

**Interaction between branched polyethylenimine (PEI), sodium dodecyl sulfate (SDS) and cations during copper recovery from water using polymer-surfactant aggregates**

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**Abstract:** The application of polymer–surfactant aggregates (PSAs) to recover heavy metal ions from water is a novel treatment process for aqueous metallic effluents. To better employ this strategy, branched polyethylenimine (PEI), sodium dodecyl sulfate (SDS) and copper ions were selected to investigate their interaction in water and to improve the recyclable PSAs process for metal removal and recovery. Electrostatic association between PEI and SDS caused the formation of PSAs, and addition of SDS to a partially protonated PEI solution caused a pH increase; however, re-dispersal of PSAs could be achieved via an increase in pH. Precipitation of PSAs depended on pH, SDS/PEI concentration ratio and the total concentration of PEI; the optimal SDS/PEI ratio decreased as pH increases, and a higher concentration of PEI showed a greater potential to precipitate. PEI formed a strong complex with  $\text{Cu}^{2+}$ , with the most stable complex at a PEI/Cu chelation ratio of 4. Acidification decreased the chelation capacity of PEI to  $\text{Cu}^{2+}$ , because of the competition from protons for amino groups. Complexation with  $\text{Cu}^{2+}$  in turn reduced the proton buffer capacity of PEI in a non-acid solution. The removal of  $\text{Cu}^{2+}$  increased by increasing the total PEI concentration, or by increasing pH from 1 to above 4. Ionic strength and hardness had no marked effect on  $\text{Cu}^{2+}$  removal using the PSAs process. Following the initial interaction among PEI, SDS and  $\text{Cu}^{2+}$ , the  $\text{Cu}^{2+}$  could then be released from the PSAs by acidification and the reuse of the PSAs material could be achieved by alkalization. Copper removal and recovery were still up to 98% and 88% after three reuse cycles of the PSAs process, respectively.

**Keywords:** Branched polyethylenimine (PEI); surfactant; sodium dodecyl sulfate (SDS); metal removal and recovery; polymer-surfactant aggregates (PSAs).

## 1. Introduction

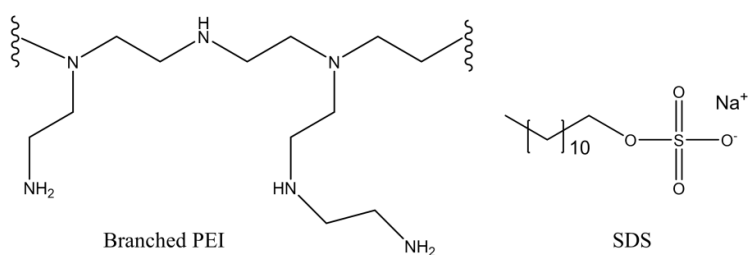
The presence of heavy metal contaminants in water has been a long-standing environmental issue that poses a severe threat to human health and a risk to ecosystems, even at very low concentrations [1]. At the same time, some heavy metals represent valuable resources and should be recovered, considering their economic value and scarcity [2, 3]. Treatment technologies including ion exchange [4], adsorption [5], coagulation [6], membrane separation [7], and electrochemical treatment [8] have been employed for the removal of heavy metals and their recovery for decades. Among these strategies, surfactant micelles or soluble polyelectrolyte assisted/enhanced membrane separation processes provide a high metal removal [9-13], but the efficiency is challenged by membrane cost, chemical dosage and reuse, and energy consumption. Based on studies of surfactant and polyelectrolyte systems, a novel heavy metal treatment process that applies polymer-surfactant complexation and aggregation has been developed in previous works [14, 15], and has been shown to offer a promising approach to remove and to recover valuable metal ions from water and wastewater. Its advantages include low operational cost, high treatment speed and operational stability. The process uses oppositely charged polymer (or polyelectrolyte) and surfactant to form aggregates referred to as polymer-surfactant aggregates (PSAs), due to electrostatic interaction. The PSAs bind with the heavy metal ions and subsequently form flocculates in the water due to charge neutralization and subsequent hydrophobic interactions; these flocculates can be separated via gravity sedimentation or coarse filtration. As a result of pH adjustment, the flocculated PSAs are made to release the associated metal ions and re-disperse in the solution, so that the PSAs can be recycled during the application process [15]. In previous studies, branched polyethylenimine (PEI) and sodium dodecyl sulphate (SDS) were used to form PSAs to remove and recover metals from metallic effluents. Shen *et al.* [14, 16] reported that up to 99% of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cr}^{3+}$  ions were removed at ppm contamination levels under optimum dosages of PSAs in the presence of inorganic and organic contaminants. Furthermore, 97% of  $\text{Cd}^{2+}$  was removed at ppb contamination

