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Heavy Metal Flocculation by Phosphonomethylated-Polyethyleneimine and Calcium Ions

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ABSTRACT

Removal of various heavy metal ions such as Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solutions by induced flocculation of phosphonomethylated-polyethyleneimine (PPEI)–heavy metal complex with Ca^{2+} ions was studied. Considerable floc formation accompanying metal sequestration was demonstrated, even at low initial concentration of the target metals. The PPEI–Ca^{2+} flocculant system was also effective for heavy metal scavenging purposes. Applications in actual waste streams, particularly in the treatment of wastewaters, such as rinse solutions from electroless Ni plating, which contain competing

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complexing species such as EDTA, highlighted some of the advantages of the process over traditional alkali precipitation methods. The ability of spent PPEI flocculant to be regenerated by 2 N HCl has also been confirmed with slight effect on its metal sequestration ability.

Key Words: Calcium; Chelation; Flocculation; Heavy metals; Phosphonomethylated-PEI; Wastewater treatment; Phosphonate.

INTRODUCTION

The removal of heavy metals is still a major concern for waste treatment-related studies. In a recent report released by the U.S. EPA,[1] heavy metals such as lead, cadmium, mercury, chromium, copper, zinc, and nickel have been listed at the top of priority pollutant ranking, hence, demanding strict monitoring by concerned agencies. The persistency, bioaccumulative property, and toxicity (or PBT, which was the basis of EPA ranking) of heavy metals requires, for maximum removal from point sources, that close to zero emission of these pollutants would be achieved. Advanced techniques of heavy metal sequestration previously applied for analytical purposes, such as the use of chelating agents, are, therefore, being incorporated into various treatment processes to meet strict a environmental standard for the disposal of heavy metal loaded streams.

With their high metal affinity, chelating polymers have been widely employed in various metal separation and scavenging technologies, such as ion-exchange, solvent extraction, and ultrafiltration.[2–5] However, despite the wide applications of chelating agents in metal removal, traditional methods of precipitation with alkali are still preferred in the field of wastewater treatment due to inherent mechanical convenience, operational flexibility, and relatively lower cost. Nevertheless, perennial problems regarding sludge handling and disposal and, more importantly, the insufficient metal removal ability, particularly for extremely toxic metal streams containing strong complexing agents, limits the effectiveness of traditional precipitation process.

The use of water-soluble chelating polyelectrolytes to precipitate metals from solution is one application that has improved the status of precipitation for heavy metal removal from waste streams. As a common procedure, metal binding is allowed to occur in a homogeneous phase and then upon equilibration, and, in some cases, aided by the addition of a secondary polyelectrolyte of opposite charge, floc formation occurs. Factors such as charge neutralization as well as metal bridging contribute to the subsequent precipitation and separation of the polymer–metal complex. To date, numerous biopolymers and synthetic polyelectrolytes had been employed and novel methods for application have been developed.[6–8]

In our recent research, a novel approach for metal sequestration by combining the chelating and flocculating capabilities of a water-soluble phosphonomethylated polyethyleneimine (PPEI) was introduced using Cu^{2+} as the target metal ion.[9] The heart of the process is a soluble PPEI heavy metal chelating polymer, which precipitates in the presence of Ca^{2+} ions. Though the use of PPEI as a metal chelating polymer in ultrafiltration and ion exchange has been well documented,[10,11] its use as a metal flocculating agent has not been acknowledged. The branched structure of the PPEI, with its numerous nitrogen and phosphonate groups, contributes to the formation of strong coordinate bonds, specifically with the toxic transition metal ions. The phosphonate section provides the polymer with the required flocculation property. Phosphonates are known to form relatively insoluble metal salts at a high concentration of divalent Ca^{2+} ions. For comparative purposes, solubility product constant in the order of 10^{-50} had been reported for calcium methylene phosphonate salts.[12] Nitrogen-type chelating groups have been shown to exhibit high specificity for transition metals so that even in the presence of high Ca^{2+} ions, the metal chelating ability of PPEI would be considerably maintained.[13,14] In this research, evaluations of flocculation capabilities of the PPEI for a wider range of heavy metals was made. A mechanism governing the removal of heavy metals by this polymer is proposed. Finally, additional advantages of the PPEI–Ca^{2+} flocculant system in terms of its regenerating ability is discussed.

MATERIALS AND METHODS

Materials

Polyethyleneimine (PEI MW 70000), phosphorus acid, and formaldehyde (37%) were purchased from Wako Pure Chemicals Co., Japan. All reagents, unless otherwise specified, were obtained from the same chemical company.

