

# Heavy metal precipitation by polycation–polyanion complex of PEI and its phosphonomethylated derivative

Ronald R. Navarro<sup>a</sup>, Shinji Wada<sup>b</sup>, Kenji Tatsumi<sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering, College of Engineering and Agro-Industrial Technology, University of the Philippines, Los Banos College, Laguna 4031, Philippines

<sup>b</sup> Advanced Remediation Group, Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba-shi, Ibaraki 305-8569, Japan

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## Abstract

The removal of various heavy metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions by precipitation with polyelectrolyte complex of PPEI and PEI was conducted. Heavy metal binding with PPEI was initially allowed to occur and then upon equilibration, PEI was added to initiate precipitation of the polyelectrolyte complex together with the heavy metal ion. The PPEI–PEI system was found effective for heavy metal scavenging purposes even in the presence of high concentrations of non-transition metal ions like  $\text{Na}^+$ . Heavy metal concentration may be reduced beyond emission standards for industrial wastewaters. The PPEI–PEI polyelectrolyte complex was found to be more effective than traditional precipitation methods for the treatment of a representative electroless Ni plating waste solution.

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## 1. Introduction

In this research, the use of polyethyleneimine (PEI) and its phosphonomethylated derivative (PPEI) for heavy metal precipitation was evaluated. With their strong metal affinity, these chelating polymers have been employed in various unit operations for heavy metal removal from aqueous systems. Specifically, PEI has been incorporated in matrices for the synthesis of heavy metal adsorbents [1–3]. It has been utilized as metal complexing polymer for polyelectrolyte enhanced ultrafiltration (PEUF) process [4,5]. Recently, we have also reported a novel approach for utilizing PPEI for the precipitation of heavy metals. In this method  $\text{Ca}^{2+}$  ion are added to the system to induce the precipitation of the PPEI–heavy metal complex [6,7].

As a continuation of such work, this research hopes to contribute yet another approach in utilizing PEI for heavy

metal removal by precipitation. Specifically, precipitation-based heavy metal removal using PPEI in combination with PEI by polyelectrolyte complex (PEC) formation will be applied. In this method, interaction between oppositely charged functional groups in the two polyelectrolytes would cause them to be drawn together to form larger molecules and then consequently precipitate. In the process of polyelectrolyte interaction, heavy metals, which may serve as crosslinking agent for the two polymers, are trapped in the flocs and hence are also separated from the bulk solution. Since the added polymers are generally precipitated out together with the heavy metal ion, this process provides a non-contaminating approach to heavy metal removal. Past researches on this approach to heavy metal precipitation has been reported using anionic xanthate as well as carboxyl-containing polymers in combination with cationic polymers such as PEI [8–11]. This work is the first time that such process would be applied for PPEI as the anionic component of the polyelectrolyte complex. PPEI is actually a polyampholyte, which can contain both negatively charged phosphonate groups and positively

\* Corresponding author. Tel.: +81 298 61 8325; fax: +81 298 61 8325.  
E-mail address: ken.tatsumi@aist.go.jp (K. Tatsumi).

charged imino groups depending on solution pH. The use of both nitrogen-containing anionic and cationic polymer may contribute to the enhancement of heavy metal affinity and selectivity by virtue of its strict coordination type interaction for metal binding [12].

## 2. Materials and methods

### 2.1. Materials

Polyethyleneimine (PEI MW 70000) was purchased from Wako Pure Chemicals Co., Japan. Phosphonomethylated-polyethyleneimine was synthesized following our previous papers [6,7]. All reagents unless otherwise specified were purchased from Wako Pure Chemical Co., Japan.

### 2.2. Preliminary precipitation experiments with PPEI

Different amounts of 1% PPEI solution were added into a 25 ml of  $100 \text{ mg l}^{-1}$   $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Hg}^{2+}$  solutions. The metal removal at different concentrations of PPEI was obtained. At the end of each run, the precipitate was separated by a cellulose acetate filter paper and the equilibrium metal and phosphorus concentrations in the filtrate were assayed. Precipitation experiment at different initial pH conditions was also conducted using  $\text{Zn}^{2+}$  as a model system.

