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ENHANCEMENT OF PHOSPHONOMETHYLATED PEI–Cu^{2+} COMPLEX FLOCCULATION BY Ca^{2+} IONS: A NEW APPROACH FOR HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT

Removal of Cu^{2+} ions from aqueous solutions by induced flocculation of PPEI with Ca^{2+} ions was studied. Considerable floc formation accompanying Cu^{2+} sequestration was demonstrated even at low initial metal concentration of $5\,mg\,L^{-1}$. Flocculation capacity as high as 4.7 mmol Cu^{2+}/g PPEI at pH 6 was obtained. Ca^{2+} showed minimal competition with Cu^{2+} ions for adsorption sites in the polymer. The PPEI–Ca^{2+} flocculant system was effective over a wide range of pH so that at an equilibrium pH of 1.5, more than 50% Cu^{2+} removal was possible. The [$CaCl_2$]/[PPEI] ratio is a significant parameter with regards to achieving

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complete Cu^{2+} removal. At optimized condition, the process is capable of scavenging Cu^{2+} ions to background levels.

Key Words: Phosphonomethylated-polyethyethyneimine; Flocculation; Copper removal; Calcium; Chelation; Wastewater treatment

INTRODUCTION

Chelating polymers have been widely used for heavy metal separation. Their ability to scavenge metals to background levels make them highly useful in the field of wastewater treatment. These compounds have been employed in various metal separation processes such as ion-exchange, solvent extraction and recently in ultrafiltration technologies. For higher metal–ligand reaction rates and to maximize chelating flexibility, techniques based on homogeneous processes are generally considered ideal (1). However, with regards to the recovery of the complexed polymer, heterogeneous methods are considered advantageous due to inherent mechanical convenience and operational flexibility.

The use of a water-soluble chelating polyelectrolyte to flocculate metals from solution is one application that may combine the advantages of both homogeneous and heterogeneous processes for heavy metal sequestration. As a common procedure, metal binding is allowed to occur in a homogeneous phase and then upon equilibration a secondary electrolyte of opposite charge is added to induce floc formation. Factors such as charge neutralization as well as metal bridging contribute to the subsequent precipitation and separation of the polymer–metal complex. Among the polyelectrolytes that have been utilized for this purpose are naturally derived polymers, such as polygalacturonic acid (2) and starch xanthate (4–8). Depending on the solubility of metal–polymer complex, a secondary polyelectrolyte may not be necessary for floc formation such as in the case of alginic acid (2,3). However, with the above class of polyelectrolytes the lack of heavy metal specificity due to the ionic nature of metal bonding process contributes some limitations when applied to the treatment of wastes containing a mixture of transition and non-transition metal ions.

In this research, we propose a novel approach for metal sequestration by combining the chelating and flocculating capabilities of a water-soluble phosphonomethylated derivative of polyethyleneimine (PEI). PEI had been recently employed a lot in metal ultrafiltration technologies for the concentration of heavy metals (1,9,10,17). The branched structure of the parent PEI, with its numerous nitrogen groups, contributes to the formation of strong coordinate bonds specifically with the toxic transition metal ions. Modifications of PEI by the incorporation of additional functional groups such as acetate, methylthiourea, phosphonate and the like have been made to improve its metal specificity and metal capacity even at low pH conditions (9,11,12). Now, it has come to our attention that certain functional groups may contribute another equally significant purpose with regards to the separation process. In this work, we have considered exploiting the phosphonate section of a phosphonomethylated-PEI (PPEI) to effect flocculation of heavy metal–polymer complex. Phosphonate ions are known to form relatively insoluble metal salts with a non-transition metal ion such as Ca^{2+}. But as past researches had also established, amine chelating groups exhibit high specificity for transition metals so that the presence of Ca^{2+} ions would have a minimal effect on the performance of these sites for metal sequestration (13–15). Separation factors in excess of 1000 in favor of Cu^{2+} over Ca^{2+} metals had been reported for some nitrogen-containing chelating agents (14). Separation factor is a dimensionless measure of relative selectivity between two competing ions. Now, a combination of both heavy metal chelating and non-transition metal flocculating properties may provide a single polymer with some interesting qualities for heavy metal removal particularly for wastewater treatment applications.