Synthesis of Phosphonomethylated-PEI

Polyethyleneimine (0.06 mole ethyleneimine repeating units) was dissolved in 6 M hydrochloric acid (80 mL).[15,16] Phosphonic acid (0.3 mole) necessary for complete phosphonomethylation of amino hydrogen was added and then completely dissolved. The solution was brought to reflux at around 90°C, followed by the dropwise addition of corresponding amount of formaldehyde (0.47 mole) within a period of 1 hour under constant stirring. After the addition, the reaction was allowed to proceed for an additional hour. The resulting mixture was transferred into a beaker and left to stand overnight to allow the PPEI to separate from the mother liquor. The precipitate was collected, combined with water, and then dissolved by adjusting the pH to neutral with sodium hydroxide. The resulting solution was purified by ultrafiltration through an Amicon membrane with a cut-off molecular weight of 10,000. The remaining filtrate was then subjected to rotary evaporation and the collected solid product was dried under vacuum. An aqueous solution containing 1.0% purified PPEI was prepared and used for the entire flocculation experiments.

PPEI of different phosphonomethylation degrees were also synthesized by varying the amounts of phosphonic acid (0.058, 0.066, 0.1, 0.2 moles) and formaldehyde (0.029, 0.034, 0.061, 0.30 moles) at constant PEI (0.06 moles) during reaction to evaluate optimum PPEI for flocculation experiments. For phosphonomethylation degrees, which resulted to a homogeneous system, the pH of the whole solution was adjusted and subjected to ultrafiltration afterward.

Removal of Different Heavy Metals with PPEI–Ca^{2+} Flocculant

Different amounts of 1% PPEI solution were added into 25 mL of 100 mg L^{-1} metal solutions ($CuCl_2$, $PbCl_2$, $ZnCl_2$, $CoCl_2$, and $NiCl_2$) under mild stirring with a magnetic stirrer. After approximately 15 minutes, Ca^{2+} (from 10% $CaCl_2$) was added to a resulting [$CaCl_2$]/[PPEI] weight concentration ratio of 1.5 to initiate floc formation following our previous procedure.[9] The pH of the system was adjusted to about pH 5.5, either with HCl or NaOH as required. The mixture was allowed to equilibrate for an additional 15 minutes after which the precipitate was separated by filtration through 5C Advantec filter papers (Toyo Roshi Co., Japan). The metal concentrations of the filtrate were assayed. The scavenging ability of the PPEI–Ca^{2+} flocculant system was determined by conducting flocculation runs with 15-mL metal solutions of relatively lower initial concentrations (<5 mg L^{-1}). The selectivity of PPEI was also investigated by simultaneous removal of the above heavy metals from mixed metal systems. In these experiments, the concentrations of each metal were constant at approximately 0.15 mmol L^{-1}. The influence of pH on the sequestration capacity of PPEI was evaluated by studying the solubility of the PPEI–Ca^{2+} complex at different pH conditions.

Finally, application of the PPEI–Ca^{2+} flocculant system in the treatment of actual waste streams, such as an electroless Ni plating rinse solution, was conducted. This wastewater is generated during the washing of the plated materials just after they are removed from the plating liquor. Since the wash solution is repeatedly used, the concentrations of the Ni^{2+} and compounds in this wastewater increase up to about 1/100 of the original plating solution concentration. Aside from the presence of Ni^{2+} and reducing agents, this wastewater is also reported to contain traces of organic acids, such as acetic acid, malic acid, and citric acid, as well as chelating agents, such as ethylenediaminetetraacetic acid (EDTA), to maintain the plating solution's suitable stability and pH. We confirmed presence of EDTA by capillary electrophoresis analysis (CAPA-300, Otsuka Electronics Co.). The pH of this solution is approximately neutral from pH 6 to 7. These properties, particularly the presence of chelating agents, generally accounts for the difficulty in removing Ni^{2+} from this waste solution. For this section, the performance of PPEI–Ca^{2+} flocculant system was compared with traditional alkali precipitation methods, which employs $Ca(OH)_2$ for Ni^{2+} removal.