### 2.3. Heavy metal removal and scavenging with PPEI–PEI polyelectrolyte complex

Different amounts of 1% PPEI solution were added into a 25 ml of  $100 \text{ mg l}^{-1}$   $\text{Co}^{2+}$  and  $\text{Hg}^{2+}$  solutions. PEI solution (0.5%) was added in small amounts until flocs start to develop. For metal scavenging purposes, different amounts of 1% PPEI solution were added into a 100 ml of  $5 \text{ mg l}^{-1}$   $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  solutions and then PEI was added to initiate floc formation. The precipitate was separated and the equilibrium metal concentrations in the filtrate were assayed.

The effect of a non-transition metal ion on the performance of the process was also evaluated by conducting precipitation experiments with  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  solutions containing varying amounts of  $\text{Na}^+$  ions.

### 2.4. Treatment of actual waste streams

Different amounts of 1% PPEI solution were added into a 25 ml of actual heavy metal-containing wastewater from an electroless  $\text{Ni}^{2+}$  plating factory. PEI solution (0.5%) was added in small amounts until flocs start to develop. The precipitate was separated and the equilibrium metal concentrations in the filtrate were assayed. A check on the residual PPEI in the solution was also made by analyzing the TOC of the filtrate.

## 2.5. Analytical methods

Heavy metal and phosphorus concentrations were determined using a Seiko Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (Model 757 V). Mercury concentrations were measured by the use of Cold Vapor Atomic Absorption Spectrophotometer.

## 3. Results and discussion

### 3.1. Heavy metal precipitation by PPEI

Among the different anion functional groups, such as phosphates, acetates and sulfates, phosphate-containing compounds have been considered to exhibit a high flocculation tendency [13]. For example, 10–100 times smaller concentrations of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are necessary for the coagulation of phosphate colloids than for coagulation of carboxyl colloids of similar charge density. For the coagulation of sulfate colloids, 5–10 times larger concentrations of the same bivalent metals are needed than for coagulation of carboxyl colloids. Such a sequence finds its analogy in the relative solubilities of the metal phosphates, acetates and sulfates. Close to the structure phosphates are phosphonates, which are also known to form relatively insoluble metal salts. As an example, solubility product constant in the order of  $10^{-50}$  had been reported for calcium methylene phosphonate salts [14]. Preliminary analysis in this research has also confirmed the ability of phosphonate to precipitate out other toxic metals such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  in aqueous solutions. It was our initial hope that by its incorporation into a strong chelating polymer such as PEI, a polymer (PPEI), which is capable of removing heavy metals by chelation and subsequent precipitation, would be developed.

Indeed results from the precipitation of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  by PPEI have shown positive results. Upon the addition of PPEI in  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  solutions, formation of small and non-gelatinous flocs that readily settled was observed. Metal-complex formation has been especially visible with  $\text{Cu}^{2+}$  by the formation of deep-blue colored flocs. White flocs formed in  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ . After filtration, the metal concentration of the filtrate had been reduced. Up to a certain PPEI limit, a direct relationship existed between the amount of PPEI added and  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  removed. However, upon increasing the PPEI concentration beyond the certain limit for each heavy metal, a reversal in heavy metal concentrations to a higher value occurred (Fig. 1). Among the three heavy metals evaluated, a much lower residual concentration for  $\text{Pb}^{2+}$  of approximately  $1.5 \text{ mg l}^{-1}$  had been attained. In the case of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , higher values for minimum heavy metal concentration ( $>15 \text{ mg l}^{-1}$ ) was attained. For all the three metals evaluated, however, a narrow range for the amount of PPEI necessary for maximum metal removal was evident. With this result, it would be quite difficult to optimize PPEI amount in order to come up with much