MATERIALS AND METHODS

Materials

Polyethyleneimine (PEI MW 70000) was purchased from Wako Pure Chemicals Co., Japan. All reagents unless otherwise specified were purchased from Wako Pure Chemical Co., Japan.

Synthesis of Phosphonomethylated-PEI (16,17)

Polyethyleneimine (0.06 mol) was dissolved in 6 *M* hydrochloric acid (80 mL). Phosphonic acid (or phosphorous acid) (0.30 mol) was added and then completely dissolved. The solution was brought to reflux followed by the dropwise addition of formaldehyde (0.47 mol) within a period of 1 hr under constant stirring. After the addition, the reaction was allowed to proceed for an additional hour under reflux. The PPEI precipitate, which had been allowed to separate overnight, was collected by decantation. It was re-dissolved in water by altering the pH of the resulting solution to neutral with sodium hydroxide.

Purification of PPEI

The solution obtained from the synthesis section was purified by ultrafiltration through an Amicon membrane (NMWL: 10,000 MW). Repeated cycles of washings with distilled water were conducted until the final phosphorus content of the effluent was close to background values. The remaining filtrate was then subjected to rotary evaporation and the final precipitate was dried under vacuum. An aqueous solution containing 1% of purified (PPEI) was prepared and used during the entire process of flocculation experiments.

Removal of Cu^{2+} with PPEI–Ca^{2+} Flocculant

Different amounts of 1% PPEI solution were added into a 25 mL of 100 mg L^{-1} Cu^{2+} solutions (as $CuCl_2$) under mild stirring with a magnetic stirrer. After approximately 15 min, a measured amount of Ca^{2+} (10,000 ppm as $CaCl_2$ solution) was added to initiate the floc formation. The pH of the system was adjusted with either HCl or NaOH as required. The mixture was allowed to equilibriate for an additional 15 min after which the precipitate was separated by filtration through 90 mm 5C Advantec filter papers. The metal concentrations of the filtrate were assayed. Corrections on the metal concentrations due to the dilution by PPEI and Ca^{2+} solutions were made. The influence of pH and Ca^{2+} concentration on the sequestration capacity of PPEI was evaluated. Flocculation experiments with PPEI and Ca^{2+} in the absence of Cu^{2+} were also conducted to determine the capacity of PPEI for Ca^{2+} ions. Finally, to evaluate the scavenging ability of the PPEI–Ca^{2+} flocculant system, experimental runs with 15 mL of 5 mg L^{-1} Cu^{2+} solution were made.

Analytical Methods

The degree of phosphonate substitution in PEI was analyzed using a Perkin–Elmer Elemental Analyzer (Model 2044 CHN). Phosphorus content of PPEI as well as the heavy metal concentrations of solutions were determined by a Seiko Inductively Coupled Argon Plasma Spectrophotometer (Model SII SPS 3000S).

RESULTS AND DISCUSSIONS

Chemical Analysis of Phosphomethylated PEI

The Mannich-type reaction of an amine, formaldehyde and phosphorous acid proceeds according to the equation:

$$R_{3-n}NH_n + nCH_2O + nHP(O)(OH)_2 \rightarrow R_{3-n}N[CH_2P(O)(OH)_2]_n + nH_2O \quad (1)$$

where $n = 1$, 2 or 3. The hydrogen atom directly bonded to the phosphorus in phosphorus acid is the 'acidic' hydrogen required for this reaction. In this experiment, the amino and phosphorus compounds used for the reaction were PEI and phosphonic acid, respectively.

