

# Ammonium Perchlorate–Binding Poly(allylamine hydrochloride) Hydrogels for Wastewater Remediation

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**ABSTRACT:** Systems that are capable of removing highly toxic anions from wastewater effluents, even at extremely low concentrations, are a major need in the defense industry. This study reports on the features of two new batch and continuous-flow sorption processes with regard to ultimate removal and recovery of the perchlorate ( $\text{ClO}_4^-$ ) anion from ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) wastewater. The sorbent developed is a crosslinked poly(allylamine hydrochloride) (PAA·HCl) polymeric hydrogel. The pH-sensitive PAA·HCl hydrogels were synthesized by chemically crosslinking a solution of linear PAA·HCl chains with epichlorohydrin (EPI). The perchlorate-binding capacity of the polymer gels was measured in standard solutions and studied as a function of gel synthesis parameters. Equilibrium perchlorate loadings of  $5770 \pm 870$  mg  $\text{ClO}_4^-/\text{g}$  gel were calculated from measurement of the decrease in perchlorate concentration in aqueous standard solutions using UV-Vis spectrophotometry. Batch experiments in wastewater originating from the Naval Surface Warfare Center (NSWC) Indian Head Division showed that perchlorate concentrations decreased by 85%. Preliminary lab-scale packed-column experiments in wastewater achieved up to 40% reduction in total perchlorate content. The regeneration ability of the gels was demonstrated by release of the bound perchlorate anions, upon washing with a 1N NaOH solution, providing opportunities to recover and reuse the hydrogel over multiple regeneration cycles. The PAA·HCl hydrogels are demonstrated to be appropriate materials for treating wastewaters that contain ammonium perchlorate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2073–2083, 2001

**Key words:** polymer hydrogel; perchlorate binding; wastewater; regeneration; fixed-bed

## INTRODUCTION

Ammonium perchlorate [AP ( $\text{NH}_4\text{ClO}_4$ )] is a highly toxic, inorganic chemical primarily used as

a component in explosive or pyrotechnic mixtures and as a solid-propellant fuel for missiles, jets, and rockets.<sup>1</sup> Crystals of AP are the oxidizers and primary ingredients in solids used to produce propulsive thrust in a broad range of applications that include rocket, gun and air-breathing propulsion systems, high-pressure air bags, matches, high-temperature gases for joining heavy-duty electrical cables, and other propulsion systems.<sup>1</sup>

AP is a primary ingredient for most U.S. Air Force large rocket motors.<sup>2</sup> AP has a limited shelf life, so that inventories must be periodically re-

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placed with a fresh supply, creating large quantities of AP waste that need to be disposed of. The end of the Cold War left the U.S. Department of Defense with a projected 140 million pounds of rocket propellant to be disposed of between 1993 and 2005.<sup>2</sup> AP is removed from the rest of the propellant mixture by a high-pressure water washout system because AP is highly soluble in water. The resulting AP-containing wastewater is stored in large steel storage tanks in military facilities throughout the United States. The highly toxic wastewater is subsequently diluted and released into natural waterways. This process is very inefficient in that it only dilutes the AP present in the wastewater instead of removing it; approximately 4500 gallons of water are required in one shift (6-h process), depending on the warhead system. The initial AP concentration in the wastewater is approximately 3400 ppm. After passing the wastewater through the case reclamation water-treatment process, the resulting diluted waste streams still contain high concentrations of AP (approximately 260 ppm), which are acceptable for discharge in surface waters, but are orders of magnitude higher than the maximum allowable concentration in drinking water (e.g., 18 ppb is the current maximum acceptable level in California). Large volumes of the compound have been disposed of since the 1950s and detected in the states of Nevada, California, Utah, Maryland, New York, and likely other states, thus potentially causing a serious environmental hazard.<sup>3-5</sup>

The perchlorate ( $\text{ClO}_4^-$ ) anion is exceedingly mobile in aqueous systems. It can persist for many decades under typical groundwater and surface water conditions because of its resistance to react with other chemicals.<sup>4</sup> This mobility and persistence may pose a threat to ecological receptors and entire ecosystems, either by directly harming the organisms or by indirectly affecting their ability to survive and reproduce.

AP was recently found in drinking-water wells in areas where aerospace materials and munitions have been manufactured and tested.<sup>3</sup> The currently available database on the health effects and toxicology of  $\text{ClO}_4^-$  is very limited.<sup>4</sup> Nonetheless, AP is known to interfere with the thyroid gland's ability to use iodine for hormone production. Genotoxic studies are under way to establish whether  $\text{ClO}_4^-$  has any activity relevant to carcinogenicity.<sup>4</sup> Current data suggest that an exposure level range of 4 to 18 ppb is acceptable in drinking water.<sup>3</sup>

Treatment methods that will remove  $\text{ClO}_4^-$  from wastewater effluents are a major need in the U.S. defense industry. Technologies such as chemical reduction, ozone/peroxide, nanofiltration, and reverse osmosis have had limited success and have unknown costs.<sup>4</sup> An anaerobic biochemical reduction process that was developed by the Air Force Research Laboratory has been able to reduce  $\text{ClO}_4^-$  concentrations in groundwater from over 5000 ppb to the low hundreds of ppb.<sup>4</sup> In the biochemical reduction process, microbes are employed to convert  $\text{ClO}_4^-$  to a less-toxic or innocuous form. However, biological processes are characterized by high operating costs, unreliability, microorganisms that can be severely affected by fluctuations in operating conditions (i.e., temperature, pH, feed composition), and uneven public acceptance of this technology.<sup>4,6,7</sup>

In this study we synthesized polyelectrolyte hydrogel materials that can selectively bind  $\text{ClO}_4^-$  anions from the AP wastewater into the polymer matrix. Hydrogel materials are hydrophilic, crosslinked polymer networks that are able to absorb large amounts of water but remain insoluble because of the presence of crosslinks, entanglements, or crystalline regions.<sup>8</sup> Fully ionized hydrogels are a class of materials receiving increasing commercial attention in a wide range of technologies including superabsorbents, separations media, and controlled release of pharmaceuticals and agricultural agents.<sup>9-11</sup>

Poly(allylamine hydrochloride) (PAA·HCl) is a water-soluble polymer, which can be crosslinked by a variety of methods to produce a highly swollen hydrogel material.<sup>12</sup> To be effective in removing  $\text{ClO}_4^-$  from wastewater effluents, the rate of transport of  $\text{ClO}_4^-$  into the gels must be large enough so that efficient binding can be achieved. The transport process must also be reasonably insensitive to pH changes so that  $\text{ClO}_4^-$  can be bound from effluents of varying acidities. In addition, the ability of the gels to bind  $\text{ClO}_4^-$  should not be limited by the presence of particulates and counterions, which are common fouling constituents of AP wastewater effluents.