Regeneration of PPEI Flocculant

The possibility of spent PPEI regeneration was evaluated by conducting cyclic metal flocculation and desorption experiments using Cu^{2+} as a representative metal ion. Following the previously described procedure, coagulation experiments involving the addition of sufficient amount of PPEI and $CaCl_2$ into 25 mL of $100\,mg\,L^{-1}$ Cu^{2+} ions was initially made. The mixture was filtered under vacuum through a glass filter. The flocs were washed sufficiently for traces of metal ions not chemically bonded to the PPEI flocculant. The washed flocs were carefully collected and subjected to metal stripping using a 2-M HCl solution. The glass filter was also rinsed with the stripping agent and the washings were combined with the bulk acid solution. The metal contents of the filtrates from the flocculation and regeneration cycle were determined.

Analytical Methods

The degree of phosphonate substitution in PEI was analyzed using a Perkin-Elmer Elemental Analyzer (Model 2044 CHN). Phosphorus (for PPEI) and heavy metal concentrations of solutions were determined by a Seiko

Inductively Coupled Argon Plasma Spectrophotometer (Model SII SPS 3000S).

RESULTS AND DISCUSSIONS

Flocculation Properties of PPEI at Different Phosphonomethylation Degree

Polyethyleneimine forms a highly soluble complex with metal ions so that the degree of metal flocculation of the PPEI–Ca^{2+} flocculant system, as well as its solubility in acidic systems, is considered a function of phosphonate substitution degree. To evaluate the influence of this factor for flocculation purposes, modification of PEI at different phosphonomethylation degrees was conducted. In a PEI chain, it has been reported that approximately 25% are primary amines, 50% are secondary amines, and the remaining 25% are tertiary amines.[17] At this ratio, the reaction product at 100% phosphonomethylation degree would contain approximately equimolar amounts of nitrogen and phosphorous components. In the synthesis experiments, PPEI phosphonomethylation degrees attained are shown in Table 1. From synthesis and flocculation experiments, it is interesting to mention that PPEI of different phosphonate content exhibited varying solubilities and flocculation properties in acid solutions and in the presence of Ca^{2+} ions, respectively. Specifically, PPEI above 50% phosphonomethylation was found to separate readily from the mother liquor during synthesis. Furthermore, the polymer also flocculates in the presence of Ca^{2+} ions. In contrast, partially functionalized PPEI, particularly those below 50% phosphonomethylation degree, were soluble even at highly acidic conditions. It is also not capable of forming flocs with

Table 1. Elementary analysis of PPEI at different phosphonomethylation degrees.

Lot	%C	%H	%N	%P	Phosphonomethylation degree (%)
1	31.30	9.28	14.96	9.73	29
2	27.74	8.66	12.74	11.30	40
3	23.43	6.39	10.12	12.11	54
4	21.97	6.85	8.41	14.77	80
5	16.37	6.87	6.29	13.95	100

Ca^{2+} ions at any concentration. These observations can be explained in terms of established mechanisms of floc formation of polyelectrolytes through charge neutralization and solubility properties of the PPEI–Ca^{2+} complex. Higher phosphonate groups results in better flocculation due to the formation of more phosphonate–Ca^{2+} complexes within the PPEI chain, particularly in the presence of competing heavy metal ions. This is discussed further in a later section, which deals on the mechanism of heavy metal removal by PPEI–Ca^{2+} flocculant system.

PPEI Flocculation with Different Metals

In accordance with previous results with Cu^{2+} ions,[9] the incorporation of PPEI polyelectrolyte alone into Zn^{2+} and Pb^{2+} solutions results to subsequent precipitation and separation of the metal ions (data not shown). Other metals, such as Co^{2+} and Ni^{2+}, do not form flocs with PPEI. However, floc formation was found to occur within a narrow range of PPEI concentrations. Expectedly, there is an optimum concentration that results to visible floc formation and considerable metal removal that is difficult to determine effectively, particularly at low concentration of the target metal ion. Increasing the PPEI content beyond this optimum value leads to redissolution of the metal–polymer complex. This property has also been observed by other researchers working with heavy metal–polyelectrolyte systems. This has been identified as one of the limitations of the process.[8] It was suggested that for such heavy metal–polyelectrolyte systems where the metal exhibits high solubility product constant (Ksp) with the anionic polymer section, charge neutralization is responsible for the observed formation of flocs. However, the reversal in metal sequestration at higher doses beyond the optimum flocculation condition could be attributed to the net negative charge prevailing in the metal–polyelectrolyte complex due to the unreacted anionic sections that hinder particle aggregation.