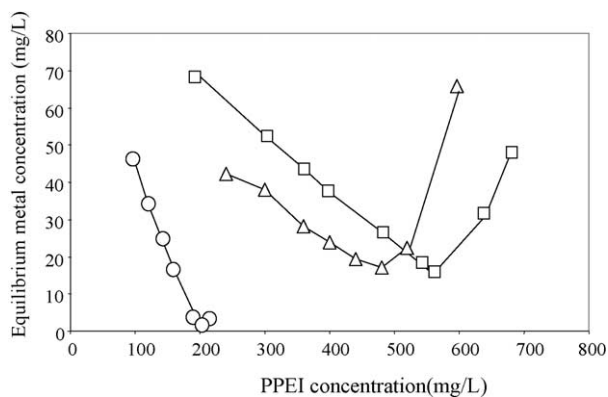


Fig. 1. Precipitation of heavy metals at different PPEI concentration: (○) Pb<sup>2+</sup>; (□) Zn<sup>2+</sup>; (△) Cu<sup>2+</sup>.

lower heavy metal concentrations. Furthermore, a check on the residual phosphorous in Zn<sup>2+</sup> system beyond the reversal point showed that a considerable amount PPEI now remained in the filtrate suggesting possible re-dissolution of the PPEI–heavy metal complex at these conditions (Fig. 2).

To describe the precipitation of these metals by PPEI, clearly three regions of polymer concentration may be visualized: a region at low concentration, an optimum region and a region of re-stabilization at high concentration, which results to the disappearance of flocs. At the third region the polymer–metal complex has become soluble so that flocs did not appear despite the formation of metal–polymer complex as qualitatively confirmed by color changes particularly in the Cu<sup>2+</sup> solution as well as by ultrafiltration runs.

In parallel experiments regarding the precipitation of Cu<sup>2+</sup> with phosphonate ions, however, further reduction of Cu<sup>2+</sup> beyond the observed limit (>15 mg l<sup>-1</sup>) upon the addition of more phosphonate ions was observed. For example, at about 85 mg l<sup>-1</sup> phosphonate (as sodium phosphonate) concentration the residual Cu<sup>2+</sup> content is approximately 6.9 mg l<sup>-1</sup>. However, at similar phosphonate concentration from PPEI, no significant precipitation occurred so that the Cu<sup>2+</sup> content of the final solution remained the same as the initial. This observation indicates that the solubility product principle, which governs the precipitation of phosphonate–metal com-

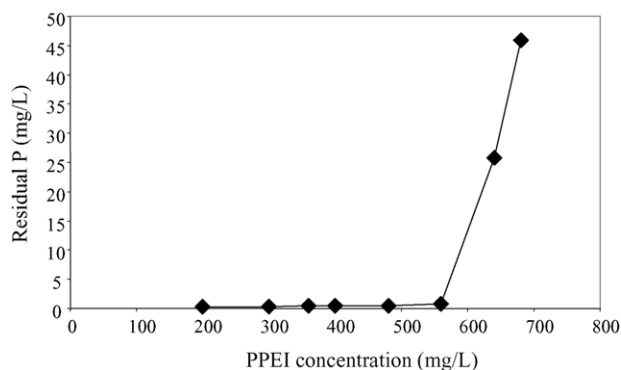


Fig. 2. Residual phosphorus of filtrate at different PPEI concentrations during Zn<sup>2+</sup> precipitation.

plex, does not apply exclusively in the precipitation of metal with phosphonate containing polymer. It has been suggested that for heavy metal–polyelectrolyte systems where the metal exhibits high solubility product constant (K<sub>sp</sub>) with an anionic polymer section, charge neutralization is responsible for the observed formation of flocs. Now in the case of PPEI–heavy metal complex, the reversal in metal sequestration at higher doses beyond the optimum precipitation condition seem to indicate also the significance of charge neutralization in the precipitation of the heavy metal–polymer complex. Re-dissolution of heavy metal–polymer complex at high polymer dose could be attributed to the net negative charge prevailing in the metal–polyelectrolyte complex due to unreacted phosphonate sections in PEI that hinders particle aggregation. This behavior has also been observed for other heavy metal–polyelectrolyte systems particularly in cadmium and starch xanthate interactions. Xanthate groups are known to form highly insoluble heavy metal complexes, yet at excessive amounts of starch xanthates, redissolution of starch xanthate–cadmium complexes occurs. The mechanism can be compared to a colloid–cationic polyelectrolyte system, where the positively charged metal species resemble the colloid and the PPEI as the polyelectrolyte [15].