To optimize the  $\text{ClO}_4^-$ -binding capacity and mechanical integrity of the PAA·HCl gels, synthesis parameters such as the amount of crosslinker were varied. Perchlorate removal experiments were run in both the batch and continuous (fixed-bed) modes. An economically feasible method for desorption of  $\text{ClO}_4^-$  and regeneration of the spent hydrogel was also investigated in this study. The PAA·HCl hydrogels' practicality for AP effluent

remediation could have a very large market. Moreover, they will be methods of controlling one of the most difficult environmental problems facing the U.S. defense industry.

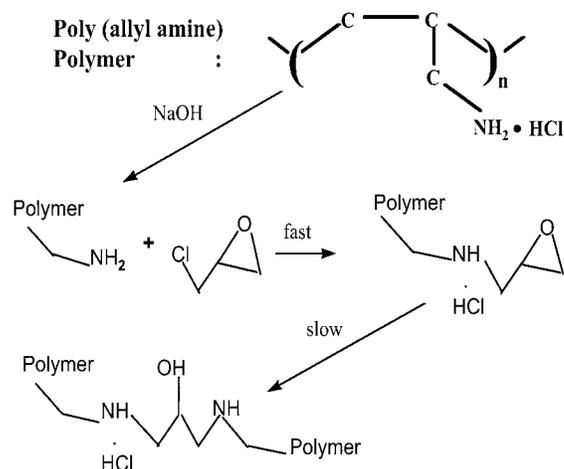
## EXPERIMENTAL

### Materials

Poly(allylamine hydrochloride) (PAA·HCl) powder (25 g), sodium hydroxide (NaOH) pellets (97%), epichlorohydrin (EPI; 99+% pure), and ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) crystals (25 g) reagents were purchased from Aldrich Chemicals (Milwaukee, WI). All reagents were ACS grade and were used without further purification. AP-containing wastewater used in the AP-binding experiments was supplied by the Naval Surface Warfare Center (NSWC) Indian Head Division at Indian Head, Maryland. The wastewater originated from AP steel storage tanks at the NSWC site. This wastewater has an average pH of 7.5 and contains high concentrations of dissolved metal cations such as cadmium ( $\text{Cd}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ), and sodium ( $\text{Na}^+$ ), as well as other compounds such as ammonia ( $\text{NH}_3$ ), nitrates ( $\text{NO}_3^-$ ), and nitrites ( $\text{NO}_2^-$ ). Before experimentation, the AP wastewater samples were stored in large 2-gallon containers away from direct light at room temperature. The AP wastewater samples were filtered using Millipore (Bedford, MA) Millex-GS filter units (particle retention  $> 0.22 \mu\text{m}$ ) prior to use in the  $\text{ClO}_4^-$ -binding experiments. Milli-Q reagent grade distilled water (Millipore) was used for washing PAA·HCl gels, preparing standard/buffer solutions, and diluting samples prior to analysis.

### Preparation of PAA·HCl Networks

The randomly crosslinked PAA·HCl networks were prepared by the aqueous reaction of 20% (or 25%) w/v solution of linear PAA·HCl chains and EPI, which served as the crosslinking agent. The PAA·HCl used in the synthesis of the gels had average molecular weights of 9750, 15,000, and 57,500 g/mol. PAA·HCl chains have hydrochloric acid (HCl) ionically associated with allyl amine ( $\text{NH}_2$ ) groups along the polymer chain backbone. Before crosslinking the polymer chains a portion of the HCl groups of PAA·HCl were neutralized with NaOH to provide free  $\text{NH}_2$  sites for the EPI crosslinking reaction. The chemical crosslinking



**Figure 1** Hydrogel synthesis by chemical crosslinking with EPI.

reaction steps are shown schematically in Figure 1.

A typical batch of hydrogel was synthesized as follows: a 20% w/v solution of PAA·HCl was mixed with 0.36 g NaOH/g PAA·HCl until the NaOH dissolved. When the temperature of the solution dropped below  $27^\circ\text{C}$  (the dissolution of NaOH is exothermic), 0.196 mL of EPI was added. EPI reacted with the free  $\text{NH}_2$  groups produced from the neutralization of HCl by NaOH. The PAA·HCl/NaOH/EPI reaction mixture was stirred for 6 to 20 min, depending on the amount of NaOH or EPI that was added. The reaction mixture was poured into a petri dish to set into a gel slab. Upon curing for an additional 18–24 h, the gel slab was washed with deionized water to remove residual NaCl (produced from the neutralization of HCl by NaOH), unreacted PAA·HCl, and EPI. Finally, the washed hydrogel slab was air-dried in an oven at  $40\text{--}50^\circ\text{C}$ . The final water content of the dry gels, as determined by thermogravimetric analysis, was 5 to 8 wt %. The dried gel slab was ground into small pieces for use in the  $\text{ClO}_4^-$ -binding experiments.

The relative amounts of the reagents used in the gel synthesis steps were independently varied to determine their possible influence on the final structure and  $\text{ClO}_4^-$ -binding properties of the resulting gel. For example, the crosslink density, which could affect both the mechanical properties and the solute transport through the hydrogel, was controlled via the amount of crosslink agent (EPI) added during the synthesis or via the number of free  $\text{NH}_2$  sites available for crosslinking to occur, that is, varying the amount of NaOH (neutralizer) added.

The structure and anion-binding capacity of the hydrogels can be influenced by parameters such as

1. The amount of EPI for gel formation.
2. The number of neutralized  $\text{NH}_2$  sites per gram of gel available for crosslinking and anion binding (amount of NaOH).
3. The pH level of the sample.
4. The PAA·HCl molecular weight.