Elementary analysis of PPEI indicated nitrogen and phosphorous contents of 8.41 and 14.77%, respectively (Table 1). This corresponds to approximately 4.8 mmol of phosphate and 6.0 mmol of amino groups per gram of the polymer. Considering that each mole of phosphonate section in PPEI contributes 2 mol of oxygen chelating group (Eq. (1)), the total moles of ligand available for metal coordination would be close to 15.6 mmol/g PPEI. Based on a Cu^{2+} coordination number of 4, this would correspond to an ideal theoretical Cu^{2+} capacity of approximately 3.9 mmol Cu^{2+}/g PPEI.

PPEI Flocculation with Metal Ions

The mechanism governing the metal flocculation by PPEI was initially studied. Throughout the experiments, Cu^{2+} was used as a representative metal due to the distinct blue color of the PPEI–Cu^{2+} complex, which allows for a quick qualitative evaluation on the performance of the flocculation process. Though preliminary experiments had shown the possibility of removing Cu^{2+} by the incorporation of PPEI polyelectrolyte alone, floc formation was found to occur within a narrow range of PPEI content (Fig. 1). At an initial Cu^{2+} concentration of 100 mg L^{-1}, increasing the PPEI concentration beyond 300 and 420 mg L^{-1} at pH 6 and 3, respectively, resulted in the re-dissolution of PPEI–Cu^{2+} complex as indicated by the increase of both Cu^{2+} ions and phosphorus of the filtrate. This is considered a limitation with regards to establishing the optimum amount of PPEI for maximum Cu^{2+} removal. Furthermore, from experiments conducted at lower initial Cu^{2+} concentration (<5 mg L^{-1}), floc formation was difficult to monitor qualitatively, so that this contributes additional complications with regards to the separation process.

Table 1. Elementary Analysis of Synthesized PPEI Polymer

Element	Percent
Carbon	21.97
Hydrogen	6.85
Nitrogen	8.41
Phosphorus	14.77

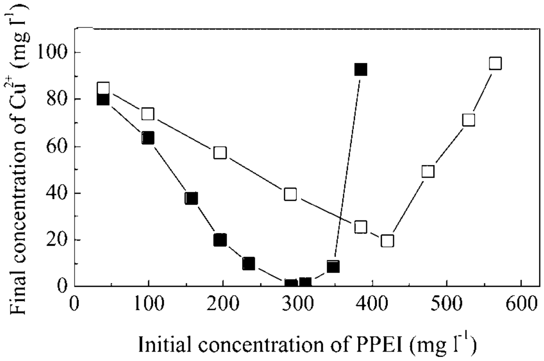

Figure 1. Flocculation of Cu^{2+} by PPEI polymer at different pH conditions. —■- pH 6; – –□ pH 3.

As an alternative procedure to separate the heavy metal–polymer complex from the mother solution, enhancement of floc formation and floc size by the addition of external non-transition metal ions was considered. For example, Ca^{2+} is known to form relatively insoluble salt with the phosphonate ions so that by bonding with the phosphonate section of PPEI, flocculation of the polymer with the attached metal ion may be achieved. By this approach, flocculation of PPEI would be dependent on the amount of the enriching metal ion so that this becomes more flexible when optimizing the flocculant requirement even at initially low concentration of the target metal ($<1\,\mathrm{mg\,L^{-1}}$). Though this method introduces another foreign metal to the waste stream, the lesser toxicity of the additional metal, however, may not be a big concern from the point of view of wastewater treatment. In fact, Ca^{2+} had long been applied for metal removal through alkali treatment.

During the preliminary experiments, we have evaluated different non-transition metals on their ability to flocculate PPEI. Among the metals tested, only Ca^{2+} exhibited floc formation with PPEI. In the case of Mg^{2+}, the formation of cloudy solution was observed but floc separation by the simple filtration was not possible. Furthermore, an additional experiment involving another type of PEI-derivative had also generated negative results. In this particular experiment, a carboxylic derivative of PEI was synthesized by its reaction with bromoacetic acid under alkali conditions (17). However, results showed that Ca^{2+} does not induce the flocculation of such carboxylic-PPEI derivative both in the presence and absence of Cu^{2+} ions. The above results thus give credence to our assumption that the flocculation of PPEI polymer with Ca^{2+} ion is basically inherent of the solubility properties of the phosphonate–Ca^{2+} complex.