levels. Previous research results have also shown that the PSAs process is capable of both removing and recovering 90% of the metallic cations into a 20–50 times more concentrated solution [15]. PSAs formed by an anionic polymer and a cationic surfactant have also been developed for the removal and recovery of metallic anions. Shen *et al.* [17] reported that 99% of 0.1 mM  $\text{Fe}(\text{CN})_6^{3-}$  and 80% of 0.2 mM  $\text{CrO}_4^{2-}$  were removed using PSAs consist of poly(acrylic acid) (PAA) and myristyltrimethylammonium bromide (MTAB). In addition, using a cationic surfactant with a longer tail group facilitates the formation of PSAs and the removal of metallic anions [18]. Research results on the overall recycle process have shown that up to 94% of both  $\text{CrO}_4^{2-}$  and the PAA-MTAB can be recovered and reused, respectively, via addition of NaOH and  $\text{H}_2\text{SO}_4$  at the optimum dosage [19].

To better apply the PSAs process for metal removal and recovery from water, the interaction among polymer, surfactant and metal needs to be more deeply investigated and more clearly understood. The interactions between polyelectrolyte and surfactant [20-22], between polyelectrolyte and ions [11, 23], and between surfactant and ions [24-27], have been studied extensively in various fields, driven by both fundamental interest and their applications. However, studies focusing on the interaction among all three of them, a so-called ‘three-body problem’, and on the mechanism of the recyclable PSAs process based on their interactions are still sparse. The present study aims to address this gap in understanding.

In previous studies, PEI has been used as the cationic polymer to form PSAs [14-16]. As is known, PEI, with repeated amino groups, presents as a positively charged polyelectrolyte in an acidic environment, while it presents as a neutral polyelectrolyte at high pH; consequently, its interactions with surfactants or with metals can vary depending on the pH. Based on this property, the recyclability of the PSAs process can be achieved. Branched PEI is used widely as an ingredient in pharmaceutical formulations, food products, industrial detergents, nanoparticle synthesis and water treatment chemicals [28, 29], and **Figure 1** shows its structure. Unlike with linear PEI, branched PEI contains primary, secondary, and tertiary amino groups, and the amount of primary amino groups equals that of

the tertiary ones. The interaction between branched PEI and oppositely charged surfactants is distinct from that of linear ones with surfactants [28, 30]. For example, the sodium dodecyl sulphate (SDS, shown in **Figure 1**) binding structure with linear PEI depends on the pH value, while that with branched PEI is independent of pH in the range from 3 to 10 [28]; adsorption of SDS is more pronounced for branched PEI than for linear PEI; and branched PEI displays more complex layered surface structures [22]. Meanwhile, considering the cost of chemicals, branched PEI has an economic advantage over linear PEI in industrial applications.