These potential influences on the gel's chemical structure and properties raise the question of batch-to-batch reproducibility, which is an important issue for the commercialization of this product for AP wastewater remediation. The following issue was therefore addressed: How sensitive is the gel structure and its anion-binding capacity to perturbations in any of these parameters? The detailed elucidation of a gel's properties is an indirect but effective way to document the influence of all the aforementioned parameters on the mechanical integrity and  $\text{ClO}_4^-$ -binding ability of the resulting gel.

### Parameters Influencing the Binding Capacity and Structure of the Gels

#### Variation in NaOH Content

The aqueous 20% w/v PAA·HCl solutions were partially neutralized using NaOH to cleave off HCl ionically associated with  $\text{NH}_2$  groups. The pH of the reaction medium became more basic with increasing amount of NaOH added. Gels were synthesized with 20% w/v PAA·HCl and 0.36, 0.28 (−20% NaOH), 0.30 (−15% NaOH), and 0.43 (+20% NaOH) g NaOH/g PAA·HCl. The time to gelation, upon the addition of EPI, decreased with increasing amount of NaOH. The samples synthesized with 0.43 g NaOH per g PAA·HCl gelled within 8 min after addition of EPI to the stirred solution of NaOH and PAA·HCl. In comparison, samples synthesized with 0.28 g NaOH/g PAA·HCl required 20 min to reach the gelation point after the addition of EPI to the stirred reaction medium.

#### Variation in EPI Content

PAA·HCl gels of varying crosslink densities were prepared by changing the amount of EPI added during the crosslinking reaction step. Gels were synthesized with 1.26, 1.57 (+25% EPI), 1.76 (+40% EPI), and 1.88 (+50% EPI)  $\times 10^{-3}$  mol

EPI/g PAA·HCl. All other synthesis parameters were kept constant.

#### Variation in PAA·HCl Molecular Weight

The effect of PAA·HCl molecular weight used to synthesize the gels was investigated. Gels were prepared with 20% w/v PAA·HCl solutions having molecular weights of 9750 and 57,500 g/mol. The amounts of EPI and NaOH used in the crosslinking reaction were kept constant.

#### Anion-Binding Mechanism

The PAA·HCl hydrogel networks contain amine groups. Amines are nucleophiles because their lone pairs of nonbonding electrons can form a bond with an electrophile. An amine can also act as a Bronsted–Lowry base by accepting a proton ( $\text{H}^+$ ) from a proton acid (i.e., HCl). Therefore the aqueous solutions of amines are basic. An amine can abstract an  $\text{H}^+$  from water, giving an ammonium ion ( $\text{NH}_3^+$ ) and a hydroxide ( $\text{OH}^-$ ) anion.

The gels are pH sensitive.<sup>2,13,14</sup> At acidic pH values the primary ( $\text{NH}_2$ ) and secondary ( $\text{NH}$ ) amine groups present on crosslink junction units and along the PAA·HCl chains, respectively, become protonated, that is,  $\text{NH}_3^+$  and  $\text{NH}_2^+$  state. The  $\text{pK}_a$  value of PAA·HCl is 9.67.<sup>11</sup> Hence, at pH values lower than 9.67 the degree of swelling of PAA·HCl gels increases as a result of electrostatic repulsion (positive charge) of the chains within the network. The attracted  $\text{ClO}_4^-$  anions form clusters around  $\text{NH}_3^+$  and  $\text{NH}_2^+$  sites in the network. At more alkaline pH values, in excess of 9.67, the  $\text{NH}_3^+$  and  $\text{NH}_2^+$  groups lose a hydrogen (become deprotonated) and exist in their uncharged  $\text{NH}_2$  and  $\text{NH}$  forms; hence, the gel network collapses, resulting in little or no  $\text{ClO}_4^-$  binding because there is also no electrostatic attraction between the network and  $\text{ClO}_4^-$  anions. This charging and discharging of the network will affect the swelling behavior as well as the  $\text{ClO}_4^-$  removal ability of the PAA·HCl gels. However, wastewater effluents typically exhibit a pH in the range of 5.0 to 8.0, where the gels exhibit high  $\text{ClO}_4^-$ -binding capacity.<sup>2,13,14</sup>

#### UV-Vis Spectrophotometry Measurements

Perchlorate anion concentration levels of the various standard solution and wastewater samples were measured using the Hach Company (Loveland, Colorado) PhosVer 3 method on a Hach DR/2010 UV-Vis spectrophotometer.<sup>15</sup> The detection

procedure used by the spectrophotometer is equivalent to USEPA method 365.2/Standard Method 4500-P-e for natural water and wastewater. This method was determined to be the most suitable detection method for  $\text{ClO}_4^-$ . A calibration curve was obtained using AP standard solutions of known molarity (0.050, 0.010, 0.005, and 0.001M). The slope of the plot of absorbance versus  $\text{ClO}_4^-$  concentration gave the conversion factor from UV-Vis absorbance to  $\text{ClO}_4^-$  concentration. NSWC wastewater was filtered before any experimentation to reduce interference of particulates with the concentration measurements.

During the various experimental runs, the  $\text{ClO}_4^-$  concentration was measured by transferring a 1- to 5-mL aliquot of the sample to a 25-mL Hach 1-in. sample cell (cuvette). Distilled/deionized water was added to the sample cell, until the 25-mL fill mark was reached, to dilute the  $\text{ClO}_4^-$  concentration to the PhosVer3 method detection range. Samples were diluted because the initial concentration of  $\text{ClO}_4^-$  was higher than the range of the detection procedure (i.e.,  $2 \times 10^3$  mg/L in the NSWC wastewater). Once the dilution step was completed the contents of a PhosVer 3 reagent powder pillow were added to the sample cell. The sample mixture was swirled to dissolve the solid powder and allowed to stand for 5 min. A reaction occurred that gave the sample a blue color. The  $\text{ClO}_4^-$  anions react with molybdate contained in the powder pillow, in an acid medium, to produce a perchloromolybdate complex. Ascorbic acid, also in the powder pillow, then reduces the complex, producing an intense molybdenum blue color, whose intensity was measured by the UV-Vis spectrophotometer, with the wavelength set at 890 nm. Perchlorate concentration data were obtained from absorbance data by using the Beer-Lambert law correlation and subsequently multiplying by the dilution factor.