As an alternative procedure to separate the heavy metal–polymer complex from the mother solution, enhancement of flocculation of PPEI–Cu^{2+} complex by the addition of Ca^{2+} ions was tested in recent research with positive results. The low solubility of Ca^{2+}–phosphonate complex, as well as the function of neutralizing net negative charges, particularly at an excess amounts of the polymer, which renders this flocculation process more flexible in determining the polymer requirement. In this research, aside from Cu^{2+} ions, the addition of Ca^{2+} ions in excess was also found to enhance floc formation of PPEI complexes with other heavy metals ions, such as Co^{2+},

Ni^{2+}, Pb^{2+}, and Zn^{2+}. Qualitative evaluation showed that flocs formed in Cu^{2+}, Co^{2+}, and Ni^{2+} solution were colored blue, pink, and green, respectively, which suggests the formation of corresponding amine complexes, which accompany the interaction of Ca^{2+} with phosphonate groups. Floc size was sufficiently large to allow for rapid settling and subsequent separation by decantation and filtration. Figure 1 shows the removal of the different heavy metals by PPEI–Ca^{2+} flocculation. Metal removal increased correspondingly with increasing the PPEI concentrations so that redissolution of PPEI–metal complex was not observed, even at a relatively higher polymer concentration. A narrow optimum range for maximum metal removal, which is observed in the absence of Ca^{2+} ions, does not exist for this system. This is expected since the flocculation property of the polymer has become a function of the additional Ca^{2+} ion.

Further experiments at lower initial concentration ($<5\,\mathrm{mg\,L^{-1}}$) demonstrated the ability of PPEI–Ca^{2+} flocculant system for metal scavenging. The flocculation experiments were conducted initially at a pH of approximately pH 5.5 for all metal systems. This was to ensure that the heavy metals would not precipitate as hydroxides, which can complicate the analysis of flocculation by a PPEI–Ca^{2+} system. At an equilibrium pH of 5.5, the concentrations of the Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} had been

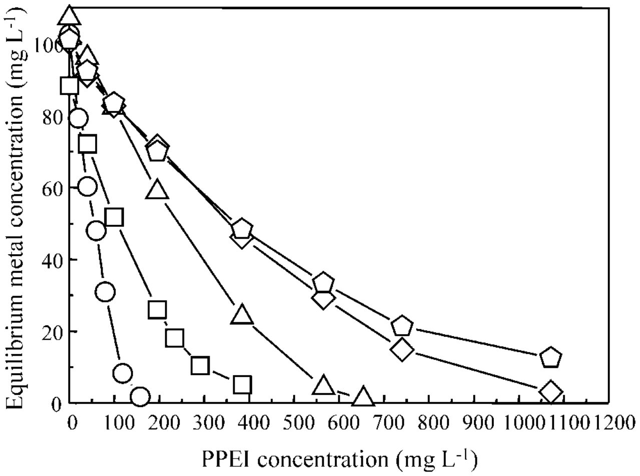

Figure 1. Isotherms for the removal of different heavy metals by PPEI–Ca^{2+} flocculant system. □ = Cu^{2+}, ○ = Pb^{2+}, △ = Zn^{2+}, ◇ = Ni^{2+}, and ⬠ = Co^{2+}.

Table 2. Scavenging of different heavy metals by a PPEI–Ca^{2+} flocculant system.

PPEI concentration ($mg\,L^{-1}$)	Equilibrium metal concentration ($mg\,L^{-1}$)				
	Cu^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}
3.3		1.62			
6.6	3.23	1.15			
13.0	2.69	—			
16.7	1.62	0.25			
20.0	0.82	—			
33.3	0.19	0.20			
50.0	0.11	—	1.09	1.93	2.23
66.7	—	0.09	—	—	1.75
100.0	—	0.02	0.11	0.38	0.97
133.3	—		0.20	0.14	0.61
166.7	—		0.09	0.06	—
200.0	0.03		0.11	0.04	0.30
266.6			0.03		0.19

Equilibrium pH was approximately 5.5.

reduced from 4.69, 4.76, 4.91, 4.82, and 4.91 $mg\,L^{-1}$, respectively, to acceptable limits for industrial wastewaters (Table 2). Though a decrease in metal removal efficiency of polymer was observed when metal concentrations were in the ppb order, the ability of the process to attain extremely low metal concentration without drastic changes in pH is still considered an advantage over the usual alkaline treatment. This is highlighted in a succeeding section involving actual wastewater streams, which contain other chelating contaminants. The PPEI content (in terms of P concentration) of the filtrate also remained considerably low enough to support the possibility of reducing heavy metal concentrations to very low concentrations. Expounding on this concept further, the presence of trace amounts of PPEI would be disadvantageous since it would translate to the limit of the effectiveness of the process. As succeeding sections indicate, pH also has an important influence on PPEI solubility so that by properly optimizing this parameter, better removal of heavy metals can be attained. The results nonetheless indicate that the combined coordinating and flocculating properties of the PPEI with Ca^{2+} can be exploited to effectively scavenge various types of extremely toxic metals from aqueous solutions.