**Figure 1.** Structure of branched PEI and SDS

In this study, a branched PEI and an anionic surfactant, SDS, were used to form PSAs for metal removal and recovery. As a petrochemical product, while some concern may pay to SDS, SDS was chosen because of its commercial availability, high stability, and low cost. The copper ion ( $\text{Cu}^{2+}$ ) was selected as an example metal to investigate the interaction among branched PEI, SDS, and metal, in order to improve and optimize the PSAs metal treatment process. The specific objectives of this study include: (1) to investigate the bonding and aggregation behavior among PEI, SDS and  $\text{Cu}^{2+}$  via titration, conductivity analysis, and turbidity measurement; (2) to understand the metal removal process and recovery strategy to operate at high efficacy, as well as to recycle PEI and SDS during the PSAs process.

## 2. Materials and methods

### 2.1 Materials

Branched poly(ethyleneimine) (PEI) solution from Sigma Aldrich, with a manufacturer-supplied average molecular weight of  $\sim 750,000$  (as 50 wt.% in  $\text{H}_2\text{O}$ ), was used directly without purification to

prepare PEI solutions for the PSAs process by dilution. Sodium dodecyl sulphate (SDS,  $\geq 98.5\%$ ), purchased from Sigma-Aldrich, was used as surfactant.  $\text{Cu}^{2+}$  solutions were prepared from copper (II) sulfate pentahydrate (ACS reagent,  $\geq 98.0\%$ ). Branched PEI, SDS and  $\text{CuSO}_4$  were prepared as 2000 mg/L, 50 mM and 10 mM stock solutions in volumetric flasks, respectively, for use in the subsequent experiments. ACS reagent grade calcium chloride dihydrate and magnesium chloride hexahydrate from Sigma-Aldrich and sodium chloride (99%) from Fluorochem were used to prepare sample solutions with different chemical compositions. Concentrated sulphuric acid (95%), hydrochloric acid (37%) and 99.5% purity sodium hydroxide pellets were used to make acid or base solutions for pH adjustment and PSAs recycle. Deionized water (18.2 M $\Omega$ /cm, Labpro water) was used in all experiments.

## 2.2 Titration of PEI solution

The protonation of branched PEI was determined by pH titration. Aqueous solutions of PEI (20 mL) with varying initial moiety concentrations ranging from 1 mM to 25 mM (the effective PEI molar concentration refers here to the concentration of individual, repeated PEI moieties and was calculated based on a molecular weight for the moiety of 43 g/mol) were prepared by diluting concentrated PEI solution, and were titrated with HCl at room temperature. Solution pH was measured using a pH meter (Orion star A211, Thermo Scientific) with a refillable Ag/AgCl pH electrode. The volume of HCl solution added to the PEI solution and the corresponding pH value were recorded, and the fractional protonation of branched PEI was calculated using **eq 1** [31].

$$\alpha = \frac{[\text{PEI}-\text{H}^+]}{[\text{PEI}]_{\text{total}}} = \frac{V' C' / (V + V') - 10^{-\text{pH}}}{C V / (V + V')} \quad (1)$$

where:  $[\text{PEI}-\text{H}^+]$  and  $[\text{PEI}]_{\text{total}}$  refer to the concentration of protonated PEI and the total concentration of PEI, respectively, both expressed in mol/L;  $V'$  and  $C'$  refer to the volume and concentration of HCl titrated, with units of L and mol/L, respectively;  $V$  and  $C$  represent the initial volume and moiety concentration of PEI solution, with units of L and mol/L, respectively; pH refers to the final pH value after each titration with HCl.

### 2.3 Interaction among PEI, SDS and copper ions

PEI solutions with varying initial pH values, adjusted by adding HCl, were prepared in a tube to complex with SDS at different molar ratios. After the addition of SDS (total solution volume of 10 mL) and mixing, the final pH of the PEI-SDS solution was recorded and plotted against the SDS/PEI molar ratio. The PEI-SDS solutions were shaken slightly and left to stand overnight, and then a turbidimeter (Lovibond, No. 194200) was used to determine the turbidity of supernatant after filtration using coarse filter papers (Fisherbrand, pore size of 15  $\mu\text{m}$ ). This latter was done in order to find the optimal SDS/PEI ratio, which is defined here as that yielding the lowest turbidity (as close as possible to zero), such that most or all of the polymer and surfactant material was precipitated.