### Batch-Mode Removal Experiments

Batch experiments were carried out in AP standard solutions to determine the  $\text{ClO}_4^-$ -binding capacity of the PAA·HCl gels. Uptake assays were carried out in standard solutions prepared in deionized water because the composition of tap water varies considerably. The standard-solution experiments allowed us to study the  $\text{ClO}_4^-$  uptake capacity of the gels without interference from other ions. The effect of varying the gel synthesis parameters (i.e., amount of NaOH) on the  $\text{ClO}_4^-$ -binding capacity was studied in both AP standard

solutions and wastewater. The AP standard solutions had a  $\text{ClO}_4^-$  concentration similar to that of the wastewater from NSWC.

Batch processes contain no inflow or outflow of reactants and products. Batch reactors were set up with volumes ranging from 40 to 100 mL. The amount of ground dry PAA·HCl gel particles added to the reactor depended on the experimental need (i.e., binding-capacity measurement or maximum  $\text{ClO}_4^-$  removal). Binding-capacity measurement reactions were allowed to run from 180 to 240 min. The decrease of  $\text{ClO}_4^-$  concentration, which occurred when a slurry of gel particles was added to the reactor, was monitored using the UV-Vis spectrophotometer. The experiment stopped when the gel reached its saturation point and the  $\text{ClO}_4^-$  concentration in the reactor remained constant. At the end of each experimental run the total  $\text{ClO}_4^-$ -binding capacity of the gel was calculated from the UV-Vis data using the following equation:

$$\frac{\text{Amount of } \text{ClO}_4^- \text{ bound (mg)}}{\text{gel (g)}} = \frac{(C_{Po} - C_{Pf})V_s}{m_0} \quad (1)$$

where  $C_{Po}$  = initial concentration (mg/L  $\text{ClO}_4^-$ );  $C_{Pf}$  = final concentration (mg/L  $\text{ClO}_4^-$ );  $V_s$  = batch reactor volume (L); and  $m_0$  = amount of dry gel used in the experiment (g).

Experiments in AP wastewater effluents were designed to evaluate the effect of the variety of particulate, dissolved organic, and counterion wastewater constituents on the  $\text{ClO}_4^-$  removal ability of the PAA·HCl gels. The initial  $\text{ClO}_4^-$  concentration of the wastewater ranged from 1.9 to  $2.6 \times 10^3$  mg/L. Batch reactors with volumes of 40, 100, and 125 mL were employed for the anion removal experiments. The amount of PAA·HCl gel required for complete removal was calculated from the initial  $\text{ClO}_4^-$  concentration and the measured binding capacity of the specific gel used. The decrease in  $\text{ClO}_4^-$  concentration that occurred when the ground dry gel particles were added to the reactor was recorded until the concentration stopped decreasing. The experiment stopped because the gel had reached its saturation point. The percentage  $\text{ClO}_4^-$  removal was calculated from the initial and final concentrations.

### Continuous-Flow Removal Experiments

A lab-scale fixed-bed column process was developed for  $\text{ClO}_4^-$  removal from AP wastewater. In

this process the AP wastewater was introduced into the top of a 1.6-cm-diameter glass column containing PAA·HCl gel packing. Subsequently the  $\text{ClO}_4^-$  anions were bound by the gel until it became saturated.

The optimum PAA·HCl gel, determined from batchwise removal experimentation and the effects of processing parameters (i.e., EPI, NaOH) was used as packing in the lab-scale glass column. This gel was prepared from 25% w/v PAA·HCl solution (15,000 g/mol), 0.28 g NaOH/g PAA·HCl, and  $1.6 \times 10^{-3}$  mol EPI/g PAA·HCl. Initially the concentration of  $\text{ClO}_4^-$  in the wastewater sample was determined. Using the  $\text{ClO}_4^-$ -binding capacity data from batch mode experiments and the initial  $\text{ClO}_4^-$  mass content of the wastewater sample, the quantity of gel required for  $\text{ClO}_4^-$  removal was calculated. Thus 0.2 to 0.5 g of gel was ground using a mortar and pestle and placed in the glass column.

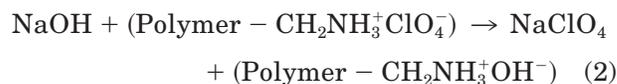
The gel packing was fixed with a glass-wool support and filter paper. Distilled deionized water was poured through the column in order for the gel to reach equilibrium swelling. NSWC wastewater effluent (400–500 mL) was then flowed through the top of the column. The wastewater sample trickled through the preswollen PAA·HCl bed at an average flow rate of 5.3 to 6.7 mL/min under the influence of gravity. The treated effluent was collected at the bottom. Both the influent and effluent  $\text{ClO}_4^-$  concentrations were monitored, and the percentage  $\text{ClO}_4^-$  removal from the wastewater was determined.

An experiment with a larger (5.1-cm-diameter) glass column was also performed. The initial  $\text{ClO}_4^-$  concentration of the wastewater was measured and the amount of gel required for 90%  $\text{ClO}_4^-$  removal was calculated. This column contained 3.5 g of PAA·HCl gel packing and was used to treat a 1-L AP wastewater sample. The average flow rate through the packed bed of PAA·HCl gel was 20 mL/min.

### Regeneration

Experiments were performed to determine whether the PAA·HCl gels could be regenerated after having bound  $\text{ClO}_4^-$  anions from NSWC wastewater. Approximately 0.1 g of wet  $\text{ClO}_4^-$  anion-saturated PAA·HCl gel was recovered by vacuum filtration following a 2-h batchwise  $\text{ClO}_4^-$  removal experiment from a 100-mL wastewater sample. The recovered gel was subsequently treated with 5 mL of 1N NaOH solution for 1 h.

