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Hybrid Properties of Alginate-PEI Adsorbent for Chromium (VI) Removal from Aqueous Solutions

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Abstract: An adsorbent consisting of polyethyleneimine (PEI) immobilized in calcium alginate gel beads was synthesized and evaluated for Cr^{6+} removal. An evaluation of the synthesis process showed the importance of the PEI molecular weight on the immobilization efficiency. Polyethyleneimine of 70,000 Da molecular weight displayed the highest immobilization percentage at 52%. Batch kinetics and equilibrium tests showed that alginate-PEI (APEI) resin displayed considerable affinity for negatively charged Cr^{6+} complexes at low pH conditions ranging from pH 1.5-pH 3. The results also indicated the reduction of Cr^{6+} to less toxic Cr^{3+} species by the APEI adsorbent. The column adsorption experiments showed the ability of APEI resin to treat a 10 mg/L Cr^{6+} solution with pH influent adjustment from pH 1.5 to pH 3 to concentrations that satisfy effluent standards for Cr^{6+} (<0.1 mg/L) and total Cr (<0.5 mg/L). Finally, comparisons with a highly aminated commercial resin Chitopearl CS-03 highlighted the unique ability of the

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hybrid APEI beads with its amine and carboxylic groups for the adsorption of Cr^{6+} as well as the retention of generated Cr^{3+} ions.

Keywords: Adsorption, alginate, polyethyleneimine, immobilization, chromium (VI), wastewater treatment

INTRODUCTION

Chromium(VI) is considered as one of the heavy metals whose high toxicity demands strict regulation. Its high water solubility and mobility in soils and sediments has been a major environmental concern (1–2). Though the natural chromium cycle allows for the conversion of Cr^{6+} to its less toxic Cr^{3+} species through reduction by organic acids (3), extremely high concentrations may impose considerable stress on such regulating process, thus allowing for relatively toxic levels of Cr^{6+} to remain and infiltrate the groundwater (4).

Currently, numerous unit operations such as ultrafiltration, reduction/precipitation and adsorption have been applied for the treatment of Cr^{6+} contaminated waste solutions. Ultrafiltration capitalizes on large molecular weight compounds particularly positively charged amine-containing polymers that exhibit high affinity for negatively charged Cr^{6+} complex at low pH (5). Separation is achieved by the use of membranes with molecular weight cut-off below the effective size of the polymer. Precipitation on the other hand initially converts Cr^{6+} to Cr^{3+} by the use of strong reducing agents such as Fe^{2+} ions and organic acids followed by removal of Cr^{3+} as hydroxides at high pH. Recently developed adsorbents for Cr^{6+} include activated carbon (6), tannin derivatives, (7) crosslinked chitosan (8) as well as organo-silica sol gels containing amino and thiol groups (9). For chitosan, the mechanism for Cr^{6+} removal include also its binding with protonated amino groups of the resin. For tannin derivatives as well as amino/thiol-containing resins on the other hand, removal involves the reduction of Cr^{6+} to the less toxic Cr^{3+} followed by its subsequent adsorption by the resin.

In this work, a novel adsorbent for sequestering Cr^{6+} ions from aqueous solutions was developed. The simplicity of its synthesis and the use of inexpensive and non-toxic reagents, particularly organic solvents, is one of its practical advantages. Specifically, the adsorbent consists of a Ca-alginate (CA) gel bead to which polyethyleneimine (PEI) had been entrapped. Protonated imino groups of PEI serve as binding sites for negatively charged Cr^{6+} ions. Alginate gel beads have been applied for the sequestration of positively charged heavy metal ions such as Cu^{2+}, Cr^{3+} and Zn^{2+} (10–12). It has also been a popular matrix for immobilizing cells as well as enzymes for biotechnological applications (13). Previous research has indicated the possibility of entrapping materials of $MW > 20{,}000$ in CA matrix, (14, 15) thus providing enough pore size for immobilization of PEI of 70,000 MW. In this paper, interesting findings regarding the performance of such alginate-PEI (APEI) adsorbent during the treatment of a model Cr^{6+} contaminated aqueous solution will be discussed. Furthermore, the mechanisms responsible for the efficient removal Cr^{6+} as well as its conversion to less toxic Cr^{3+} species will also be presented.

METHODOLOGY

Materials

Alginate, PEI (70,000 Da MW), calcium chloride, and potassium dichromate were obtained from Wako Chemicals, Japan. PEI of lower molecular weights (300, 600, 1800, 10,000, and 20,000 Da) were provided by Nihon Shokubai Corporation. All other chemicals unless otherwise specified were obtained from Wako Chemicals, Japan.

General Procedure for the Synthesis of CA and APEI Beads

Following established protocols, the CA gel beads were formed by dropping 60 ml of 3% Na-alginate aqueous solution into 100 ml of well-mixed 20% $CaCl_2$ solution using a peristaltic pump (10, 12). A pipet tip was attached at the tube outlet of the pump to generate beads of approximately 2 mm diameter size. The beads were cured overnight in the $CaCl_2$ solution. Afterwards, they were filtered and then washed thoroughly with distilled water. The beads were stored in distilled water.

The same procedure as above was applied for APEI synthesis. However, instead of dissolving Na-alginate in 60 ml distilled water, 60 ml of PEI solution was used. Specifically, the PEI-alginate solution was dropped into a 100 ml $CaCl_2$ and the formed beads were cured overnight. The different synthesis parameters studied as well as the specific procedures applied include:

1. To determine the effect of PEI molecular weight on immobilization efficiency, PEI of different molecular weights (300, 600, 1800, 10,000, 20,000, and 70,000) were employed. For all these runs, the concentrations of alginate and $CaCl_2$ were constant at 3% and 20%, respectively.
2. To determine the effect of $CaCl_2$ concentrations, 1%, 2.5%, 5%, 10%, 15%, and 20% $CaCl_2$ were used. Alginate and PEI (70,000 MW) concentrations were constant at 3% and 1%, respectively.
3. To determine the effect of PEI concentration, 0.5, 1, 2, and 3% PEI were used. The concentration of sodium alginate and $CaCl_2$ were fixed at 3% and 20%, respectively.