Conductivities of PEI/ $\text{Cu}^{2+}$  solutions with different molar ratios were determined by a conductivity test meter (Fisher Scientific, accument AE95008608), and demonstrated while maintaining a constant concentration of PEI or  $\text{Cu}^{2+}$ , respectively. For constant PEI concentration experiments, the pH was also recorded after addition of  $\text{Cu}^{2+}$  solutions to show the pH change.

### 2.4 PSAs process for $\text{Cu}^{2+}$ removal and recovery, and recycle of PSAs

**Figure 2** demonstrates the process of employing branched PEI/SDS aggregates to remove and recover copper from aqueous solution, and reuse of the PEI/SDS materials. In this case, 50 mL of 0.5 mM  $\text{CuSO}_4$  solution in a beaker is shown as an example. A certain concentration of metal ions was prepared first in the beaker, followed by addition of branched PEI solution. After mixing, the surfactant solution was added at the optimum ratio. The pH of the solution was adjusted by adding small amounts of HCl and NaOH solutions, and stirred to mix the PEI, SDS and  $\text{Cu}^{2+}$  completely in a short time (less than 1 min), until aggregates or precipitates formed. Following stirring, the sample was allowed to sit for 10 min to settle the aggregates. Finally, the sample was filtered using filter paper to separate permeate and the PSAs solid. A sample of permeate was taken to analyze the residual  $\text{Cu}^{2+}$  concentration in the aqueous phase after treatment. 5 mL of  $\text{H}_2\text{SO}_4$  (0.1 M) was used to rinse the PEI/SDS/Cu precipitate solid and

release  $\text{Cu}^{2+}$  from the aggregates into the  $\text{H}_2\text{SO}_4$  solution as a concentrated copper sulphate solution.

After the release of  $\text{Cu}^{2+}$ , white PEI/SDS precipitates were dissolved using 2.5 mL NaOH (0.2 M) to reuse in a new treatment cycle.