The  $\text{ClO}_4^-$  anions bound by the gel can be readily desorbed by treating the gel with 1N NaOH solution, as shown by the following chemical reaction:



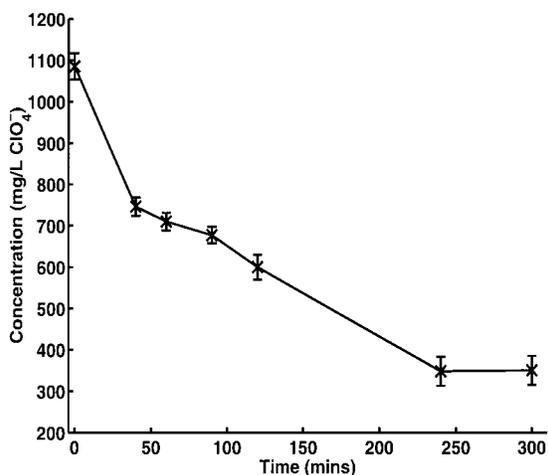
The gel was then vacuum filtered again to remove the waste regenerant solvent consisting of  $\text{NaClO}_4$ ,  $\text{NaCl}$ , and unreacted NaOH that are formed during the treatment. The gel was further washed with distilled water to remove any residual  $\text{NaClO}_4$ , NaOH, and  $\text{NaCl}$  solids that remained. The gel was then dried to prepare it for reuse in a new anion-removal experiment. The above-noted procedure thus describes a regeneration cycle, as it were, that involves a (2-h)  $\text{ClO}_4^-$  removal step, followed by gel treatment with NaOH solution for  $\text{ClO}_4^-$  release, and steps to remove residual  $\text{NaCl}$ ,  $\text{NaClO}_4$ , and NaOH formed during the regeneration. This procedure was repeated several times to determine the operational lifetime of the PAA·HCl gels.

## RESULTS AND DISCUSSION

### Measurement of Binding Capacity in AP Standard Solution

The  $\text{ClO}_4^-$ -binding capacity of PAA·HCl gels was measured in AP standard solution. The standard solution and wastewater had similar  $\text{ClO}_4^-$  concentrations. These experiments were run in the batch mode. An example of such an experiment is shown in Figure 2, in which the  $\text{ClO}_4^-$  concentration decreased with time upon addition of a small amount (0.01 g) of PAA·HCl gel to a reactor containing 80 mL of AP standard solution. A small amount of gel was used here to make sure the gel became saturated with  $\text{ClO}_4^-$  anions. Complete removal was not desired in these experiments. The gel reached its saturation point after 4 h of reaction, after which time the  $\text{ClO}_4^-$  concentration remained constant. Approximately 68%  $\text{ClO}_4^-$  removal was achieved. The binding capacity calculated was 5880 mg  $\text{ClO}_4^-$ /g gel. The unusually high binding capacity may be partly attributed to the clustering of negatively charged anions within the positively charged three-dimensional gel network.

Batchwise  $\text{ClO}_4^-$  binding in AP standards ranged from 2800 to 6640 mg  $\text{ClO}_4^-$ /g gel, depend-



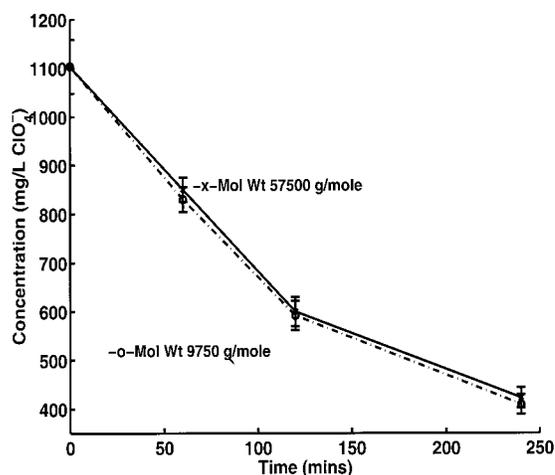
**Figure 2** Measurement of  $\text{ClO}_4^-$ -binding capacity of PAA·HCl gel in AP standard solution. PAA·HCl concentration: 20% w/v,  $M_n = 9750$  g/mol; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.88 \times 10^{-3}$  mol/g PAA·HCl.

ing on the ionic strength of the prepared standard solution and the type of chemical variation of the gel.

#### Effect of Synthesis Parameters on Binding Capacity

The hydrogels proved to be very efficient in binding the  $\text{ClO}_4^-$  anion in experiments in which AP solutions of known concentrations, made with distilled/deionized water, were used. The effects of hydrogel synthesis parameters on their binding capacity were determined in AP standard solutions.

The effect of the PAA·HCl molecular weight on  $\text{ClO}_4^-$  removal was investigated. Gels were prepared using the same amount, 10 mL, of 20% w/v PAA·HCl solution (i.e., 0.2 g PAA·HCl/mL) but with PAA·HCl of 9750 and 57,500 g/mol molecular weight. Figure 3 shows the decrease in  $\text{ClO}_4^-$  concentration with time for the two PAA·HCl molecular weights. The binding-capacity values were calculated from the concentration data. Within the limits of experimental error it was observed that the molecular weight of the PAA·HCl used to prepare the gels did not have any effect on the binding capacity of the gels. The gel prepared with 57,500 g/mol PAA·HCl bound 6640 mg  $\text{ClO}_4^-$ /g gel and the one prepared with 9750 g/mol PAA·HCl bound 6610 mg  $\text{ClO}_4^-$ /g gel. Because the total amount of PAA·HCl used to prepare the low and high molecular weight gels was the same (10 mL of 20% solution), the total numbers of  $\text{NH}_2$  groups in the resulting gel networks are equal.

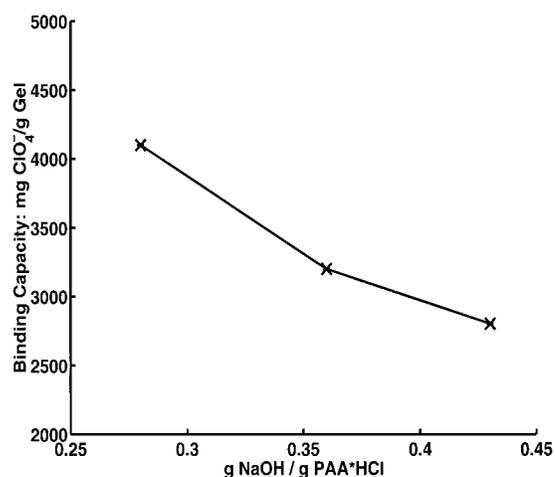


**Figure 3** Effect of PAA·HCl molecular weight on  $\text{ClO}_4^-$ -binding capacity in AP standard solution. PAA·HCl concentration: 20% w/v; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.26 \times 10^{-3}$  mol/g PAA·HCl.