Alginate-PEI was also synthesized by the atomization process. The synthesis conditions were as follows: 2% Na-alginate, 1% PEI, and 10%

$CaCl_2$. The use of Na-alginate at a lower concentration and viscosity allowed for the effective atomization of the alginate-PEI solution. A typical procedure involves filling up a water sprayer unit with the specified reagents. The chamber was pressurized and the alginate-PEI solution was then atomized through its nozzle towards a stirred $CaCl_2$ solution below. The beads were then cured, washed, and kept in distilled water prior to use.

Dry weight, yield, and elemental analysis of dried synthesized beads were made to approximate the amount of PEI immobilized.

Kinetics of Heavy Metal Adsorption

Approximately 3.0 grams of the CA and APEI adsorbents were added into 300 ml of 10 mg/L Cr^{6+} solutions (as $K_2Cr_2O_7$) at an initial pH of 1.5 (adjusted with HCl) and then stirred continuously. (For all adsorption experiments, wet form of the beads was employed. Excess water was absorbed into filter papers.) Aliquots were withdrawn at specific time intervals. The pH, Cr^{6+} and total Cr content in each sample were determined.

Equilibrium Adsorption at Different pH

Different amounts of CA-PEI beads were combined with 10 mg/L Cr^{6+} solutions then allowed to equilibrate for 1 day. Separate runs at different initial pH of 1.5, 2, and 2.5 were conducted. The mixture was filtered and the final pH as well as residual Cr^{6+} and total Cr concentrations of the filtrates were determined.

Continuous Fixed Bed Column Adsorption

Approximately 20 grams of Alginate-PEI were allowed to fill-up a 35 ml column (ID: 24 mm; column height: 85 mm). A 10 mg/L Cr^{6+} solution at an initial pH of 2 was fed from the top of the column at a flowrate of 30 ml/hr by a peristaltic pump. Samples were taken at specific time intervals at the column outlet at the bottom. The pH, Cr^{6+}, and total Cr of each sample were determined.

A continuous fixed bed experiment with pH adjustment was also performed following the above procedure. Specifically, the pH of the influent was adjusted from pH of 2.0 to pH 4.0 then finally to pH 3. The effluent pH, Cr^{6+}, and total Cr of each sample were determined.

The performance of the APEI resin was finally compared with a commercially available chitosan-polyamine resin (Chitopearl CS-03). In this run, APEI microbeads synthesized by atomization technique was employed. Approximately 20 grams of APEI microbeads and Chitopearl CS-03 were allowed to fill-up a column. (For Chitopearl, the beads were also used in the wet form in accordance with the manufacturer's instructions.) A 5 mg/L Cr^{6+} solution at an initial pH of 2 was fed to each column at a flowrate of 30 ml/hr by a peristaltic pump. Effluent samples were taken at regular time intervals. The pH, Cr^{6+}, and total Cr and of each sample were monitored.

Analytical Methods

Elemental Analysis

CHN contents of products were determined by a Perkin-Elmer Elemental Analyzer (Model 2044).

Heavy Metal Analysis

Total Cr concentrations were analyzed by an Inductively Coupled Plasma Spectrometer (Nippon Jarrel-Ash). The Cr^{6+} content was evaluated by a UV spectrophotometer at 540 nm wavelength using the Photometric diphenyl carbohydrazide method (16).

RESULTS AND DISCUSSION

Optimization of Ca-Alginate–PEI Synthesis

Preliminary synthesis runs showed the formation of stable APEI beads. In fact, the APEI beads were more firm and rigid in structure as compared with CA beads. This conforms well with previous research that shows the ability of PEI in relatively smaller amounts to improve resin stability through the cross-linking of alginate chains (17–18). In this work, however, more than being a stabilizer, PEI was utilized as an additive to introduce novel Cr^{6+} binding characteristics to the resulting product. Hence, basic studies on the quality of the gels formed at PEI to alginate ratios that are much higher than those utilized for the stabilization process were considered.

Table 1 shows the elemental analysis of CA-PEI beads synthesized at different molecular weights of PEI. Interestingly, the PEI content (as per cent N) increased with its molecular weight. Immobilization efficiency reached up to as high as 52% using a PEI-70,000 Da. Immobilization was quite minimal (<3%) at low molecular weights of 300 and 600 and 1800 Da. Though a significant immobilization was achieved with PEI of 10,000 Da (12%) and 20,000 Da (23%) molecular weight, this was less than 50% of that obtained at 70,000 Da.

As mentioned previously, the pore size of CA beads are approximately around 20,000 Da. Hence, the retention by CA matrix of molecules with

Table 1. Elemental analysis of alginate-PEI adsorbents synthesized at different molecular weights of PEI. In these runs, PEI and $CaCl_2$ concentrations were constant at 1% and 20%, respectively

Molecular weight	% Carbon	% Hydrogen	% Nitrogen	% PEI immobilized
300	31.94	4.57	0.11	0.8
600	32.07	4.69	0.13	0.9
1800	32.14	4.83	0.23	3
10,000	32.91	5.04	1.48	12
20,000	39.01	5.88	2.00	23
70,000	35.95	5.72	4.97	52

molecular weights below this value was expectedly low. Clearly, these data show the importance of PEI size during the immobilization process. These also indicate that the major mechanism of PEI immobilization in alginate beads is through entrapment. Ionic interaction may also exist between the alginate and PEI chains but their affinity may be lowered due to resulting high pH of the $CaCl_2$ solution following bead synthesis. Such relatively high pH (>pH 10) would minimize the protonation of imino groups in PEI, which is necessary for binding with negatively charged carboxylic groups of the alginate. In any case, these results do confirm the feasibility of PEI entrapment by the simple process of gel entrapment. For effective immobilization, the use of PEI with the highest molecular weight (70,000 Da) was found to be important.

