method for the precipitation of perchlorate as $KClO_4$ from the regenerant brines using methanol. Overall, the proposed method allows relatively efficient removal, recovery, and recycling of perchlorate from aquatic media.

2. Experimental

2.1. Resin columns and apparatus

The Purolite A-530E resin in the chloride form (BroTech, PA) is a dual amine bifunctional resin that exhibits high selectivity for hydrophobic anions such as perchlorate and pertechnetate [9,12]. Three different columns (11.5, 13.2 and 1.0 g) were slurry-packed into either a buret for the larger two columns or a 6.6 mm i.d. adjustable-length glass column (Omnifit) for the smaller column. The packing density was 0.73 g/mL, leading to bed volumes of 16, 18, and 1.4 mL, respectively. The smaller column was connected to an HPLC pump (Varian Model 2010) and operated at 1.0 mL/min or 0.73 BV/min. Samples collected from the column outlet were analyzed with a Metrohm-Peak ion chromatograph (Model 761, Houston, TX) using a Metrosep A Supp 5–100 column, a 7.0 mM carbonate/1.0 mM bicarbonate eluent, and ion-suppressed conductivity detection.

2.2. Loading ClO_4^- onto the columns

The columns were rinsed by running 100 mL of deionized water through the column at a rate of 1 mL/min. Once equilibrated the resins were loaded with either pure $NaClO_4$ solutions at different concentrations; or a simulated contaminated groundwater sample [15]. The simulated groundwater sample consisted of 3 mM $NaHCO_3$, 1 mM $CaCl_2$, 0.5 mM $MgCl_2$, 0.5 mM Na_2SO_4, and 0.5 mM KNO_3 in addition to 2 mM $NaClO_4$. The resins were loaded until a full breakthrough of perchlorate was obtained by analysis of 1-mL samples at the column outlet at various time intervals. The amount of ClO_4^- loaded onto the column was calculated from the breakthrough midpoint, after subtracting the void volume of the columns [16].

2.3. Regeneration of the resins/displacement of ClO_4^-

The perchlorate was displaced from the columns with either 0.1 M NaI or 0.35 M $FeCl_3$ in 2 M HCl with 35% methanol. The flow rate was similar to the loading experiments, or 1.0 mL/min for the small column. Following the adsorption of perchlorate and before displacement, the column was rinsed with 100 mL of distilled water. During regeneration, samples were collected at strategic volumes and then analyzed using IC. The concentrations obtained (moles/L) were plotted against the volume (mL) or number of bed volumes in which they were eluted. The area under the curve was determined to be the total amount of perchlorate desorbed from the resins.

2.4. Mass balance

The mass balance adsorbed and desorbed for perchlorate was obtained as one indicator of regeneration efficiency. This was measured by determining the ratio of the amount of perchlorate desorbed from the resin to the amount of perchlorate sorbed by the resin during the same regeneration cycle. Another indicator of regeneration/displacement efficiency is the number of

bed volumes required to elute the perchlorate, as well as the maximum concentration observed for this elution band.

2.5. Isolation and precipitation of perchlorate

The perchlorate-containing regenerant brine desorbed with the tetrachloroferrate solution required a neutralization step using concentrated NaOH to precipitate the iron as ferric hydroxide. The neutralized solution was then centrifuged using a Fisher Scientific Model 228 for 5 min. Following centrifugation the supernatant solution was carefully decanted from the precipitate. This procedure was used to supply a sample for IC analysis. Several combined fractions of the supernatant were then passed through a cation-exchange column to remove excess sodium. Removing sodium further facilitated the selective precipitation of perchlorate as $KClO_4$, which is almost 200 times less soluble than $NaClO_4$. The precipitation was compared under two different conditions: precipitation with KCl alone, and precipitation with KCl plus 80% (v/v) methanol. The precipitated potassium perchlorate was rinsed with 97% methanol and then re-dissolved in deionized water and tested for purity by IC. The percent recovery was obtained from the concentration of perchlorate in the collected fraction before precipitation and the recovered, re-dissolved concentration. The regenerant brine desorbed with the iodide solution did not require the neutralization, centrifugation, or cation-exchange steps.

To return the resin to the chloride form, the iodide-laden column is regenerated with 2 M NaCl. The $FeCl_4^-$-laden resin is regenerated with 0.01 M HCl to breakdown the complex while keeping iron(III) soluble enough to elute.