Mechanism of PPEI–Heavy Metal Flocculation by Ca^{2+} Ions

Earlier, it was mentioned that in the case of Ca^{2+}-induced flocculation of PPEI, higher phosphonomethylation leads to the availability of more phosphonate groups to react with Ca^{2+} ions rendering the PPEI–Ca^{2+} complex more insoluble. In the presence of a competing transition metal ion, we would indicate further that complete phosphonomethylation of primary amines may play an important role with regard to the flocculation of the PPEI–heavy metal complex by Ca^{2+} ions. As previously mentioned, nitrogen ligands exhibit high specificity for transition metals. This may be attributed to their soft base and soft metal characters, respectively. Hence, the PPEI polymer may only interact with the Ca^{2+} ions through its phosphonate groups. This has been confirmed experimentally in this research by IR spectroscopy analysis. In the case of Cu^{2+} for instance, comparisons between the spectra of PPEI and PPEI–Ca^{2+}–Cu^{2+} complex show a distinct shift of the C—N vibration from wavenumber 1090 to 1055, respectively, to indicate the binding of Cu^{2+} ions with amine groups of PPEI (Fig. 2). Note that in the case of PPEI–Ca^{2+} complex, such shift in C—N vibration is not observed, indicating that Ca^{2+} does not interact with the nitrogen groups of PPEI. In addition, phosphonate functionalities may also participate with the corresponding nitrogen ligand during complexation ions for improved stability of heavy metal–PPEI complex.[13] With this arrangement, we postulate further that with regard to the Ca^{2+} binding site, only phosphonate groups of primary nitrogen ligands may be available (Fig. 3). Unless primary amines in PEI are completely phosphonomethylated, Ca^{2+} ions would have less available sites for interaction in the PPEI polymer in the presence of any transition metal ion for that matter. But even in this case, it has to compete with the heavy metal ions for ionic type interaction. We have some data (not shown) that indicate that of the total available phosphonate groups in PPEI, less than approximately 10% is actually bonded with Ca^{2+} in the presence of another heavy metal such as Cu^{2+}. However, more detailed studies to confirm the above assumptions regarding the mechanism of PPEI interaction with Ca^{2+} and transition metals in general are necessary.

Selectivity of PPEI–Ca^{2+} Flocculant

The metal preference of PPEI chelating flocculant is presented in Fig. 4. From the graph, the selectivity trend may be best established from the removal of individual metals at PPEI content less than the minimum requirement for complete removal of all metal ions. At the lowest amount of PPEI employed,

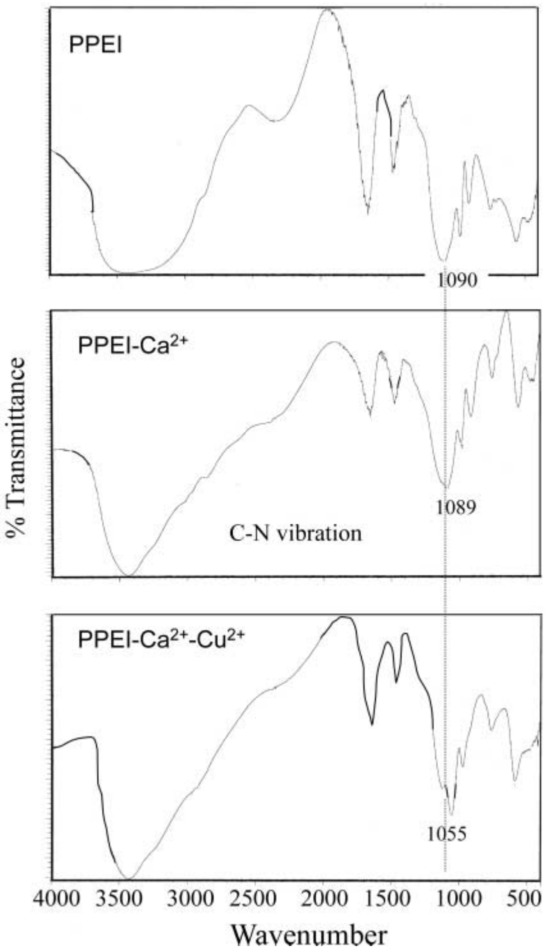

Figure 2. IR spectra of PPEI and PPEI–metal complexes.