In addition to the PEI molecular weight, the effect of $CaCl_2$ concentrations on immobilization efficiency was also studied. The results showed that $CaCl_2$ only slightly affects immobilization efficiency (Table 2). At the lowest $CaCl_2$ concentration evaluated (1%), more than 41% PEI was still immobilized whereas at the highest amount (20%), around 52% PEI was

Table 2. Elemental analysis of alginate-PEI adsorbents synthesized at different concentrations of $CaCl_2$. In these runs, PEI of 70,000 Da MW was used. PEI concentration was constant at 1%

$CaCl_2$ concentration (%)	% Carbon	% Hydrogen	% Nitrogen	% PEI immobilized
1	34.17	5.63	4.50	41
2.5	34.03	5.83	4.72	43
5	35.98	5.74	5.09	46
10	35.77	5.65	4.87	43
15	35.54	5.59	4.78	46
20	35.95	5.72	4.97	52

immobilized. Though increasing $CaCl_2$ concentration up to 5% resulted to an increasing PEI immobilization efficiency, the differences were not as pronounced as those observed on the molecular weight effect. To explain these findings, it is well understood that gel formation is a result of alginate crosslinking by Ca^{2+} ions. As long as Ca^{2+} is available in excess, considerable entrapment of PEI by the crosslinked CA beads may be achieved. Now, calculations indicated that at the given amount of alginate used during synthesis, approximately 0.125 % $CaCl_2$ is necessary to provide a 1:2 stoichiometry of Ca^{2+} ions with carboxyl groups in alginate. Since the lowest concentration of alginate considered was 1% (this still represents a considerably high concentration of Ca^{2+} ions), the PEI immobilization was still quite satisfactory at this condition. Nonetheless, the slightly higher immobilization at more than 5% $CaCl_2$ concentration somehow indicates some positive effect of higher Ca^{2+} ions. For this case, high $CaCl_2$ concentration would enhance the rate of alginate gelation. In the presence of more Ca^{2+} ions, faster gel formation may occur leading to a lesser degree of PEI leakage and dissolution. Most of the PEI is expected to leak out during the initial stage of gelation so that faster alginate solidification at higher Ca^{2+} concentration would be advantageous for improving PEI entrapment.

Finally, the effect of PEI concentration was also studied. Expectedly, higher PEI resulted in a higher nitrogen content (Table 3). However this was achieved at the expense of immobilization efficiency. Though a great amount of the PEI can be immobilized at a higher PEI to alginate ratio, the increase in percent nitrogen is not proportional to the amount of PEI utilized. This is clearly reflected on the decreasing immobilization percent at increasing PEI concentration.

To summarize, the above experiments confirmed that the molecular weight is the most significant factor that affects the efficiency of PEI immobilization into calcium alginate gel beads at the given synthesis conditions. Nonetheless, other parameters such as $CaCl_2$ and PEI concentrations, which showed a rather minimal effect on percent PEI, may become significant in large scale production to minimize reagent loses.

Table 3. Elemental analysis of alginate-PEI adsorbents synthesized at different concentrations of PEI. In these runs, PEI of 70,000 Da was used. $CaCl_2$ concentration was constant at 20%

PEI concentration (%)	% Carbon	% Hydrogen	% Nitrogen	% PEI immobilized
0.5	34.20	5.24	3.10	59
1	35.95	5.72	4.97	52
2	37.63	6.14	7.79	40
3	36.98	6.76	8.82	32

Kinetics and Equilibrium Adsorption of on Cr^{6+} by CA and APEI Resins

Polyethyleneimine is a well known chelator for a wide variety of toxic heavy metal ions such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cr^{2+}, Cd^{2+}, and Co^{2+} due to the lone pair of its nitrogen atoms (19–20). In addition, the protonation of nitrogen ligands of PEI at low pH also allow for its use in the removal of highly toxic negatively-charged metal complexes such as Cr^{6+}. The solubility of PEI in aqueous solutions however, complicates the separation of its heavy metal complexes. Hence, we evaluated the feasibility of PEI immobilization by simple entrapment in calcium alginate. Since the above results confirmed that PEI could be immobilized into alginate matrix at considerable degree, the affinity of this resin for Cr^{6+} was then evaluated next. For this purpose, a resin synthesized at 3% alginate and 2% PEI in 20% $CaCl_2$ solution and which contains approximately 7.23% N was utilized. The dry weight of this resin was 9.86% so that the theoretical Cr^{6+} capacity of this APEI is approximately 132 mg/g dry resin. Calcium alginate beads were also evaluated as control. During initial runs, the pH of the solution was set at pH 1.5 to provide a highly protonating condition for effective Cr^{6+} binding.