Based on the practical point of view, the use of PPEI as a sole precipitant would seem inapplicable for metal scavenging as the concentration of toxic metals would be difficult to reduce beyond the strict background levels. This is further complicated by technical difficulties with regards to the control of optimum precipitation conditions. Furthermore, it has also been observed that other transition metals such as Hg<sup>2+</sup> and Co<sup>2+</sup> also does not readily form flocs with PPEI.

As the above observations clearly indicate, aside from solubility characteristics of introduced functional groups in the PEI polymer with heavy metals cations, the residual charge of the polymer after metal binding also influences the efficiency of metal precipitation. This residual charge may hinder particle aggregation. With regards to this parameter, the possible influence of the coordination requirement of the metals on charge neutralization along the polymer is also being considered. In order for the flocs with the polymer to develop, we believe it important that the nature of metal coordination would be such that charge neutralization along the polymer would be maintained. It would be very interesting to elucidate how this factor would actually contribute to the precipitation properties of the different heavy metals by PPEI. At this point, however, our primary concern has been to develop a practical approach for metal precipitation utilizing PPEI so that we do not intend to explore on basic mechanisms yet. In the succeeding discussions, an alternative method of capitalizing on the chelating and flocculating property of PPEI for heavy metal removal will be presented.

### 3.2. Heavy metal precipitation by PPEI–PEI complex

As discussed in the previous section, the presence of residual charge during heavy metal sequestration limits the ability

of the process to reduce metal concentrations beyond acceptable levels. To counter this problem, the addition of other cationic species, which does not displace the adsorbed metal species from the PPEI polymer in the solution, was considered. Following the principle of PEC formation for heavy metal precipitation, the use of additional cationic polymer, particularly PEI, was specifically evaluated in this work. Aside from charge neutralization mechanism, addition of such coordinating cationic polymer may have the additional function of enhancing floc characteristics through polymer bridging.

To evaluate the feasibility of such process, initial studies with  $\text{Hg}^{2+}$  and  $\text{Co}^{2+}$  removal were conducted. From preliminary precipitation experiments with PPEI, floc formation was not observed with  $\text{Hg}^{2+}$  while longer incubation time before flocs appear was observed in the case of  $\text{Co}^{2+}$ . In these systems, therefore, the immediate effect of the addition of PEI on the development of flocs would be seen. Results confirmed the possibility of employing PEI to quickly precipitate out the soluble PPEI– $\text{Hg}^{2+}$  and PPEI– $\text{Co}^{2+}$  from the solution. By careful addition of PEI to the PPEI–heavy metal complex, readily separable flocs can be formed and a dramatic reduction in the final concentration filtrate may be achieved. The amount of  $\text{Hg}^{2+}$  and  $\text{Co}^{2+}$  removed was dependent on the amount of incorporated PPEI. It must also be emphasized that the concentration ratio of  $[\text{PPEI}]/[\text{PEI}]$  also affects the extent of removal so that individual tests to determine the optimum amount of PEI at a given amount of PPEI was found important. Interestingly, the optimum  $[\text{PPEI}]/[\text{PEI}]$  concentration ratio was also found to vary depending on the heavy metal being removed. This is postulated to be a consequence of the different coordination requirements of each metal, which determines the resulting charge speciation of PPEI–heavy metal complex. In these runs involving simulated waste streams,  $[\text{PPEI}]/[\text{PEI}]$  concentration ratio ranging from 6–10 was observed. Based on the obtained data,  $\text{Hg}^{2+}$  concentrations had been reduced up to approximately  $1.5 \text{ mg l}^{-1}$  from an initial value of about 101 at  $200 \text{ mg l}^{-1}$  PPEI concentration. A capacity above  $490 \text{ mg Hg/g PPEI}$  had been obtained at this condition. In the case of  $\text{Co}^{2+}$ , concentration was reduced up to approximately  $3.2 \text{ mg l}^{-1}$  at about  $715 \text{ mg l}^{-1}$  PPEI concentration and this corresponds to a capacity of approximately  $133 \text{ mg Co}^{2+}/\text{g PPEI}$  (Fig. 3). For  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , further reductions in concentrations have been reached beyond the limits observed in Fig. 1. Specifically, concentrations lower than  $3 \text{ mg l}^{-1}$  and  $0.1 \text{ mg l}^{-1}$  were achieved above 550 and  $740 \text{ mg l}^{-1}$  PPEI for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively. In order to evaluate the merits of the above process for metal scavenging, studies on the precipitation of these heavy metals from solutions of low initial concentrations were also made.