greatest removal of Cu^{2+} and Pb^{2+} was observed. At this condition, minimal sequestration of Zn^{2+} concentration was detected while Ni^{2+} and Co^{2+} concentrations were barely reduced. These results indicate the higher preference of PPEI–Ca^{2+} flocculant system for Cu^{2+} and Pb^{2+} ions. Upon the addition of more PPEI, the removal of other metals becomes more apparent so that a general selectivity order of Cu^{2+}, Pb^{2+} $>$ Zn^{2+} $>$ Ni^{2+} $>$ Co^{2+} may be established. It was possible to reduce concentration of all metals to

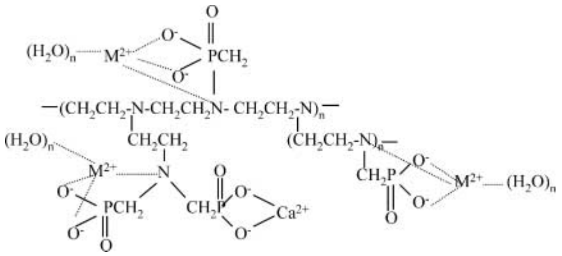

Figure 3. Mechanism for heavy metal removal by PPEI–Ca^{2+} flocculant system.

background conditions by corresponding increase in PPEI. This selectivity trend conforms with the complexity of the coordination geometry in relation to the cationic radius for each metal. The influence of the large radius of the Pb^{2+} ions (largest in the series) may contribute to its higher preference over the other metal ions. The observed pattern is consistent with the Irving–Williams order of metal preference by chelating agents, which is in the order: $Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$.[18]

Effect of pH on PPEI–Ca^{2+} Complex Solubility

In previous research, the ability of PPEI to sequester Cu^{2+} over a wide range of pH was mentioned.[9] Even at low pH condition, considerable Cu^{2+} removal has been displayed by the flocculant system. More significantly, better performance was observed at higher pH values. Among the reasons

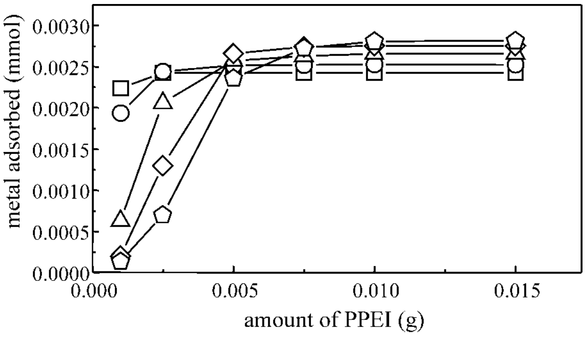

Figure 4. Selectivity of PPEI–Ca^{2+} flocculant system for different heavy metals. □ = Cu^{2+}, ○ = Pb^{2+}, △ = Zn^{2+}, ◇ = Ni^{2+}, and ⌂ = Co^{2+}.

found are the possible removal of heavy metal ions as metal hydroxide as well as the improved affinity between PPEI and Cu^{2+} ions due to lesser competition with hydronium ions. As discussed earlier, the presence of trace quantities of PPEI may also decrease the ability of the flocculant to completely remove the heavy metal ions since some heavy metal may be complexed with soluble fractions of PPEI. Now, we postulated that the solution pH may also influence the flocculation of PPEI to some extent. Hence, to evaluate any influence of pH on the complete removal of PPEI, PPEI flocculation by Ca^{2+} in the absence of heavy metal ions was conducted.

Table 3 shows the values of residual P at various pH conditions as a result of PPEI flocculation with Ca^{2+} ions. In the absence of any transition metal ion in the solution, it was observed that the residual PPEI decreases at increasing pH of the system. To explain this property, we cite the fact that at high pH, less hydronium ions would be available to compete not only with heavy metals but also with Ca^{2+} for phosphonate sites in the PPEI polymer. This would translate to improved affinity of PPEI with Ca^{2+} ions for better flocculation. Indeed, for heavy metal scavenging purposes, it would be appropriate to conduct flocculation experiments at higher pH conditions to maximize the precipitation of the PPEI polymer and minimize the concentration of soluble fractions that may bind with the heavy metals. To confirm this hypothesis, Ni^{2+} flocculation by a PPEI–Ca^{2+} system, for instance, showed better Ni^{2+} removal at higher pH values as a result of enhanced PPEI flocculation at these conditions (Table 4). Note that at increasing pH, the trend of decreasing Ni^{2+} concentration is in accordance with the decrease in residual PPEI as indicated P concentration of the solutions. It is also important to mention that any

Table 3. Residual P during PPEI flocculation at different pH levels.

pH (−)	Final P concentration (mg L^{-1})
5.7	0.245
7.2	0.054
8.3	0.059
9.3	0.031
10.2	0.033
11.1	0.030

The initial P concentration (corresponding to approximately 385 mg L^{-1} PPEI) was 57.96 mg L^{-1}.