Kinetics experiments confirmed the affinity of APEI resin for Cr^{6+} (as dichromate ion) while the pure CA gel did not exhibit any (Fig. 1). The Cr^{6+} content of the solution with APEI decreased continuously through time while that of CA remained constant. This indicates that the Cr^{6+} binding property is mainly due to the immobilized PEI in the resin. The pH in both systems increased slightly to confirm the protonation of nitrogen

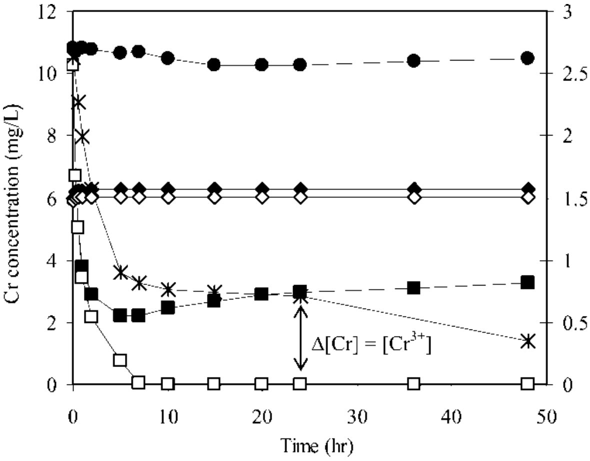
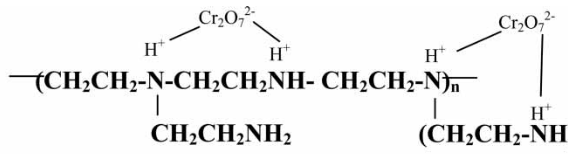


Figure 1. Kinetics of Cr^{6+} adsorption by Alginate-PEI and Ca-alginate resins. The initial Cr^{6+} concentration was 10 mg/L. Initial pH was around pH 1.5 for both resins. ■ APEI-Cr_{tot}; □ APEI-cr^{6+}; ● CA-Cr^{6+} and Cr_{tot}; * PEI-Cr^{6+}; ◆ APEI-pH; ◇ Ca-pH.

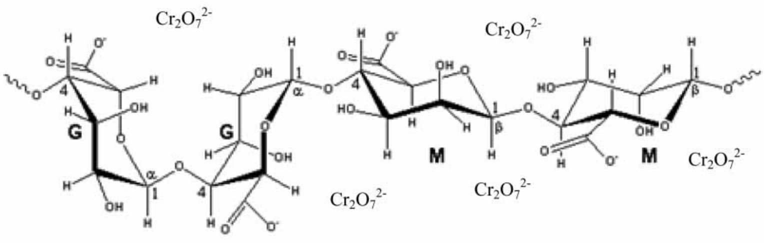
(APEI) as well as carboxylic groups (APEI and CA). Nonetheless the pH increment for both systems was minimal so that equilibrium pH was still in the highly acidic range of pH 1.5–1.6. The imino groups of PEI are readily protonated at low pH, thus providing the necessary binding sites for negatively charged dichromate ($Cr_2O_7^{2-}$) ions (Fig. 2). Qualitatively, the binding of dichromate ions was also confirmed by the transfer of its yellow complex to the APEI resin. In the case of CA beads, no color change was observed. This was expected since the CA beads basically contain carboxyl functionalities of β-D-mannuronic and α-L-guluronic residues, which do not provide binding sites for the dichromate ions at any pH condition (Fig. 2).

In addition, another interesting phenomenon observed is the slow but very clear reduction of Cr^{6+} in the APEI system. Notice in Fig. 1 that though the Cr^{6+} was almost completely removed, the total Cr content remained relatively higher. The color of the APEI-Cr complex also changed from yellow to green. These results indicate the occurrence of dichromate reduction to Cr^{3+} ions at the existing low pH of the system. (In the graphs, the difference between Cr_{tot} and Cr^{6+} concentration (ΔCr) for each sample corresponds to the concentration of Cr^{3+} in the solution.) Now, since this phenomenon was not observed in the CA beads (as indicated by the same Cr^{6+} and Cr_{tot} concentration of the corresponding solution) such reduction of Cr^{6+} may be solely attributed to the immobilized PEI. Indeed, this was confirmed by time course experiments involving Cr^{6+} and free PEI, which also showed a similar decrease in Cr^{6+} content at low pH at a slow rate (Fig. 1). Because any PEI-Cr^{6+} complex that formed in such free PEI system remains soluble, the decrease in Cr^{6+} concentration could only indicate its reduction



$-(CH_2CH_2\text{-}N\text{-}CH_2CH_2NH\text{-}CH_2CH_2\text{-}N)_n-$

A. PEI



B. Alginate

Figure 2. Interaction of Cr^{6+} with CA and CA-PEI. While APEI contains protonated imino groups in for Cr^{6+} binding, CA does not have any binding site.

to Cr^{3+} species possibly by imino groups of PEI. Such imino functionalities are weak nucleophiles, which could initiate Cr^{6+} reduction at low pH by the aid of acid catalysis. The weak nucleophilic nature, however, would probably account for the observed slow reaction of the process. Nevertheless, current available data is not sufficient to fully establish the exact mechanism for this process particularly in the APEI system. To some degree, Cr^{6+} reduction to Cr^{3+} by PEI is very significant in this case as it clearly affected the overall Cr removal by the APEI resin. The low pH suitable for Cr^{6+} binding may be inappropriate for Cr^{3+} ions due to extensive competition by hydronium ions. With regard to Cr^{3+} binding, this preferentially occurs at a higher pH particularly around pH 3–4 where less competition for hydronium ions occurs. At these conditions, unprotonated nitrogen as well as carboxyl groups of APEI serve as sites for both coordinate and ionic bond formation. Indeed, some desorption of Cr^{3+} from the resin was evident from the slightly increasing curve of the Cr_{tot} concentration in Fig. 1. Nonetheless, despite the still low equilibrium pH accompanying Cr^{3+} formation, a high percentage Cr_{tot} removal was still possible, thus indicating considerable stability of APEI- Cr^{3+} complex. Such stability may be due to the presence of free carboxyl groups in the alginate matrix that can bind ionically with the Cr^{3+} ion (12).