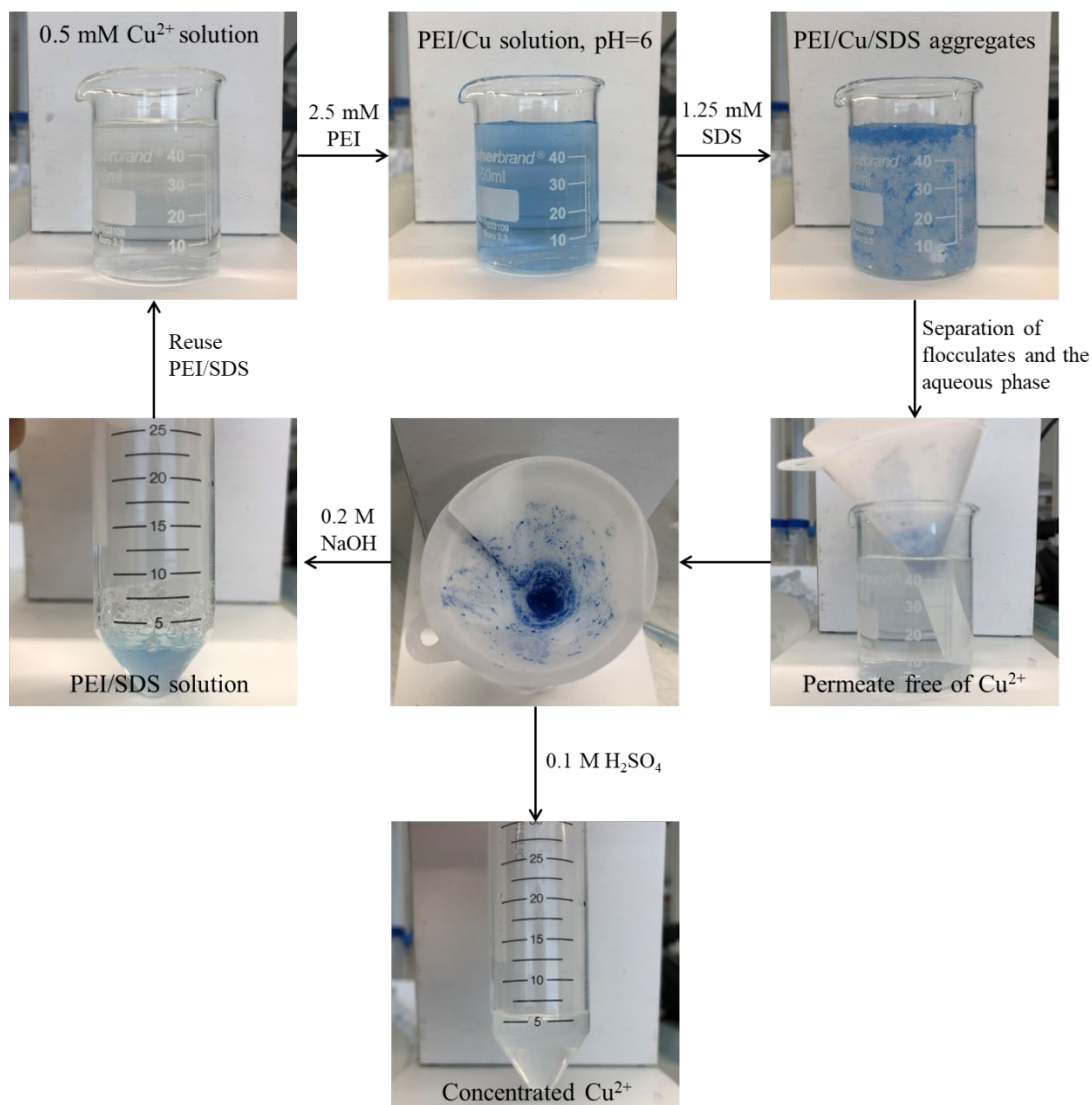
During the treatment process, fractional copper removal ( $\eta$ ) from water using the PSAs and the fractional recovery of copper ( $R$ ) from the PSAs solid were defined by eqs 2 and 3, respectively:

$$\eta = 1 - \frac{[\text{Cu}]_r}{[\text{Cu}]_{\text{total}}} \quad (2)$$

$$R = \frac{[\text{Cu}]_c V_c}{[\text{Cu}]_{\text{total}} V_0} \quad (3)$$

where:  $[\text{Cu}]_r$  refers to the residual copper in the water, i.e.  $\text{Cu}^{2+}$  not removed by the PSAs process and residing in the retentate; and  $[\text{Cu}]_{\text{total}}$  is the total feed  $\text{Cu}^{2+}$  concentration;  $[\text{Cu}]_c$  presents the concentration of  $\text{Cu}^{2+}$  in the leached solution and released from the PSAs solid using strong acid.

Copper concentrations were all expressed in mg/L.  $V_c$  is the volume of concentrated acid and  $\text{Cu}^{2+}$  salt (copper sulphate) solution, L;  $V_0$  refers to the initial effluent feed volume, L. The concentrations of aqueous copper were determined using a Thermo Scientific Orion AC2029 Colorimeter Reagent for Copper with a concentration range of 0.05 mg/L to 5.0 mg/L, based on the colorimetric chelation reaction between  $\text{Cu}^{2+}$  and biquinoline. A UV-Vis spectrophotometer (Shimadzu UV-1800) was used to analyze the absorbance of water samples with the colorimeter reagent at a wavelength of 550 nm.