3. Results and discussion

The dual amine bifunctional Purolite A-530E resin has been previously shown to have high selectivity for ClO_4^- [10,11]. This resin was packed into glass columns and loaded with perchlorate until 100% breakthrough to the feed concentration was observed. Perchlorate was loaded onto the resins in two separate experiments with either 0.1 M or 2.0 mM $NaClO_4$ alone and with 2.0 mM perchlorate in a simulated ground water sample containing Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-} as competing anions as described in Section 2. The breakthrough of perchlorate was observed by analyzing samples from the column outlet by IC. Fig. 1 is the breakthrough curve of 0.1 M perchlorate through a large column containing 11.5 g of resin without any competing ions. From the midpoint of the breakthrough and the estimated void volume (6 mL), it is determined that 0.86 meq/g of perchlorate was sorbed onto the column. This serves as an estimate of the capacity of the resin and compares favorably with the manufacturer's specifications (0.60 meq/g minimum) [9].

Fig. 2 illustrates the sorption behavior of 2.0 mM perchlorate when other anions typically in ground water are present in the perchlorate feed solution. Note that bicarbonate, although present, is not observed because a bicarbonate/carbonate buffer is used as the eluent in the IC chromatograms. These results indicate that all the other ions breakthrough earlier than perchlorate
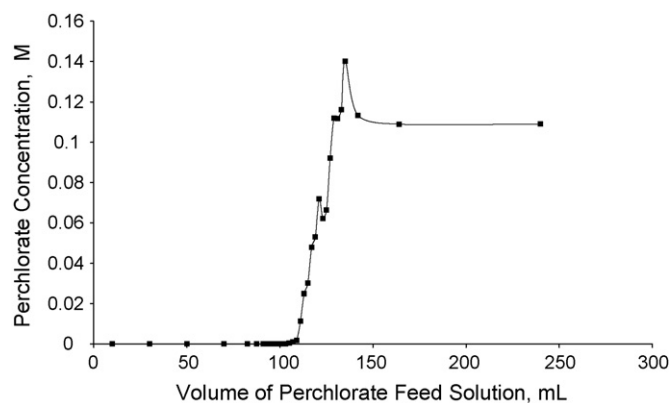

Fig. 1. Breakthrough curve of 0.1 M perchlorate on larger 11.5 g Purolite A-530E glass column.

and therefore the resin is less selective towards them. The selectivity order is $ClO_4^- > NO_3^- > SO_4^{2-} > Cl^-$. Note that chloride immediately breaks through due to it being pre-loaded on the resin. It is also noted that the competing ions breakthrough to a higher concentration before relaxing back to their feed concentrations, especially for nitrate. This is due to the displacement of additional ions from the resin by the perchlorate. The midpoint of the perchlorate front indicates a capacity of 0.84 meq/g in the presence of the other ions, which is very similar to the capacity without competition.

In the first stages of this project we utilized tetrachloroferrate as the regenerant solution; this solution was found to fully regenerate the A-530E resin after ≈6 bed volumes in Gu et al. [15]. In their experiment the resins were only loaded to 50% capacity. In our experiments the resin was loaded to 100% capacity, and less than 10 bed volumes were required for complete regeneration as shown in Fig. 3. Displacement using the tetrachloroferrate solution was considered time consuming in our work since we were interested in isolating the displaced perchlorate from solution; therefore this solution required neutralization and centrifugation to remove the precipitated ferric hydroxides from the supernatant solution. In addition, the high concentration of HCl in this solution oxidizes the stainless steel components utilized in the HPLC equipment and indeed was the principle reason for using glass columns in this study. It is desirable to design separations with the resins packed in stain-
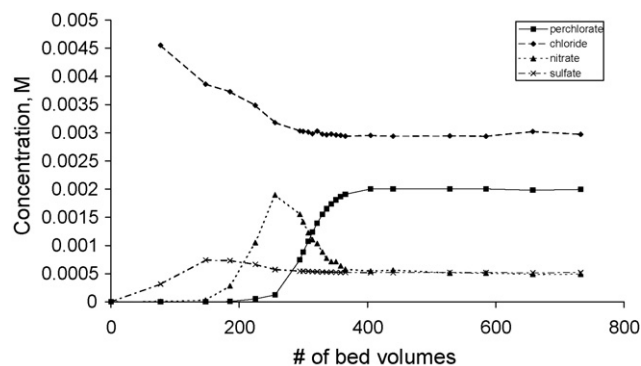