Equilibrium studies at different initial pHs also confirmed in more detail the mechanisms that affect the sequestration of Cr^{6+} by APEI resin as mentioned above. First, at an initial pH of 1.5, Cr^{6+} removal increased at increasing amounts of APEI (Fig. 3a). Again, though Cr^{6+} can be removed almost completely by increasing the amount APEI, a relatively higher amount of total Cr remained. These Cr represent the Cr^{3+} ions that were formed and which remained unbound due to the still low equilibrium pH of the filtrate at any given amount of APEI. The concentration of the residual Cr^{3+} ions in the filtrate, which is the difference (ΔCr) between Cr_{tot} and $Cr^{6+}$for each sample, also increased with APEI due the higher amount of immobilized PEI available for such redox reaction.

At an initial pH of 2.0 (Fig. 3b), the removal of Cr^{6+} was higher than that at pH 1.5 at any amount of APEI. For example, calculations show that the capacity attained at the highest amount of APEI employed at pH 2 (39 mg/g dry adsorbent) is higher than at pH 1.5 (25 mg/g dry adsorbent) (Fig. 4). This lower removal at pH 1.5 as compared to pH 2 (as well as the lower removal at both pH conditions with respect to theoretical capacity of 132 mg/g dry resin) can be attributed to lower amounts of Cl^- ions at higher pH. These negatively-charged Cl^- ions may also compete with Cr^{6+} (as Cr_2O^{7-}) ions for binding sites. It must be mentioned that HCl was used during pH adjustment, so that lower pH would correspond to a higher amount of the Cl^- ion. In addition, better removal of total Cr at higher pH of 2 was also achieved due to less competition between generated Cr^{3+} and hydronium ions. In another aspect, such pH may have also resulted to a lesser degree of Cr^{6+} reduction as such reaction has been reported to be

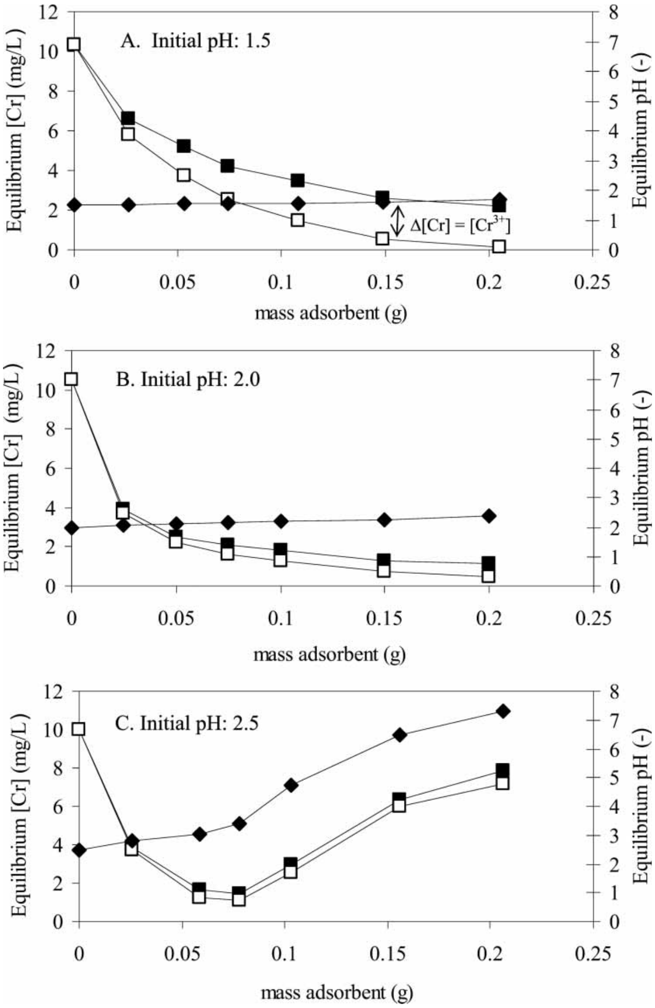


Figure 3. Removal of Cr^{6+} from aqueous solution by Alginate-PEI at different initial pH conditions. Initial Cr^{6+} concentration was approximately 10 ppm. –■–Cr_{tot}; –□–Cr^{6+}; –◆–pH.

catalyzed by low pH (7–8). All these results point to the fact that extremely low pH may result to lower performance of APEI for the total Cr removal so that less acidic conditions may be appropriate for this process.

However, there is a limit to the maximum pH by which the resin may function well for total Cr removal. The clear effect of pH particularly on Cr^{6+} reduction and sequestration by APEI at much higher equilibrium pH (>pH 3) can be seen in Fig. 3c, which shows some equilibrium data at initial pH of 2.5. Notice in Fig. 3c that contrary to Figs. 3a and 3b, higher

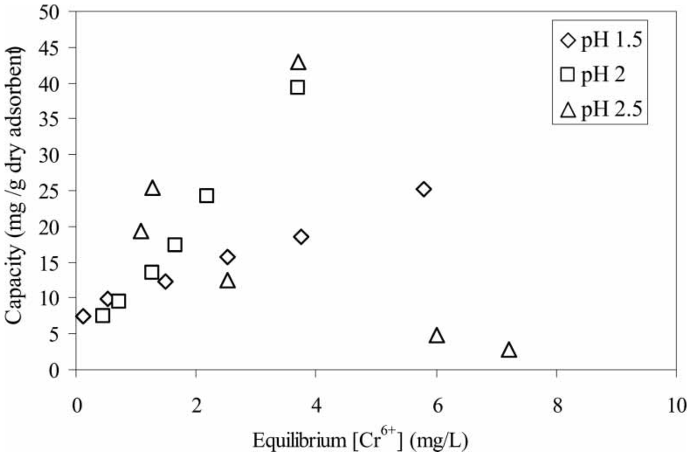


Figure 4. Isotherm for Cr^{6+} adsorption from aqueous solution by Alginate-PEI at different initial pH conditions. Initial Cr^{6+} concentration was approximately 10 ppm.