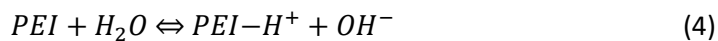


**Figure 2.** Process of copper removal/recovery and recycle of PEI/SDS materials

### 3 Results and discussion

#### 3.1 Protonation of branched PEI

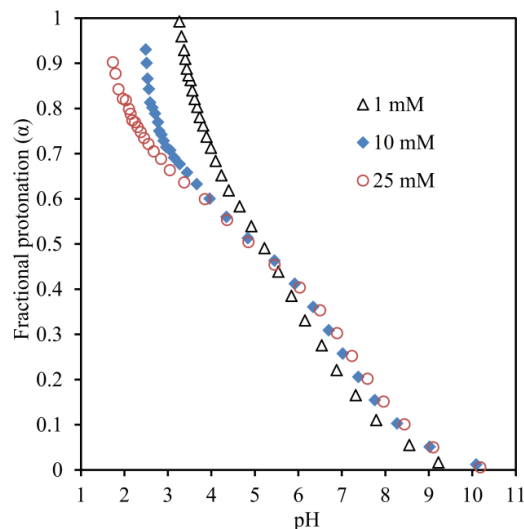
Because of the amino groups present on the PEI backbone, PEI has a proton-buffering capacity and its dissociation can be expressed simply via **eq 4** or **5**. **Figure 3** shows the protonation fraction ( $\alpha$ ) of PEI with varying initial concentrations, based on titration experiments and calculated using **eq 1**.





As can be seen from **Figure 3**, the protonation of branched PEI is a function of both amino group concentration and pH. The pH value corresponding to 50% protonation of PEI was around 5 when the amino group concentrations ranged from 1 to 25 mM. PEI with a lower moiety concentration was fully protonated at a higher pH, e.g. 1 mM PEI was fully protonated at a pH of ~3.3, while ~35% of the amino groups for 10 mM PEI were not protonated at the same pH. Suh *et al.* [32] reported a similar protonation of 10 mM PEI when pH ranged from 5 to 3 (48-82%), and they similarly indicated that the fraction of unprotonated amines of branched PEI at low pH was higher when PEI with a higher moiety concentration was presented in the polymer solution. Therefore, it is harder to protonate PEI when its moiety concentration is higher, possibly because of the greater electrostatic repulsion arising between neighbouring, already protonated amino groups and incoming H<sup>+</sup>. The dissociation of linear ionic polymer with single repeated groups can usually be described using the modified Henderson–Hasselbalch equation ( $pK_a = pH + m \log(\frac{\alpha}{1-\alpha})$ ) [33], but the equation cannot be used for the description of branched PEI, because the ionization constant of different types of amino groups (primary, secondary and tertiary amines) varies [32]. This is implied by multiple obvious changes of the titration curve slope (for 10 and 25 mM) [34], so there is no uniform  $pK_a$  for branched PEI. Previous studies also reported the  $pK_a$  value of branched PEI decreased for decreasing pH values, and for increase of protonation [30, 35].

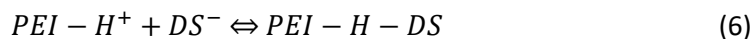
Based on the current titration results, increasing PEI concentration at low pH provides more available unprotonated amino groups to associate with metallic cations, presenting a possibility to remove metals from acidic solutions.



**Figure 3.** The plot of fractional protonation of branched PEI of varying moiety concentrations against pH values

### 3.2 Interaction between branched PEI and SDS

In **Figure 4**, the pH change is plotted against the SDS concentration added to branched PEI solutions, at varying initial pH values. As can be seen, the addition of SDS led to an increase in pH of PEI solution when PEI had partially unprotonated moieties for both 1 (pH 5-9) and 10 mM PEI (pH 3.5-9). The pH increase was caused by association between anionic surfactant molecules (dodecyl sulfate anion,  $DS^-$ ) and  $PEI-H^+$  due to electrostatic interactions (**eq 6**), thus shifting the equilibrium reaction of **eq 4** to the right hand side due to the consumption of charged amino groups (according to Le Chatelier's principle), and generating more  $OH^-$  until a new equilibrium is attained. The pH value eventually became independent of the SDS concentration after a sharp increase. Mészáros *et al.* [30] reported a similar observation, where  $DS^-$  was bound in monomer form to the protonated amine groups and caused an increase of the pH value.