Table 4. Effect of pH on the flocculation of PPEI–Ni^{2+}–Ca^{2+} complex.

pH (−)	Final Ni^{2+} concentration ($mg\,L^{-1}$)	Final P concentration ($mg\,L^{-1}$)
4.50	0.629	1.184
6.65	0.044	0.151
7.22	0.036	0.153
8.16	0.016	0.123
8.90	0.005	0.100
9.50	0.006	0.132
7.00 (no PPEI–Ca^{2+})	4.548	—
7.71 (no PPEI–Ca^{2+})	2.573	—
9.00 (no PPEI–Ca^{2+})	2.150	—

$[CaCl_2]/[PPEI] = 1.5$. (Ini [Ni]: 4.65 $mg\,L^{-1}$).

influence of pH on the flocculation of Ni^{2+} as metal hydroxide may be neglected since based on our experimental conditions, the residual Ni^{2+} concentrations at the corresponding pH values evaluated in the absence of PPEI–Ca^{2+} flocculant system showed much higher values.

Treatment of Actual Wastewater with PPEI–Ca^{2+} Flocculant

The application of PPEI–Ca^{2+} in the treatment actual waste stream from electroless nickel plating process was initially studied. As previously mentioned, this waste is generated during the rinsing of the plated materials just after they are removed from the plating liquor. Aside from Ni^{2+} and reducing agents (phosphorous ion), this wastewater also contains chelating agents such as EDTA. The presence of these additives contributes to the difficulty in removing Ni^{2+}. Based from actual experimental data, Ni^{2+} precipitation with $Ca(OH)_2$ was confirmed to be ineffective for this particular waste. Results showed that even at a high pH value of 13, residual Ni^{2+} content was barely changed from its initial concentration of 46.39 $mg\,L^{-1}$ (Table 5). This indicates the difficulty of reaction between hydroxide and Ni^{2+} ions since the latter is strongly bonded with chelating stabilizers such as EDTA and other organic acids in the system. As a common solution to this problem, disruption of Ni^{2+}–EDTA complex, as well as preliminary removal or chemical destruction of these chelating compounds, have been proposed.

As an alternative procedure, we tried to employ the chelating PPEI–Ca^{2+} flocculant system to counter the influence of chelating agents and, at the same

Table 5. Treatment of electroless Ni rinse solution by PPEI–Ca^{2+} flocculant system at $[CaCl_2]/[PPEI] = 1.5$. (Ini [Ni]:46.39 $mg\,L^{-1}$).

PPEI concentration ($mg\,L^{-1}$)	Final concentration ($mg\,L^{-1}$)
100	33.77
250	17.94
500	1.131
750	0.243
$Ca(OH)_2$ to pH 12	43.80
$Ca(OH)_2$ to pH 13	43.56

time, provide a process of separating the formed Ni^{2+}–PPEI complex. With this method, considerable reductions in Ni^{2+} concentration way below the limit of ordinary $Ca(OH)_2$ treatment was attained (see Table 5). Experimental data shows that Ni^{2+} concentration can be reduced by corresponding increases in PPEI concentration. By coordinate-type metal interaction, a much stronger affinity for Ni^{2+} was displayed by PPEI over other organic complexing agents in the solution, thus allowing for better Ni^{2+} removal over conventional alkaline treatment.

Another waste stream evaluated contains a mixture of different heavy metals, such as Pb^{2+}, Cu^{2+}, Ni^{2+}, and Fe^{2+} ions. Since the initial waste has a relatively acidic pH of 2.3, preadjustment of the pH to approximately pH 5.5 with NaOH was made. However, after pH readjustment, considerable flocculation, possibly of Fe^{2+}, was observed so that prior to treatment with PPEI–Ca^{2+} flocculant system, the actual concentration of the other heavy metals were slightly changed. Upon the addition of PPEI–Ca^{2+} flocculant, concentrations of the different metals were further reduced (Table 6). The preference of the flocculant system for Pb^{2+} and Cu^{2+}, as previously established, was also observed in this particular waste stream, though concentrations of these metals were many times lower than the Ni^{2+} ions.