The employment of the above process for advanced treatment of metal contaminated waste streams is among the main application being considered. As a polishing step, its ability to remove metal concentrations way below existing emission standards needs to be confirmed. For this evaluation, Japan's standards for industrial effluents for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ , which

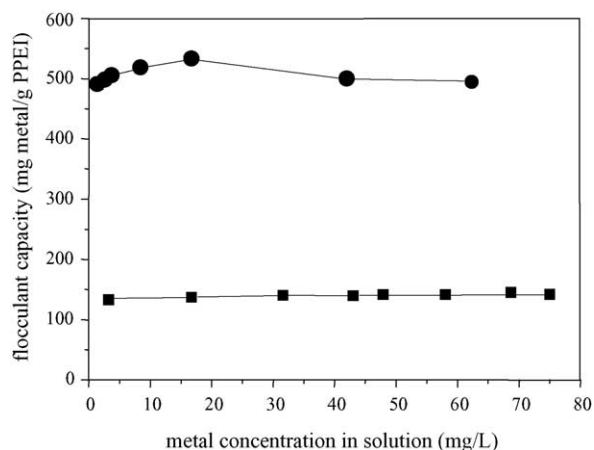


Fig. 3. Isotherms for the removal of  $\text{Hg}^{2+}$  and  $\text{Co}^{2+}$  by PPEI–PEI polyelectrolyte complex: (●)  $\text{Hg}^{2+}$ ; (■)  $\text{Co}^{2+}$ .

are  $0.1$  and  $0.005 \text{ mg l}^{-1}$ , respectively, were targeted. Traditional treatment processes involving alkaline precipitation though economical and simple in operation has numerous setbacks in terms of insufficiency of metal removal to acceptable standards particularly for wastewater-types containing other complexing species.

Results showed the ability of the process to reduce the concentrations of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  to values lower than their existing discharge limits. For example, from an initial concentration of approximately  $5 \text{ mg l}^{-1}$ , the concentrations of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  had been reduced to about  $0.002$  and  $0.025 \text{ mg l}^{-1}$ , respectively, based from the limit of our experimental conditions. Analysis of isotherms indicated a PPEI capacity of above  $412 \text{ mg Hg}^{2+}/\text{g PPEI}$  and  $350 \text{ mg Pb}^{2+}/\text{g PPEI}$  at these conditions (Fig. 4). In the case of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , concentrations have been reduced up to  $0.015$ ,  $0.009 \text{ mg l}^{-1}$  and below the detection limit, respectively, which are also way below the emission standards for these heavy metals. These results correspond to capacities above 150, 110 and  $100 \text{ mg/g PPEI}$  for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , respectively.