On average there are  $6.45 \times 10^{21}$   $\text{NH}_2$  groups/g of low or high molecular weight PAA·HCl.

The amount of NaOH added during the gel-synthesis reaction was determined to significantly affect the  $\text{ClO}_4^-$  removal performance of the resulting gel. The binding capacity of the gel was found to decrease by as much as 32% by increasing the amount of NaOH added during synthesis, as shown in Figure 4.

The NaOH was used to partially neutralize the  $\text{NH}_2$  groups of the PAA·HCl chains, by cleaving off HCl groups, to enable crosslinking of the

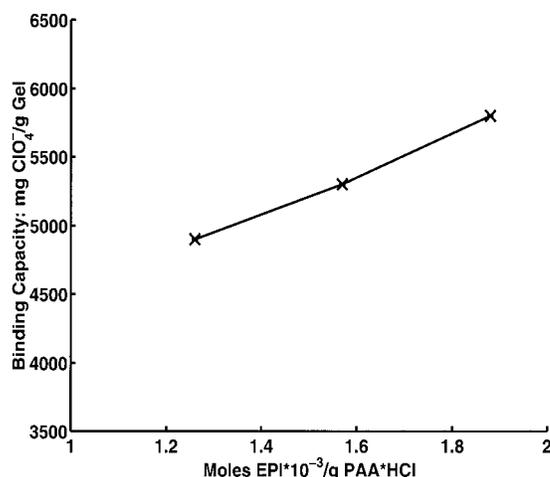


**Figure 4** Effect of NaOH amount on  $\text{ClO}_4^-$ -binding capacity in AP standard solution. PAA·HCl concentration: 20% w/v;  $M_n = 57,500$  g/mol; EPI:  $1.26 \times 10^{-3}$  mol/g PAA·HCl.

chains. By varying this parameter during synthesis, the number of neutralized  $\text{NH}_2$  groups per PAA chain available for crosslinking was altered. Because the pH of the reaction is increased by neutralizing more HCl groups with NaOH, more free  $\text{NH}_2$  sites are produced. The calculated average number of neutralized  $\text{NH}_2$  groups available for crosslinking per PAA chain increased by 33% upon increasing the amount of NaOH from 0.28 to 0.43 g NaOH/g PAA·HCl. This resulted in a larger number of crosslinks within the gel network because there were more free  $\text{NH}_2$  sites per PAA chain available for crosslinking. However, the probability of occurrence of neighboring free  $\text{NH}_2$  sites on the PAA chains also increases, which in turn may cause the EPI to react with two  $\text{NH}_2$  groups on the same chain, thus forming loops instead of crosslinks.<sup>12</sup> The structure and  $\text{ClO}_4^-$  removal characteristics of the resulting gel are negatively influenced. The gel is nonuniformly crosslinked and, hence, does not have the expected mechanical integrity of a more uniformly crosslinked network.

Another factor that must be considered when varying the amount of NaOH is the duration of the synthesis reaction itself. Gels prepared using 0.36 g NaOH/g PAA·HCl react for 20 min before the gelation point. Gels synthesized with 0.43 g NaOH/g PAA·HCl would typically react for an average of 8 min. This reduction in reaction time had an effect on the homogeneity of the crosslinking reaction. In contrast to model networks, with constant length of network chains between crosslinks, real networks exhibit a wide distribution of chain lengths between network junction points.<sup>16</sup> Furthermore, a variety of network defects, such as dangling ends, elastically ineffective loops, and crosslink agglomerations, are known to occur. These defects change the effective crosslink density and topological microstructure of the gel networks and thus influence their swelling behavior and mechanical properties. PAA·HCl gels synthesized with relatively small reaction times until gelation (larger NaOH and/or EPI contents) had an increasing amount of crosslink inhomogeneities present in the polymer matrix, which ultimately had a negative effect on their  $\text{ClO}_4^-$ -binding capacity and mechanical properties.

Experiments were performed to determine whether the amount of crosslinker (EPI) had an effect on the  $\text{ClO}_4^-$ -binding capacity of the gels. By varying the amount of EPI during gel synthesis, it was possible to produce gels with different



**Figure 5** Effect of EPI amount on  $\text{ClO}_4^-$ -binding capacity in AP standard solution. PAA·HCl concentration: 20% w/v;  $M_n = 9750$  g/mol; NaOH: 0.28 g/g PAA·HCl.

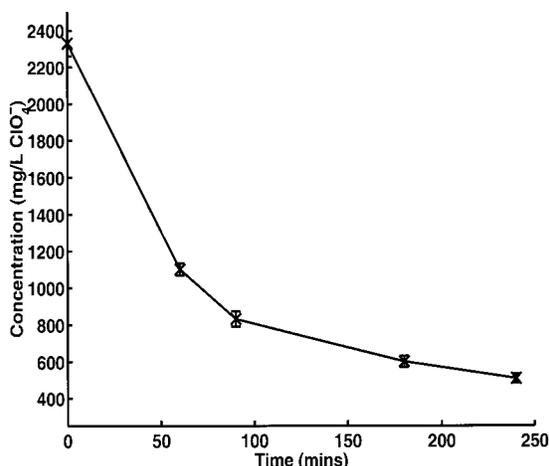
crosslink densities, and hence networks that were either loosely crosslinked or more densely crosslinked. Figure 5 indicates that the  $\text{ClO}_4^-$ -binding capacity of the gel increased by as much as 15% for a 50% increase in the amount of EPI.

The crosslink density and uniformity of the gels is directly related to their EPI content. Increasing the amount of EPI caused the resulting gel to be more tightly crosslinked. This effect reduces the gel's swelling in water, thus improving its mechanical integrity. Gels prepared with larger amounts of EPI did not break up under high stirring rates in the batch reactors, resulting in improved  $\text{ClO}_4^-$  binding by the gel.