These results confirm, to some extent, the ability of PPEI–Ca^{2+} in the treatment of actual waste streams. However, it must be emphasized that since the process was only applied to a limited type of solutions, positive results obtained from these systems may not indicate its general applicability for other wastewater types. Indeed, we have had some difficult experiences with other types of wastewaters. For example, in the case of Cu^{2+} plating wash solution, which contain stoichiometric amounts EDTA, it was found necessary to add Fe^{3+} to disrupt the strong bonding of the Cu^{2+}–EDTA complex prior to

Table 6. Treatment of a wastewater sample containing different types of heavy metals by the PPEI–Ca^{2+} flocculant system.

Concentration of PPEI ($mg\,L^{-1}$)	Equilibrium metal concentration ($mg\,L^{-1}$)			
	Cu^{2+}	Pb^{2+}	Ni^{2+}	Fe^{3+}
66.7	0.03	0.31	24.04	24.12
266.7	ND[a]	0.08	19.35	14.76
500.0	ND	0.02	13.45	6.08
1000.0	ND	ND	0.39	0.29

Initial metal concentrations after pH adjustment to pH 5.5 were approximately 0.4677, 0.427, 28.415, and 30.931 $mg\,L^{-1}$ for Pb^{2+}, Cu^{2+}, Ni^{2+}, and Fe^{3+}, respectively.

[a] Not detected.

flocculation with the PPEI–Ca^{2+}. For other systems, it is important to mention that specific pretreatment alternatives must be studied to capitalize on the chelating and flocculating property of the PPEI polymer.

Regeneration of Spent PPEI–Ca^{2+} Flocculant

One good property of the chelating PPEI polymer, which can be exploited for regeneration purposes, is its insolubility in acid conditions. By decreasing solution pH below pH 1.5, precipitation of a fully functionalized PPEI occurs. This process is reversible so that if pH is again increased, the polymer redissolves. Interestingly, this property simplifies the process of polymer regeneration by simple acid treatment. The metal is removed as the PPEI polymer reprecipitates at low pH conditions. As far as heavy metal removal by flocculation using polyelectrolytes is concerned, this is the first and only case that we can cite that is capable of such a simple regeneration method.

To evaluate whether the above property of PPEI can indeed be exploited for recycling purposes, the removal of heavy metal from the spent PPEI was conducted by its treatment with 2-M HCl acid. The regenerated polymer was reused and any significant change in its chelating ability was monitored. The results from two cycles of PPEI flocculation and regeneration using Cu^{2+} as the target metal ion were satisfactory. Initial flocculation experiments showed 98% Cu^{2+} removal ratio. From the first regeneration cycle, more than 98% Cu^{2+} recovery was attained with the use of a 2-M HCl stripping agent. Reuse of the recycled PPEI showed a slight reduction in metal sequestering ability during the second stage, so that only 94% metal removal was achieved. A decline in metal recovery to 89% during the second regeneration stage was also observed. At this point, possible polymer loss during the filtration stage might be attributed to such decline in polymer performance. Since a small amount of polymer was employed during the regeneration experiments, minor losses in PPEI may be greatly reflected in the performance evaluation. It must also be emphasized that the synthesis of PPEI polymer was conducted at a relatively higher HCl concentration of 6 M, therefore, any adverse effect of polymer decomposition at such highly acidic condition may be discounted. Hence, these results, particularly in the second stage, may not reflect the actual efficiency of the regeneration process. From the fact that during the first stage a satisfactory regeneration performance was demonstrated, acid treatment of the PPEI thus represents an effective approach for PPEI recycling.

CONCLUSION

A novel procedure for a rapid and simple method of employing a water-soluble, nitrogen-containing chelating polymer for metal separation by flocculation was introduced. Detailed analysis revealed considerable flocculation capacity of the chelating polymer for a wide range of transition metal ions. The ability of the process for metal scavenging was also confirmed. The heavy metal preference of the flocculant, which is in the order of Cu^{2+}, $Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ was found to be consistent with the Irving–Williams series. The process was found to be effective at a wide range of pH conditions. In relation to actual wastewater treatment, the PPEI–Ca^{2+} flocculant system also showed promising qualities for scavenging different metal, even in conditions where traditional methods of alkaline treatment may not be effective. Finally, the treatment of spent polymer with HCl was found to be an effective recycling process.

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