Cr removals were attained at lower amounts of APEI. Initially, at lower APEI content (<0.075 g), the resin performance was found comparable, if not better than that at pH 2.0. (Again, this can be attributed to a lower amount of competing Cl- species at the given pH of the solution.) However, at much higher APEI, both the removal of Cr^{6+} as well as Cr_{tot} decreased. To explain such seemingly anomalous behavior, we can cite the considerable rise of pH to alkaline region at a higher amount of APEI, which becomes less favorable for sequestering Cr^{6+} ions. Furthermore, the resulting alkaline pH also lead to less Cr^{6+} reduction to Cr^{3+} as indicated by the very slight difference between Cr_{tot} and Cr^{6+} for all samples.

To summarize the above results, two modes of Cr^{6+} removal by APEI are possible and these include the adsorption and reduction by protonated amine groups of PEI. These are sequential reactions which are both favored at low pH conditions. However, considerable pH lowering is also accompanied by the increase in co-anion concentration and this may influence considerably Cr^{6+} removal. An equilibrium pH of around pH 2 appears to be sufficient for the efficient performance of the resin. The readiness for Cr^{6+} reduction has also been the basis for the removal of the more toxic Cr^{6+} species even by some adsorbents (7–9). Similarly, the APEI beads exhibit the same ability to bind Cr^{6+} ions, reduce it to the less toxic Cr^{3+} species, which then remains entrapped in the gel beads. For some cases, Cr^{6+} reduction has been a major limitation since it inevitably leads to incomplete Cr removal due to the differences in adsorption conditions for Cr^{6+} ($<$pH 2) and Cr^{3+} ($>$pH 3) ions. However, based from the low residual total Cr concentration attainable with APEI at the workable pH condition, it shows that the hybrid composition of APEI—with its imino and carboxyl groups—allows it to bind both negatively charged Cr^{6+} and positively charged Cr^{3+} ion. Indeed, there are many individual reactions that occur during the removal of initially present Cr^{6+} ions by APEI that consequently affects its overall performance for total Cr removal. In this paper however, evaluations were primarily carried out to evaluate whether it is feasible to adjust adsorption parameters to come up with effluent concentrations that readily satisfy existing environmental standards. The following discussions in continuous systems show how this can be achieved. Nevertheless, in the future it would undoubtedly be very important to quantify the individual effects of these reactions on the overall performance of the resin at specific pH conditions to maximize the potential of the resin for various applications.

Continuous Fixed Bed Adsorption Experiments

The ability of APEI for Cr^{6+} removal to achieve environmental standards was also confirmed in a continuous fixed bed system. In fact, an even better performance of the resin was observed during such continuous operation. During the first run, an initial pH of 2 was employed since batch tests showed considerable removal of both Cr^{6+} and Cr^{3+} species at this condition. In the particular time period covered by the column experiment (corresponding to 6 days operation at 30 ml/hr for a 20 g APEI column), much lower residual concentrations of Cr^{6+} below the 0.5 mg/L effluent standard (Environment Agency, Japan) for wastewaters has been achieved (Fig. 5). Except in the initial stage where slightly higher Cr^{6+} concentrations

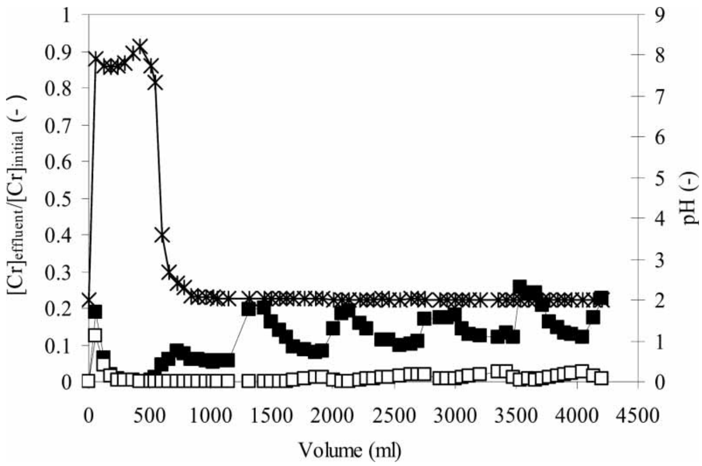


Figure 5. Breakthrough curve for Cr removal by APEI resin. Initial Cr^{6+} concentration was approximately 10 mg/L. Flowrate was 30 ml/hr. –■–Cr_{tot}; –□–Cr^{6+}; *pH.

were observed, the reduction of Cr^{6+} to concentrations below 0.01 mg/L were possible.

In the case of Cr_{tot} (mostly Cr^{3+} since Cr^{6+} were very low), however, slightly higher residual concentrations were achieved but the values were still within the effluent standard limit of 2 mg/L (Environment Agency, Japan) during most of the operation (21). Clearly, despite the occurrence of Cr^{6+} reduction, most generated Cr^{3+} ions were retained by the resin. The effect of pH on Cr removal was also very evident at different stages. In the initial stage where the pH of the effluent increased drastically to around pH 7, much lower total Cr concentrations of below 0.1 mg/L was possible. During such a brief period of time (corresponding to 500 ml of Cr solution), the concerted effects of Cr^{6+} ionic binding, Cr^{3+} coordinate binding and Cr^{3+} precipitation as hydroxide may have enhanced the total Cr removal.