#### Batch-Mode $\text{ClO}_4^-$ Removal from Wastewater

Perchlorate binding studies in AP wastewater were performed to determine the  $\text{ClO}_4^-$  removal ability of the gels in propellant washout system effluents from NSWC. Analysis of the UV-Vis spectrophotometry data from experiments showed that within 4 h the hydrogels were able to remove between 50 and 85% of  $\text{ClO}_4^-$  anions initially present in the AP wastewater. An example of such an experiment is shown in Figure 6. Within 4 h of reaction, 80% of all  $\text{ClO}_4^-$  initially present in the wastewater sample was bound by the PAA·HCl gel.

The  $\text{ClO}_4^-$ -binding capacity in the AP wastewater was determined to be in the range of 200 to 930 mg  $\text{ClO}_4^-$ /g gel, approximately one order of magnitude lower than the binding capacity of the



**Figure 6** Variation of  $\text{ClO}_4^-$  concentration with time in NSW wastewater effluent. PAA·HCl concentration: 20% w/v;  $M_n = 9750$  g/mol; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.57 \times 10^{-3}$  mol/g PAA·HCl.

gels in AP standard solutions. This resulted from the presence of high concentrations of contaminants (particulates, counterions, dissolved organic matter, other inorganics) in the NSW wastewater that could have influenced the binding capacity of the PAA·HCl gels. The hydrophobic, electrostatic, and ligand properties of the individual fouling agents influence the  $\text{ClO}_4^-$  anions' ability to compete for sorption sites in the PAA·HCl gel networks. Experiments were carried out to determine how these fouling agents affected the  $\text{ClO}_4^-$  removal ability of the gels. By varying the amount of crosslinker added to prepare the gel, one can vary the crosslink density of the networks. Larger amounts of EPI produced more tightly crosslinked gel networks. This effect caused the mesh size of the network (the space between two adjacent crosslink units) to decrease. Therefore it was thought that larger fouling agents, such as complexed metal cations and particulates, would not penetrate into the networks and shield available  $\text{NH}_2$  sites from binding  $\text{ClO}_4^-$  anions.

The effect of EPI content on  $\text{ClO}_4^-$  binding was therefore investigated in AP wastewater. The experimental data are presented in Table I. Within the limits of experimental error the  $\text{ClO}_4^-$  uptake was found to remain constant with increasing EPI content. This suggested that the fouling agents present in the wastewater were smaller than the mesh size of the network, even when EPI content was increased by 50%. However, the mechanical integrity of the gels significantly improved with increasing EPI content.

### Regeneration of Exhausted PAA·HCl Gel

The ability of the PAA·HCl gels to be amenable for regeneration and reuse was investigated. Experiments were conducted in AP wastewater to investigate how the  $\text{ClO}_4^-$ -binding capacity of the gel would change after five regeneration cycles. Following a 100-mL batchwise removal experiment, the saturated gel was recovered and treated with 5 mL 1N NaOH solution to desorb the bound  $\text{ClO}_4^-$  anions. The  $\text{ClO}_4^-$  anions reacted with  $\text{Na}^+$  cations and were transferred to the solvent phase. Hence, the  $\text{ClO}_4^-$  anions were removed from the 100-mL waste sample by the PAA·HCl gel and released into the 5-mL waste regenerant solvent. The total volume reduction of the waste sample was 95% after a regeneration cycle was completed.

Perchlorate binding values oscillated slightly for the five binding/regeneration experiments run in AP wastewater. The binding is not constant in the AP wastewater as a result of the presence of counterions and dissolved organics that can potentially foul the gel by reacting chemically with free  $\text{NH}_2$  sites from cycle to cycle, thus causing variations in the  $\text{ClO}_4^-$ -binding data. However, as shown in Figure 7, the perchlorate-removal capability of the PAA·HCl gels remained constant within experimental error throughout the five regeneration cycles. These experiments are indicative of the ability of the PAA·HCl gels to be regenerated and were not aimed at achieving high  $\text{ClO}_4^-$ -binding capacities.

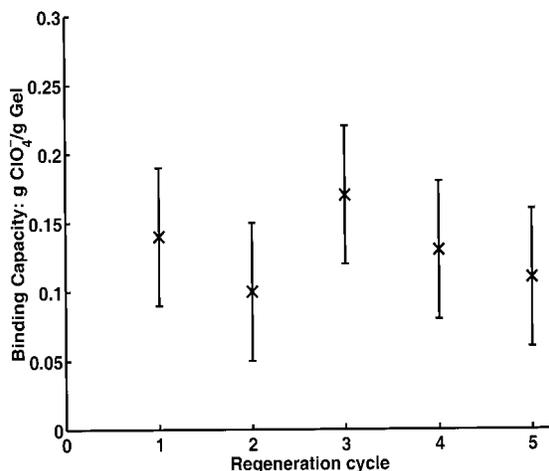
### Fixed-Bed Column Experiments with NSW Wastewater

Perchlorate removal from NSW wastewater was also investigated using a lab-scale packed-column process. The optimum PAA·HCl hydrogel was placed in a glass column and filtered NSW

**Table I** Effect of EPI Content on  $\text{ClO}_4^-$ -Binding Capacity (mg/g Gel) in NSW Wastewater Effluent

Moles EPI ( $\times 10^{-3}$ /g of Gel)	Binding Capacity (mg $\text{ClO}_4^-$ /g Gel)
1.26	500
1.57	500
1.88	510

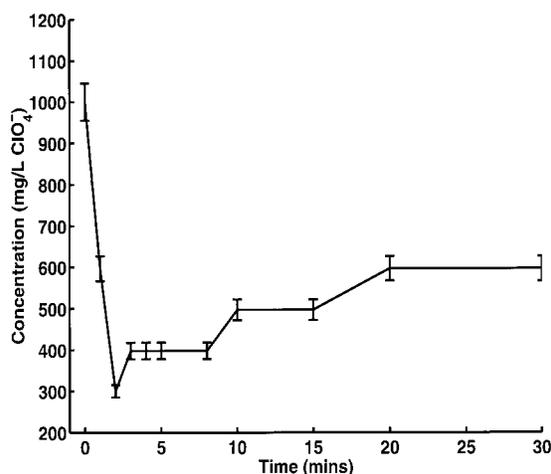
PAA · HCl concentration: 20% w/v;  $M_n = 9750$  g/mol; NaOH: 0.28 g/g PAA · HCl.