Removal of Cu^{2+} with PPEI–Ca^{2+} Flocculant

As expected, the addition of Ca^{2+} to enhance floc formation in Cu^{2+} solution was also confirmed. The flocs were bluish in appearance, thus qualitatively indicating the stability of PPEI–Cu^{2+} complex despite the presence of high concentration of Ca^{2+} in relation to the Cu^{2+} ion. Floc size was sufficiently large to allow for rapid settling and subsequent separation by decantation and filtration. Results at higher initial Cu^{2+} concentration did confirm the flexibility of the process with regards to the optimization of PPEI content and pH. As shown in Fig. 2, the concentration of Cu^{2+} in the filtrate decreased in correspondence to the increasing PPEI concentrations even beyond the optimum value that was reflected in Fig. 1 data. When PPEI was added beyond 420 and 300 mg L^{-1} at equilibrium pH 3 and 6, respectively, the residual Cu^{2+} content decreased indefinitely. At lower initial Cu^{2+} concentrations, the same trend was observed so that the Cu^{2+} concentration was also reduced to relatively lower values (Table 2). The PPEI content (in terms of P concentration) of the filtrate also decreased thus confirming that metal removal is indeed a consequence of PPEI flocculation.

Experiments were further conducted to evaluate in detail any significant effect of Ca^{2+} on the capacity of PPEI for Cu^{2+} flocculation. Figure 3 summarizes the flocculation capacity of PPEI for Cu^{2+} at different Ca^{2+} concentrations. The sequestration of Cu^{2+} was found to be dependent on solution pH and ratio of PPEI to Cu^{2+} ions. Capacities close to 2.2 mmol Cu^{2+}/g PPEI and 4.7 mmol Cu^{2+}/g PPEI at pH 3 and 6, respectively, had been attained. These data indicate the comparable performance of our method with ultrafiltration, which can achieve a

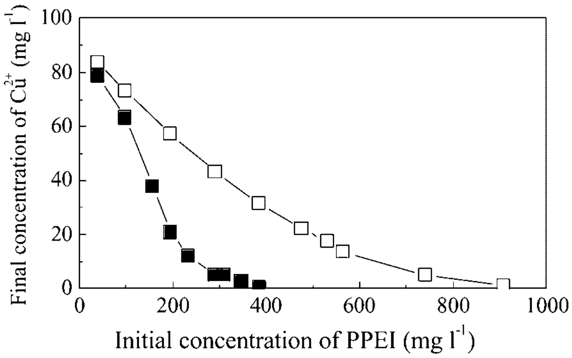

Figure 2. Removal of Cu^{2+} by PPEO–Ca^{2+} flocculant system. Ca^{2+} was added to final concentration of 100 mg 1^{-1}. —■- pH 6; – –☐ pH 3.

Table 2. Removal of Cu^{2+} by PPEI–Ca^{2+} Flocculant System at an Initial Cu^{2+} Concentration of 4.618 mg L^{-1}. $CaCl_2$ Was Added to an Initial Concentration of 80 mg L^{-1}. The Equilibrium pH of the Solution was Approximately pH 4

		[P] (mg l^{-1})	
[PPEI] (mg l^{-1})	Final [Cu^{2+}] (mg l^{-1})	Initial	Final
16.5	2.171	2.35	0.185
33.3	0.863	4.71	0.288
66.7	0.302	9.41	0.449
100.0	0.220	14.1	0.464
133.0	0.168	18.8	0.509
166.0	0.166	28.2	0.486

capacity of approximately 2.46 mmol Cu^{2+}/g PPEI at pH 4 (9). The higher metal sequestration based on the ideal coordination capacity of 3.9 mmol Cu^{2+}/g PPEI indicates the possible occurrence of pure Cu^{2+} ionic bonding as well as chelate formation with less coordination number due to some steric factors. Though a significant decrease in adsorbed Cu^{2+} at increasing Ca^{2+} concentration was evident, the relative differences in capacity at the lowest and highest Ca^{2+} concentration for both pH conditions was minimal. Calculations from Fig. 3 data