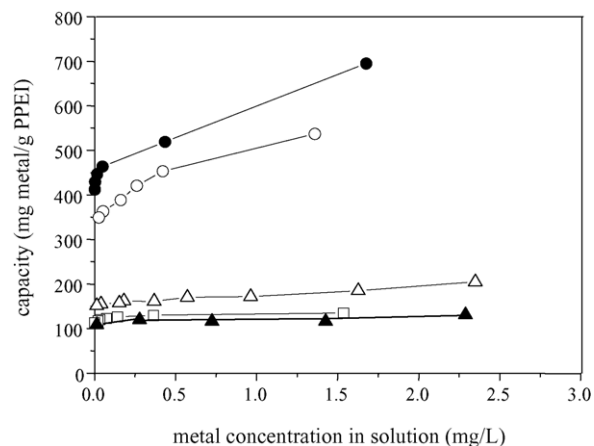


Fig. 4. Isotherms for heavy metal scavenging by PPEI–PEI polyelectrolyte complex: (○)  $\text{Pb}^{2+}$ ; (□)  $\text{Zn}^{2+}$ ; (△)  $\text{Cu}^{2+}$ ; (●)  $\text{Hg}^{2+}$ ; (▲)  $\text{Ni}^{2+}$ .

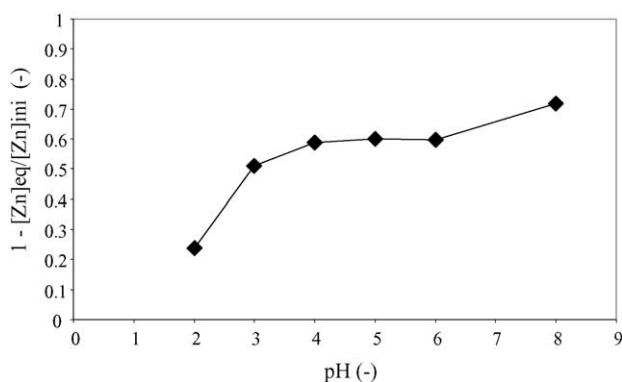
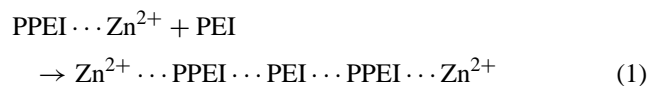


Fig. 5. Effect of pH on the removal of  $Zn^{2+}$  by PPEI-PEI polyelectrolyte complex.

### 3.3. Effect of pH and mechanism for heavy metal precipitation by PPEI-PEI polyelectrolyte complex

The influence of pH on metal precipitation using  $Zn^{2+}$  model metal ion was also studied. Qualitative evaluation of flocculation initially revealed the insignificant effect of pH on the quantity of flocs that were formed. However, floc characteristics were found to vary with pH. At very acidic pH conditions (e.g. pH 2–3), flocs were more compact and rather sticky. At higher pH, flocs were more dispersed. In terms of  $Zn^{2+}$  sequestration, considerable differences at various pH conditions were also observed. Expectedly, less removal was attained at lower pH due to extensive competition with hydronium ions for imino and phosphonate groups. At pH higher than neutral, a considerable enhancement in capacity was observed due to the formation of insoluble metal hydroxides in addition to precipitation with PPEI (Fig. 5).

The above observations indicate that at low pH, floc formation may not directly translate to  $Zn^{2+}$  sequestration since considerable generation of floc was still observed at low pH despite the low removal of  $Zn^{2+}$ . It is well known that PPEI polyampholyte precipitates at acidic pH. Hence, observed floc formation at this condition may not be directly attributed to PEC formation. Furthermore, PEC formation between PPEI and PEI would be minimal at low pH since most phosphonate groups are protonated (neutral charge), thus preventing its ionic interaction with protonated imino groups of PEI. Upon the increase of solution pH, PPEI-PEI complex starts to develop as phosphonate groups become deprotonated. Now, in the presence of a heavy metal like  $Zn^{2+}$  and depending on the relative amounts of PPEI and  $Zn^{2+}$  as well as solution pH, PPEI-PEI complexes may form through any of the following mechanisms:



In the above reactions, PEC complex between PPEI and PEI may be due to binding between (a) protonated imino groups of PEI with unprotonated phosphonate, (b) unprotonated imino groups of PEI with  $Zn^{2+}$  ions that are complexed with phosphonate groups of PPEI and (c) unprotonated imino groups of PEI with  $Zn^{2+}$  that are complexed with imino groups in PPEI. The imino groups in PEI may also coordinate with  $Zn^{2+}$  ions that are already attached with PPEI provided that coordination requirements of the heavy metal is not yet completely satisfied by the PPEI polymer.