From the above discussions, we can summarize the following sequence of reactions during Cr^{6+} removal by the fixed APEI bed column: First, at the low pH of the entering Cr^{6+} solution, protonation of imino groups occurred to generate binding sites for Cr^{6+} ions. This also results in the increase in effluent pH at the early stage. Furthermore, since APEI protonation is a prerequisite for Cr^{6+} binding, this could account for the lag in Cr^{6+} removal during the first few hours of column operation. Initially, less protonated sites were available in the resin so that some amount of Cr^{6+} remained. Now upon binding of Cr^{6+} with protonated nitrogen groups, its reduction to Cr^{3+} occurred. The occurrence of these consecutive phenomena was also confirmed qualitatively, where the color of APEI resin initially changed to yellowish brown and then finally to green. At this point, the generated Cr^{3+} ions can still be retained through interaction with free carboxylic groups of the resin. However, pH conditions generally determine the equilibrium concentration of Cr^{3+} in the effluent, with higher pH resulting to lower Cr^{3+} content. We have thus observed much lower Cr^{3+} concentrations during the initial stage where protonation of amine and carboxyl groups resulted to relatively higher effluent pH (Fig. 5). Now, when the pH of the solution started to decrease again, the Cr^{3+} equilibrium concentration shifted to higher concentration due to more extensive competition with hydronium ions.

For the efficiency of Cr removal, the breakpoint ($Cr_{tot} > 2$ mg/L) for this particular run is approximately 116 hrs or a total effluent volume of 3.48 L. This corresponds to a resin capacity of around 17.0 mg/g APEI (dry basis). Considering that the theoretical capacity of the resin for Cr^{6+} is 134.0 mg/g (dry basis), this represents approximately 12.7% adsorbent efficiency. However, it must be mentioned that the actual capacity was based on the breakpoint for Cr_{tot}, which also includes Cr^{3+} ion. With regards to Cr^{6+}, however, effluent concentrations were still below environmental standards even beyond Cr_{tot} breakpoint.

To further improve total Cr removal during continuous operations, a re-adjustment of influent pH upon complete protonation of the APEI resin was therefore considered. During batch runs, the use of an initially higher pH of around 2.5 resulted in the reduction in the sequestration performance of the resin due to considerable rise in equilibrium pH at a higher amount of APEI. In continuous systems, however, this can be prevented by initially running the system at low pH to initially allow protonation to take place and thus favor the removal of Cr^{6+} ions. Now, when the resin has been saturated (as indicated by the reduction in pH afterwards), the influent pH may then be increased to provide a favorable condition for Cr^{3+} binding as well as to minimize Cr^{6+} reduction to Cr^{3+}. To evaluate the feasibility of this approach for efficient removal of both Cr^{6+} and Cr^{3+} ions, pH readjustments at certain periods during the operation were carried out.

During the first stage, Cr^{6+} solution at pH 1.5 was fed to the APEI column to accomplish the initial PEI protonation. When the pH of the effluent started to decrease, the influent pH was first readjusted to pH 4. The results showed that by this approach, the total Cr concentrations are reduced to much lower concentrations (Fig. 6). Comparing Figs. 5 and 6, notice that as the pH was adjusted to pH 4 just after the 500 ml mark in the latter, the total Cr removal was improved. This could either indicate that less reduction of Cr^{6+} to Cr^{3+} occurred or less desorption of formed Cr^{3+} occurred due to relatively higher pH. With regards to the response of effluent pH to such feed pH readjustment, it is interesting to point out that its value increased rather slowly. Such a trend may indicate the gradual release of some protons by the APEI bead. As a consequence, the Cr^{6+} binding ability of the column started to deteriorate as indicated by the rise in Cr^{6+} concentration in Fig. 6. These results clearly show that, in the hope to achieve better conditions for Cr^{3+}

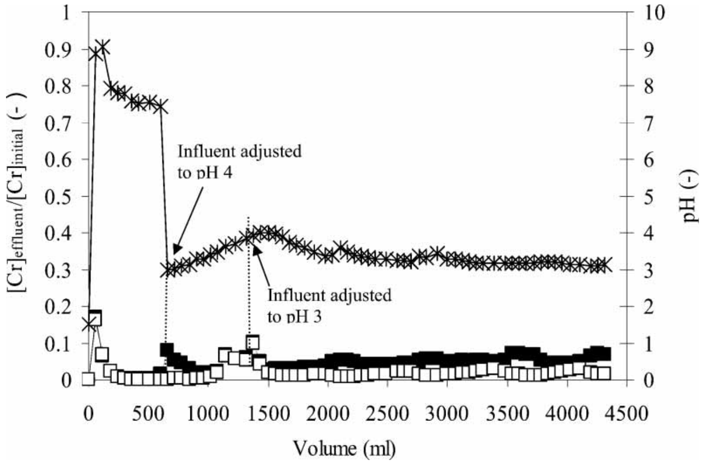


Figure 6. Breakthrough curve for Cr adsorption by APEI resin with pH adjustment. Initial Cr^{6+} concentration was approximately 10 mg/L. Flowrate was 30 ml/hr. –■– Cr_{tot}; –□–Cr^{6+}; *pH.

removal in this case, the Cr^{6+} sequestration may be sacrificed upto some point. Specifically, the Cr^{6+} concentration increased up to more than 1 mg/L, which is above the standard limit of 0.5 mg/L. To counter this problem, the influent pH was again readjusted this time to pH 3. At this condition, Cr^{6+} removal again improved due to increased protonated sites. Re-protonation of APEI is evident from the gradual decrease of pH from pH 4 to pH 3. More importantly, the total Cr was also dramatically reduced suggesting more favorable pH conditions. In fact as compared to the previous run without pH adjustment, the Cr_{tot} concentration has been maintained at a much safer value of 0.5 mg/L even beyond the breakpoint achieved in Fig. 5. This would ultimately lead to a higher experimental capacity than that achieved without pH adjustment. These results thus confirmed that by simply adjusting the influent pH, much lower total Cr effluent conditions may be achieved and the service life of the APEI resin can be extended.