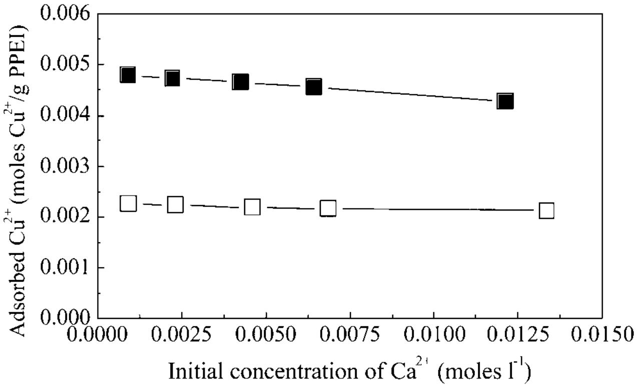

Figure 3. Effect Ca^{2+} concentration on the sequestration capacity of PPEI–Ca^{2+} flocculant system for Cu^{2+} at different pH conditions. —■- pH 6; – –□ pH 3.

revealed that when the Ca^{2+} content was increased by approximately 3×10^{-4} mol, the corresponding decrease in adsorbed Cu^{2+} of PPEI was less than 2×10^{-6} and 4×10^{-6} mol at pH 3 and 6, respectively. Clearly, such a decrease in Cu^{2+} adsorption does not correspond stoichiometrically to the increase in the Ca^{2+} concentration. The above observations may suggest the displacement by Ca^{2+} ions of some ionically bonded Cu^{2+} ions with phosphonate groups. Nonetheless, coordinate bond formation between Cu^{2+} and nitrogen group of PPEI would remain stable. Therefore, despite the possible competition with Ca^{2+}, it was still possible for the process to favor Cu^{2+} sequestration at a satisfactory level.

Another interesting observation that perhaps reflect the above assumption is the fact that the amount of Ca^{2+} ions that were required to initiate floc formation was found to be below the Ca^{2+} capacity of PPEI. For comparisons, Fig. 4 shows the flocculation capacity of PPEI for Ca^{2+} in the absence of Cu^{2+} cations at approximately pH 3.0. From this data, the amount of Ca^{2+} adsorbed is approximately 2 mmol/g PPEI. However, in the presence of Cu^{2+}, the apparent amount of Ca^{2+} that seemed necessary to flocculate PPEI–Cu^{2+} complex was lower. Based on the calculations of Ca^{2+} ions that were simultaneously removed with Cu^{2+}, a value of 0.2 mmol Ca^{2+}/g PPEI was obtained. This is just roughly 10% of the actual capacity of PPEI for Ca^{2+}, which implies that only a small amount of Ca^{2+} is actually required to induce floc formation of PPEI–Cu^{2+} complex. Hence, Ca^{2+} does also exhibit minimal competition for phosphonate sections of PPEI. However, as what we will show in the succeeding sections some degree of PPEI–Ca^{2+} solubility requires for a relatively higher ratio of Ca^{2+} to PPEI for maximum Cu^{2+} removal from the solution.