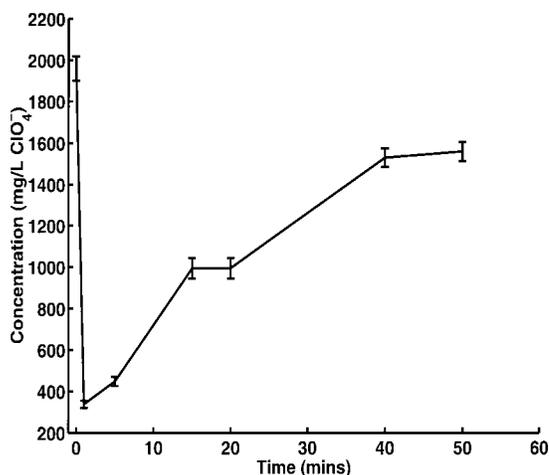
**Figure 7** Regeneration of PAA·HCl gel after  $\text{ClO}_4^-$  removal from NSWC wastewater effluent. PAA·HCl concentration: 20% w/v;  $M_n = 57,500$  g/mol; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.57 \times 10^{-3}$  mol/g PAA·HCl.

wastewater effluent was allowed to trickle under the influence of gravity through the preswollen gel packing.

Several  $\text{ClO}_4^-$  removal runs were performed with the 1.6-cm-diameter column. Preliminary results, as shown in Figure 8, demonstrate the ability of the gel to bind  $\text{ClO}_4^-$  anions from AP wastewater, successfully, under continuous operation. Startup time for the process is very fast (1–2 min) and effluent  $\text{ClO}_4^-$  concentrations initially decreased by as much as 70% of the influent. The



**Figure 8**  $\text{ClO}_4^-$  concentration decrease in the continuous-flow process. Amount of gel used: 1 g/L of NSWC wastewater. PAA·HCl concentration: 25% w/v PAA·HCl;  $M_n = 15,000$  g/mol; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.6 \times 10^{-3}$  mol/g PAA·HCl.



**Figure 9**  $\text{ClO}_4^-$  concentration decrease in the continuous-flow process. Amount of gel used: 3.5 g/L of NSWC wastewater. PAA·HCl concentration: 25% w/v PAA·HCl;  $M_n = 15,000$  g/mol; NaOH: 0.28 g/g PAA·HCl; EPI:  $1.6 \times 10^{-3}$  mol/g PAA·HCl.

effluent concentration remained between 400 and 600 mg/L (60–40% removal) and slightly increased with time because the gel packing was becoming saturated with  $\text{ClO}_4^-$  anions as well as other fouling agents present. The breakthrough point of the experiment was after 30 min, at which time the effluent concentration started to increase more rapidly. Approximately 25 bed volumes of wastewater were run through the packed column. Even after 90 min of operation the effluent  $\text{ClO}_4^-$  concentration was still lower than the influent  $\text{ClO}_4^-$  concentration. The concentration profile shows that the  $\text{ClO}_4^-$  anions as well as other counterions and contaminants are rapidly bound by the gel. If larger gel quantities were packed into the column, more  $\text{ClO}_4^-$  would be bound. However, gel quantities greater than 0.5 g would clog the (lab-scale) column and wastewater would hardly flow through the swollen gel packing. Overall, the  $\text{ClO}_4^-$  concentration of the NSWC sample decreased by 35%.

Column runs were carried out using a larger (5.1-cm-diameter) column that could treat larger volumes of wastewater samples (1 L). The wastewater effluent was poured through the top of the column and allowed to trickle through the gel packing. The average flow rate was approximately three- to fourfold higher than the flow rates of the smaller column setups. Figure 9 shows the  $\text{ClO}_4^-$  concentration decrease with process operation time. The concentration decrease profile was similar to that obtained with the

smaller columns. Startup time for the process was negligible, and within the first 10 min the effluent  $\text{ClO}_4^-$  concentration decreased by 75–83%. Approximately 50 bed volumes of wastewater were run through the packed column. The overall  $\text{ClO}_4^-$  concentration decrease achieved was 40% of the initial value. In the continuous mode, the  $\text{ClO}_4^-$ -binding capacity of the gels ranged from 200 to 1200 mg  $\text{ClO}_4^-/\text{g}$  gel, depending on the ionic strength, the type of counterions, and the amount of particulates present in the AP wastewater.

## CONCLUSIONS

This study demonstrated that the PAA·HCl hydrogels are efficient in binding more than 80% of  $\text{ClO}_4^-$  from NSWC wastewater samples, and that the gels are amenable to regeneration multiple times without significant fouling.

Synthesis parameters were varied during the gel-synthesis reaction, and their effects on the  $\text{ClO}_4^-$ -binding capacity of the resulting gel were evaluated. It was found that increasing the amount of EPI crosslinker, while concomitantly decreasing the NaOH (neutralizer) amount, produced gels with higher  $\text{ClO}_4^-$ -binding capacities and better mechanical integrity. The molecular weight of PAA·HCl used had no significant effect on the binding properties of the resulting gel. The optimum PAA·HCl solution concentration for the crosslinking reaction was determined to be between 20 and 25% w/v.

In batch mode the maximum  $\text{ClO}_4^-$ -binding capacity achieved was 6640 mg  $\text{ClO}_4^-/\text{g}$  gel in AP standard solution. The average  $\text{ClO}_4^-$ -binding capacity measured in AP standards was  $5770 \pm 870$  mg  $\text{ClO}_4^-/\text{g}$  gel. In NSWC wastewater the binding capacity ranged between 200 and 930 and between 200 and 1200 mg  $\text{ClO}_4^-/\text{g}$  gel for batch and continuous-flow experiments, respectively. The binding capacity of the gels was determined to drop by one order of magnitude when used in  $\text{ClO}_4^-$  removal from the NSWC effluents. This was attributed to the AP wastewaters' varying ionic strength and high content of dissolved organics, particulates, and counterions that interact with potential binding sites in the gel networks, thus

reducing their  $\text{ClO}_4^-$ -binding capacity. However, even in the wastewater, the  $\text{ClO}_4^-$ -binding capacity of the gels is high enough to ensure the removal of a significant portion of the  $\text{ClO}_4^-$  anion present.

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