### 3.4. Heavy metal selectivity of PPEI-PEI polyelectrolyte complex

As mentioned earlier, one of the main factors why we particularly selected nitrogen-type chelating compounds for heavy metal sequestration is their high preference for heavy metals over alkali and alkaline earth metals. This unique property is inherent to the strict coordination type of binding that forms between the electron pair of nitrogen donor and the heavy metal ion. In the field of wastewater treatment, this property is especially advantageous for the reason that non-transition metals as well as other cationic species that may be present in the solution would not compete with the target heavy metals for binding sites in the polymer. Previous researches have in even confirmed that even at low concentration of the heavy metals, the heavy metal preference was hardly influenced despite high concentration of the competing non-transition metal cations [8,12].

To confirm whether the PPEI-PEI polyelectrolyte complex also exhibits such property, evaluations on the preference of the synthesized adsorbent for heavy metals over alkaline and alkaline-earth metals were conducted. Evaluations on this particular characteristic were based on  $Cu^{2+}$  and  $Zn^{2+}$  precipitation in the presence of  $Na^+$  ions (as NaCl). As expected,  $Cu^{2+}$  removal by PPEI-PEI complex was not reduced even in the presence of high concentrations of  $Na^+$  ions. Equilibrium  $Cu^{2+}$  concentration at different  $Na^+$  content remained almost uniform in all the runs (Table 1). Though slight reductions in  $Cu^{2+}$  precipitation was observed at high  $Na^+$  concentrations evaluated, such reductions do not seem to correlate well with the considerable increases in  $Na^+$  concentrations. Furthermore, for some data, an enhancement of  $Cu^{2+}$  sequestration was even observed at higher  $Na^+$  content. We have some interesting data at higher initial heavy metal concentration that show that the addition of  $Na^+$  do really improved metal removal. Specifically in the case of  $Zn^{2+}$  precipitation by PPEI, relatively lower equilibrium  $Zn^{2+}$  concentration was observed at higher  $Na^+$  concentrations (Table 2). This property conforms well with our previous work on heavy metal sequestration by nitrogen-type chelating adsorbent where the addition of alkali and alkaline earth metal salts even resulted to better metal removal [12]. This seemingly anomalous property can well be explained in terms of the enhancing effect of anionic species ( $Cl^-$  in this case) that was also added to together with the  $Na^+$  ion. In any case, however, the above

Table 1  
Precipitation of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by PPEI–PEI complex in the presence of different amounts of  $\text{Na}^+$

Metal	[PPEI] ( $\text{mg l}^{-1}$ )	[PEI] ( $\text{mg l}^{-1}$ )	$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	Equilibrium [ $\text{Cu}^{2+}$ ] and [ $\text{Zn}^{2+}$ ] ( $\text{mg l}^{-1}$ )
$\text{Cu}^{2+}$	20	2.50	0	0.841
$\text{Cu}^{2+}$	20	2.50	325	0.735
$\text{Cu}^{2+}$	20	2.50	1300	0.765
$\text{Cu}^{2+}$	20	2.50	3250	0.949
$\text{Zn}^{2+}$	29	4.75	0	0.046
$\text{Zn}^{2+}$	29	4.75	325	0.022
$\text{Zn}^{2+}$	29	4.75	1300	0.071
$\text{Zn}^{2+}$	29	4.75	3250	0.136

Initial  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentration were approximately  $5 \text{ mg l}^{-1}$ .