Fig. 2. Breakthrough curves of 2 mM ClO_4^-, 3 mM Cl^-, 0.5 mM SO_4^{2-}, and 0.5 mM NO_3^- on smaller 1.0 g Purolite A-530E glass column at 1.0 mL/min.
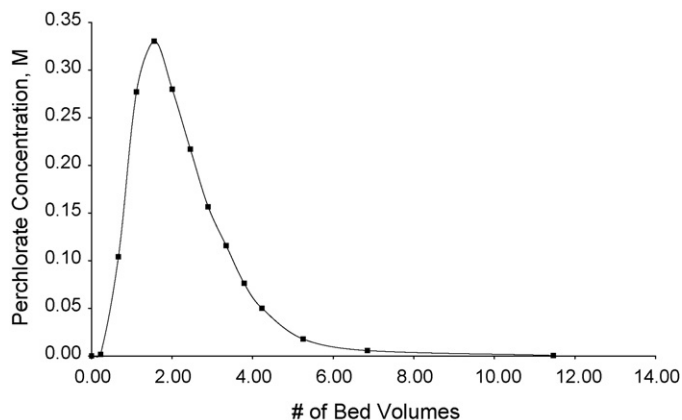
Fig. 3. Displacement of perchlorate from perchlorate-saturated Purolite A-530E column with 0.35 M $FeCl_3$ + 2 M HCl + 35% methanol displacer solution.

less steel columns to allow smaller particles and larger columns with their concomitant higher pressures and flows.

To circumvent the negative aspects of the tetrachloroferrate solution, we investigated iodide as a displacing ion and regenerant solution. The toxicity of perchlorate is based on the competitive ion-exchange mechanism in which perchlorate replaces iodide. This is possible because of the similarities in size and charge distribution between these two ions. The reverse process, iodide competing for ion-exchange sites with perchlorate, may be a good displacement ion for purposes such as the one discussed here as well as an intermediate ion in a regeneration method for highly perchlorate-selective resins such as Purolite A-530E. Although still a corrosive halide, lower concentrations may be successfully utilized to allow usage of stainless steel components.

In Fig. 4, the displacement/regeneration using 0.1 M iodide solution is shown for the small column experiment that was loaded with competing ions present. The results obtained show that the A-530E resin was regenerated after approximately 70 bed volumes of 0.1 M iodide, with a long tail of perchlorate elution with respect to the $FeCl_4^-$ data. Approximately 82% of
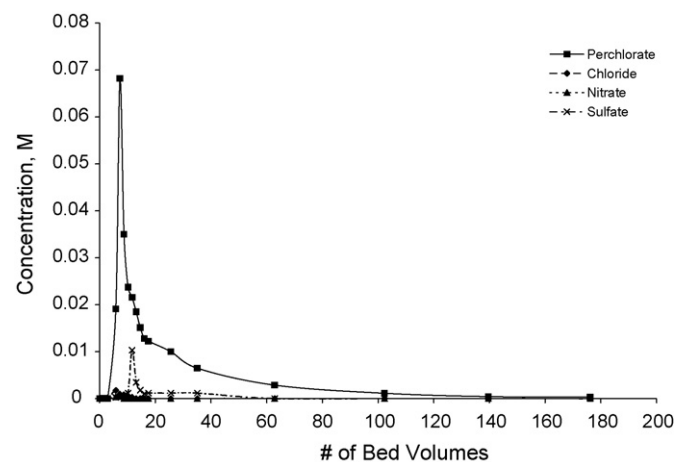
the resin is regenerated in 35 BV. The amount of ClO_4^- removed from the column was 0.89 meq/g, approximately 6% greater than that observed in the loading experiment. This could be due to perchlorate from previous experiments with this column not completely removed or to an underestimate of the loading capacity from the midpoint method. A small sulfate peak was also observed after the perchlorate peak maximum. There is a significantly greater solution volume required to regenerate the resin than with the tetrachloroferrate solution. Note however, that regeneration/displacement flow rates are generally suggested to be significantly lower than loading or service flow rates, and the flow rate of 1.0 mL/min for this experiment would be considered to be too large. A lower flow rate may allow more complete displacement in a lower volume. Also higher concentrations of NaI may be attempted without compromising stainless steel hardware to improve these figures. However it is still far more efficient than regeneration of perchlorate-laden resins with a concentrated NaCl solution [6], which is too concentrated for stainless steel stability. In addition, displaced bands of perchlorate in the NaI eluent may simply be evaporated to yield a residue of $NaClO_4$ and NaI, circumventing the need for precipitation of $KClO_4$ for IRMS analysis. There is no interfering source of chlorine and oxygen in the residue obtained.