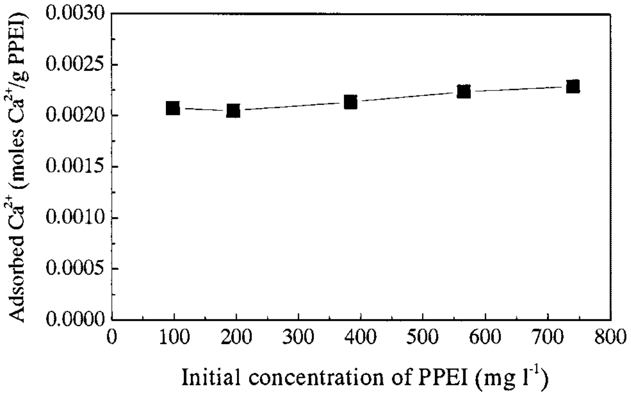

Figure 4. Flocculation of Ca^{2+} ions by PPEI polymer. The initial concentration of $CaCl_2$ was approximately 150 mg/L.

Effect of pH on the Removal of Cu^{2+} by PPEI–Ca^{2+} Flocculant

Though the above experiments were conducted at a slightly acidic and a relatively neutral pH, a more detailed evaluation on the sequestration of Cu^{2+} by PPEI at different pH conditions was also conducted. Results from this experiment are shown in Fig. 5. Experimental data revealed that PPEI is effective in removing Cu^{2+} over a wide range of pH. The optimum pH occurs above pH 4 but a relatively strong metal–ligand affinity of PPEI is still evident at much lower pH. The decrease in capacity is expected due to increased concentration of hydronium ions that compete with Cu^{2+} for both phosphonate and amine chelating sites in PPEI. But considering that at a pH of 1.5, more than 50% Cu^{2+} removal was attained still, this process does provide an interesting option for metal removal at low pH conditions. The higher performance at highly basic pH conditions expectedly reflects the influence of Cu^{2+} removal through as $Cu(OH)_2$ precipitates, which increases relatively the amount of amino and phosphonate groups available for metal chelation.

Scavenging of Cu^{2+} with PPEI–Ca^{2+} Flocculant

Following the positive results on Cu^{2+} sequestration by a phosphonate–Ca^{2+} flocculant system, the ability of the process for heavy metal scavenging to meet strict environmental standards was finally studied. For aqueous systems containing Cu^{2+} ions, US EPA has specified that solutions containing more than 1.0 mg/Cu^{2+} are considered unsafe due to its consequences to public health (18). Other regulating bodies such as WHO International implements a more strict level of 0.05 mg L^{-1} (18). In Japan, regulations prohibit the discharge of wastewaters containing Cu^{2+} content of more than 3 mg L^{-1}. But since heavy

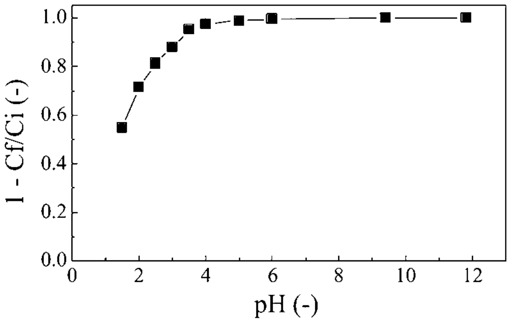

Figure 5. Effect of pH on the removal of Cu^{2+} by PPEI–Ca^{2+} floccuulant system.

metals have the ability to accumulate in living systems, close to zero emissions from point sources are considered ideal to maintain the safety of water environments. This is perhaps the major reason why, chelating agents with their strong and specific heavy metal affinity have been the most reliable agents for heavy metal scavenging.