Table 2  
Precipitation of  $\text{Zn}^{2+}$  by PPEI in the presence of different amounts of  $\text{Na}^+$

$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	Equilibrium $\text{Zn}^{2+}$ ( $\text{mg l}^{-1}$ )
0	35.44
325	33.28
1300	32.59
3250	31.11

Initial PPEI and  $\text{Zn}^{2+}$  concentration were 400 and  $97.89 \text{ mg l}^{-1}$ , respectively.

data do establish another useful property of the PPEI–PEI complex for heavy metal sequestration.

### 3.5. Treatment of actual wastewater with PPEI–PEI system

As a chelating flocculant system, the performance of the PPEI–PEI polyelectrolyte complex may be best evaluated by its application to wastewaters known to exhibit some treatment difficulty. In this case, an electroless  $\text{Ni}^{2+}$  plating rinse solution was considered. This wastewater contains  $\text{Ni}^{2+}$  ions that are strongly complexed with organic ligands. These compounds are generally added to the solution in order to stabilize  $\text{Ni}^{2+}$  concentration in the plating solution. Unfortunately during the treatment process, the presence of these compounds makes it rather difficult to completely remove  $\text{Ni}^{2+}$  ions by traditional hydroxide precipitation. As confirmed by preliminary precipitation runs, the adjustment of solution to pH 12 by the addition of  $\text{Ca}(\text{OH})_2$  still results

Table 3  
Treatment of electroless Ni-plating rinse solution with PPEI–PEI polyelectrolyte complex

[PPEI] ( $\text{mg l}^{-1}$ )	[PEI] ( $\text{mg l}^{-1}$ )	Final [ $\text{Ni}^{2+}$ ] ( $\text{mg l}^{-1}$ )	TOC ( $\text{mg l}^{-1}$ )	
			Initial	Final
195	39	15.82		
232	50	6.44		
269	63	3.90		
287	71	2.74		
323	84	1.09		
341	91	0.55		
377	94	0.30	403	409
$\text{Ca}(\text{OH})_2$ to pH 12		25.68		

Initial  $\text{Ni}^{2+}$  concentration was  $57.54 \text{ mg l}^{-1}$ .

to a relatively high residual  $\text{Ni}^{2+}$  content of approximately  $25.68 \text{ mg l}^{-1}$ . By employing the PPEI–PEI flocculant system, however,  $\text{Ni}^{2+}$  concentration can be easily reduced quite considerably (Table 3). Nickel concentration has been reduced up to  $0.30 \text{ mg l}^{-1}$ . Further reduction of  $\text{Ni}^{2+}$  is expected by corresponding increases in PPEI and PEI concentrations. The almost constant TOC before and after treatment at the highest amount of PPEI used, confirms the almost complete removal of added PPEI and PEI. These results do confirm the potential application of the PPEI–PEI system actual wastewater treatment.

## 4. Conclusions

In this work, the ability of PPEI for heavy metal precipitation was initially studied. Heavy metals such as  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were found to readily form precipitate with PPEI alone. Other heavy metals such as  $\text{Hg}^{2+}$  and  $\text{Co}^{2+}$  did not readily form flocs with PPEI. Furthermore, the existence of optimum PPEI dosage which when exceeded, results to the dissolution of the heavy metal–PPEI complex. This property indicates that heavy metal removal by PPEI may follow the behavior of colloid–polyelectrolyte system.

To counter the limitation of the above system for heavy metal scavenging, the use of polyelectrolyte complex of PPEI in combination with PEI was therefore evaluated. Results indicated that by this approach heavy metals may be precipitated, hence their concentrations reduced even further so that re-stabilization of flocs beyond a particular concentration of polymer was not observed. Concentrations of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  were reduced beyond their emission standards for industrial wastewaters. The high preference of the PEI–PPEI system for heavy metals over non-transition metal ions such as  $\text{Na}^+$  was also observed suggesting its ideal application to actual wastewaters that contain a wide variety of organic and inorganic ions that may compete with the process. Indeed, application of the process for the treatment of actual heavy metal containing wastewaters such as an electroless Ni plating rinse solution also yielded positive results. The concentration of  $\text{Ni}^{2+}$  was reduced beyond target standard limits despite the presence of complexing agents in the waste stream.

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