The results of Figs. 3 and 4 also show that the maximum concentration of perchlorate displaced is 0.33 M with the tetrachloroferrate solution and approximately five times lower at 0.068 M for iodide. A suitable fraction of perchlorate may be obtained free of sulfate in 4–10 bed volumes, yielding over 30 mg with the small column. For complete displacement of perchlorate with 70 BV of 0.1 M NaI, almost 17 g of NaI would be required per gram of perchlorate. With the tetrachloroferrate method, complete displacement with 10 BV of the reagent costs about 13 g $FeCl_3 \cdot 6H_2O$, 23 mL HCl, and 47 mL of methanol per gram of perchlorate. Considering the price of NaI is approximately 8 times that of iron(III) chloride, the proposed method would only be economically advantageous if stainless steel pumps, columns, and hardware were required to process large volumes and flow rates.

For the purposes of obtaining an analytical sample of purified $KClO_4$ with the sodium iodide method, subsequent to the iodide ion exchange, the collected perchlorate fraction was precipitated from solution by the addition of potassium chloride and methanol. Due to the lower concentration of perchlorate from the NaI displacement, methanol was used to further decrease the solubility of $KClO_4$. After the addition of excess 4 M KCl and enough methanol to make a solution that is 80% methanol (v/v), the solution was gently boiled down to approximately one half of the original volume. The potassium perchlorate precipitated as expected, leaving NaCl, KCl, NaI and KI in solution (note that the iodides are more soluble than both the chlorides and the perchlorates). The recovered $KClO_4$ was rinsed with 97% methanol, re-dissolved in deionized water, and tested for purity with IC, as described for the tetrachloroferrate method in Section 2. The results are shown in Fig. 5. As can be seen, the perchlorate recovered is free of chloride, nitrate, and sulfate. A yield of 46% of the perchlorate originally in the collected fraction was recovered, as compared to 47% obtained with the $FeCl_4^-$

Fig. 4. Displacement of ClO_4^-, Cl^-, SO_4^{2-}, and NO_3^- from perchlorate-saturated Purolite A-530E column with 0.1 M iodide as displacer solution at 1.0 mL/min.
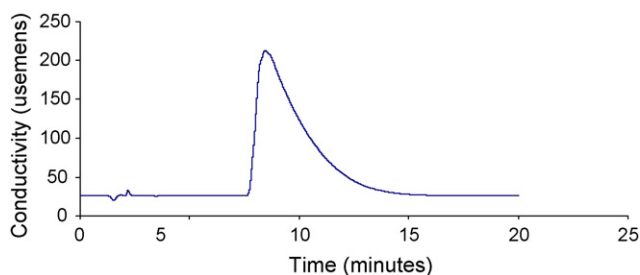
Fig. 5. Ion chromatogram of re-dissolved potassium perchlorate residue precipitated from a collected fraction displaced from Purolite A-530E by 0.1 M iodide.

method with cation exchange, without evaporation. This is a sufficient amount for an IRMS sample [13] with the NaI method and the small column; approximately four times more $KClO_4$ is obtained with the yield in the $FeCl_4{}^-$ method because of the similarly higher displaced perchlorate concentration (comparing equal fraction volumes collected).

This method could be used to recover and recycle perchlorate from contaminated groundwater samples. Although the sodium iodide required is more costly than the iron(III) chloride, savings (especially time) are recouped by circumventing the neutralization, centrifugation, and cation-exchange steps used in the $FeCl_4{}^-$ method. Most noteworthy among these is the neutralization/centrifugation step and the subsequent cleanup of the $Fe(OH)_3$ generated. The NaI method is cleaner.

4. Conclusions

Perchlorate was extracted from a simulated groundwater sample using a selective commercial resin and subsequently displaced with 0.1 M NaI with only minimal contamination by sulfate. A clean fraction of perchlorate was obtained within 10 BV and a pure $KClO_4$ salt with the addition of KCl and methanol. The method may be used without precipitation of $KClO_4$ for IRMS analysis if desired. For the purposes of complete removal of perchlorate from the resin, the sodium iodide method requires greater amounts than the more selective tetrachloroferrate displacer solution. The method including precipitation and recovery of $KClO_4$ may be more appealing overall than the $FeCl_4{}^-$ method due to the elimination of the iron removal step. An iodide

displacer solution may be used as an alternative to $FeCl_4{}^-$. This may be most advantageous when stainless steel high pressure pumps and columns are required for higher flow rates and volumes that may be used in field applications or for applications in which non-acidic conditions are desired.

Acknowledgements

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