From the preliminary flocculation experiments conducted at low initial Cu^{2+} concentration of $5\,mg\,L^{-1}$, slight shortcomings of the process PPEI were observed (Table 2). Indeed, the performance of the flocculant system may be considered satisfactory with regards to eliminating considerable amount of Cu^{2+} below existing regulations for wastewater treatment. Nevertheless, some concerns on other aspects of the process may be raised. For one, the Cu^{2+} concentration particularly at low concentration conditions does not seem to decrease correspondingly with the increase in PPEI content. Also, a check on the residual PPEI (as phosphorus) of the filtrate had pointed out traces of residual PPEI in the solution. Aside from being a possible source of additional contaminant, this could also become a limitation when concerns for complete metal removal are considered. Such residual PPEI would contain the trace amounts of the Cu^{2+} ions. To counter this problem, we tried to increase further $[CaCl_2]/[PPEI]$ concentration ratio in order to vary the flocculation equilibrium to higher PPEI–Ca^{2+} floc formation. Going back to the previous section, it was mentioned that Ca^{2+} slightly reduced the capacity of PPEI for Cu^{2+} so that increasing Ca^{2+} concentration may seem contrary to the goal of improving the performance of the process for Cu^{2+} scavenging. However Ca^{2+} ions compete only for a fixed number of sites in PPEI, particularly the phosphonate sections. Now, by adding Ca^{2+} and PPEI at an optimum ratio, that is, with the concentration of the latter in excess of the available Cu^{2+}, maximum PPEI and

Table 3. Removal of Cu^{2+} by PPEI–Ca^{2+} Flocculant System at Different Initial Ca^{2+} Concentrations. The Initial Cu^{2+} Concentration Was $4.856\,mg\,l^{-1}$. The Concentration of PPEI Was Fixed at $133\,mg\,L^{-1}$. The pH of the Solution Was Approximately pH 4

Initial $[CaCl_2]$ ($mg\,l^{-1}$)	Final $[Cu^{2+}]$ ($mg\,l^{-1}$)
40	2.171
80	0.188
160	0.065
330	0.037
660	0.023

Table 4. Removal of Cu^{2+} by PPEI–Ca^{2+} Flocculant System at Different Initial PPEI Concentration. The Initial Cu^{2+} Concentration Was 4.856 mg L^{-1}. Ca^{2+} Was Added to a Constant [$CaCl_2$]/[PPEI] Mass Concentration Ratio of 1.5. The Equilibrium pH was Adjusted to pH 6

Initial [PPEI] mg L^{-1}	Final [Cu^{2+}] (mg L^{-1})
6.7	1.089
33.3	0.512
50.0	0.159
66.7	0.063
100.0	Not detected
166.0	Not detected

Cu^{2+} removal may be achieved. Accordingly, the concentrations of Cu^{2+} were indeed reduced further by increasing the Ca^{2+} content (Table 3). At a relatively neutral pH 6 and using an estimated [$CaCl_2$]/[PPEI] mass concentration ratio of close to 1.5 based from Table 3 data, the process was able to reduce the Cu^{2+} concentration to values undetected by our employed method of metal analysis (Table 4). Correspondingly, much lower residual PPEI concentrations were also observed at these conditions.

CONCLUSION

To summarize, what we have basically introduced in this work is a novel procedure for a rapid and simple method of employing a water-soluble nitrogen-containing chelating polymer for metal separation. The basic qualities that had distinguished nitrogen-containing polymers from other type of chelating polyelectrolytes, such as their high affinity for transition metals, had been exploited to the full advantage of providing a simple separation method by floc formation with a non-transition metal ion. Detailed analysis had revealed that the sequestration capacity of the chelating polymer is not considerably affected by Ca^{2+} ions. The process was found to be effective at a wide range of pH conditions so that even at a solution pH of 1.5, more than 50% Cu^{2+} removal can be achieved. In relation to wastewater treatment, the PPEI–Ca^{2+} flocculant system was also applicable for Cu^{2+} scavenging by considering optimum concentrations of the Ca^{2+} and the PPEI polymer. Though the experiments had concentrated basically on the sequestration of Cu^{2+}, experiments with other heavy metals such as Pb^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} had also yielded positive results. Evaluations with actual metal bearing wastewater were also encouraging so that we are currently in the process of consolidating data from a wide range of applications to establish the flexibility of the PPEI–Ca^{2+} flocculant system. Furthermore, in the future we also hope to conduct more in-depth mathematical analysis of the flocculation process in order to attain the full potential of the established method for heavy metal removal.

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