Finally, the ability of the APEI resin in Cr sequestration was compared with a commercially available resin Chitopearl CS-03. Chitopearl is a chelating resin made from chitosan. It has been further modified with polyamines, thus resulting in its high nitrogen content of around 12.41%. Past research has evaluated the performance of chitosan-based adsorbents for Cr^{6+} removal with positive results. The protonated amino groups of chitosan also serve as the binding sites. In addition, reduction of Cr^{6+} species to Cr^{3+} has also been reported (8). For this experiment, an APEI resin synthesized by the atomization technique was employed. This is to come up with more or less comparable particle size with the Chitopearl resin (<100 μm) and thus minimize differences particularly on kinetics parameters during Cr^{6+} sequestration. Specifically, the APEI microbeads used contained around 4.19% N. This was relatively lower than that synthesized by the drop technique due to the lower amount of Na-alginate employed. Nonetheless, this was considered sufficient enough for comparative purposes.

Preliminary comparative tests using column experiments revealed the better performance of the APEI beads over Chitopearl-03 resin particularly in maintaining Cr effluent concentrations below the environmental standards for longer time period. This was despite the lower nitrogen content of APEI as compared to Chitopearl-03 (Fig. 7). (In these runs, Cr^{6+} concentrations for both resins were almost the same so that the total Cr alone was used as the basis for comparison.) In the case of Chitopearl, after only around 1100 ml of solution, the Cr_{tot} concentration has already started to increase and for some time has gone beyond the total Cr standard value of 2 mg/L. This is despite the low initial Cr^{6+} concentration of 5 mg/L employed. In the case of APEI, total Cr concentrations were maintained even below the standard for Cr^{6+}. With the Chitopearl resin, the release of higher amounts of Cr^{3+} generated during Cr^{6+} reduction was clearly evident. The nitrogen ligands alone may not be sufficient to establish a stable complex with the Cr^{3+} ions at the prevailing low pH of the solution. Indeed, these initial comparisons show the advantage of the hybrid composition of APEI with its imino

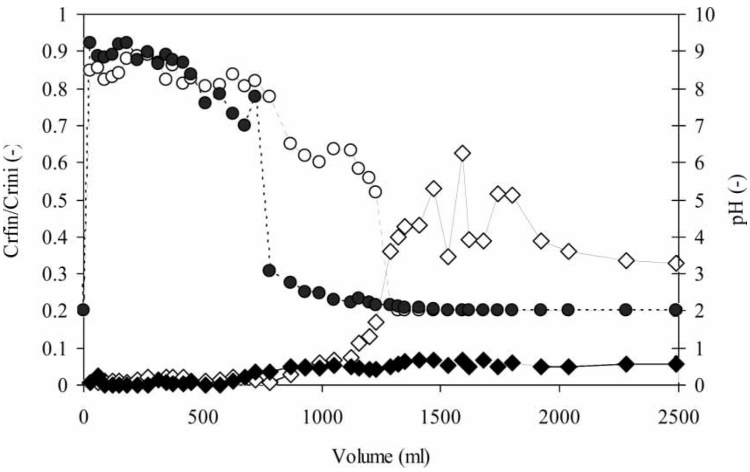


Figure 7. Breakthrough curve for total Cr removal by APEI and Chitopearl CS-03 resin. Initial Cr^{6+} concentration was approximately 5 mg/L. Flowrate was 30 ml/hr. —◇— APEI; – – ● – – pH (APEI); —◇— Chitopearl (CS-03); – –○– – pH (CS-03).

and carboxyl groups. For a resin with a reductive ability for Cr^{6+}, the ability to retain the formed Cr^{3+} species becomes significant. The hybrid composition of APEI allows it to sequester both types of Cr species to satisfy environmental standards at the specified experimental conditions.

CONCLUSION

A Cr^{6+} adsorbent made from PEI polymer immobilized in Ca-alginate gel beads was synthesized and evaluated. Optimization experiments show the importance of PEI molecular weight on the efficiency of immobilization. PEI of 70,000 Da molecular weight displayed the highest immobilization percentage of 52%. The $CaCl_2$ and PEI concentrations have very minimal effect on the immobilization efficiency except in practical applications where economics of the process become very significant. Batch adsorption experiments showed the considerable affinity of APEI for binding negatively charged dichromate ions at low pH. Conversion of Cr^{6+} to the less toxic Cr^{3+} species by APEI was also evident at the low pH of the solution. Nonetheless, the APEI resin displayed considerable retention of formed Cr^{3+} ions with its hybrid composition of amine and carboxyl groups. With this initial success, it is important to conduct more detailed studies on the exact contribution of individual reactions during Cr binding on the overall performance of the resin. Furthermore, evaluations on the resulting physical stability of the resin as a result of such reactions—particularly the redox reaction—will also be useful. With regard to the concern of what to do with the saturated resin afterwards, the final physical state of the material may have a significant effect on the feasibility of its regeneration. But with the simplicity of the synthesis procedure, disposal may be a practical alternative. In this case incineration as well as stabilization methods are among the possible disposal procedures that are being considered and which we also hope to evaluate in future research work.

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