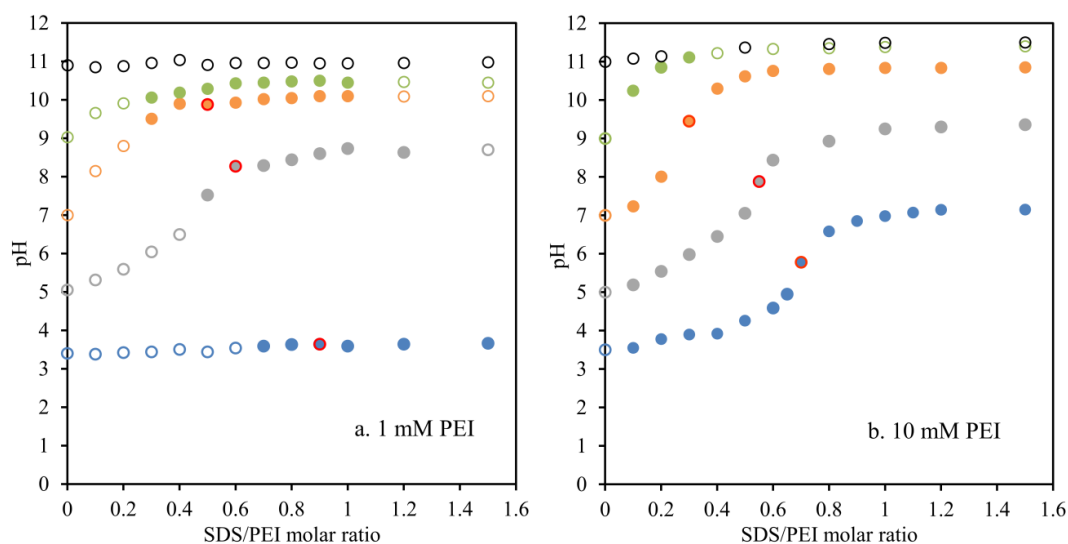
However, when PEI was close to full protonation (e.g., ~pH 3.4 of 1 mM PEI) or full un-protonation (e.g., ~pH 11), a strong buffering effect was evident and the pH remained stable with the addition of SDS.

For example, 1 mM branched PEI was almost fully associated with  $H^+$  at pH 3.4, and there was no marked pH change after adding SDS ranging from 0.1 to 1.5 mM (**Figure 4a**). On the other hand, the pH increased rapidly when adding SDS into 10 mM branched PEI at pH 3.5 at molar ratios between 0.6 and 0.8 (**Figure 4b**), because only around 65% of the amino groups were protonated at pH 3.5. When the solution pH was adjusted to 11, where both 1 mM and 10 mM branched PEI polymers were fully unprotonated, there was no electrostatic association between PEI and SDS, so that the pH remained at around 11. This lack of association at high pH provides a good opportunity to recover the SDS from the PEI/SDS aggregates via the addition of alkaline solution.

Comparing **Figures 4a** and **4b**, it can be seen that precipitation of the PSAs depends on both the SDS/PEI concentration ratio and the total concentration of PEI. Precipitation (visible turbidity) occurred at an SDS/PEI ratio of 0.7 for 1 mM PEI at  $\sim$ pH 3.5, but it already started to precipitate at a ratio of 0.1 for 10 mM PEI, possibly because higher polymer and surfactant concentrations have a higher tendency to aggregate in a more crowded molecular environment (by exceeding their mutual solubility limit) and form larger flocculates, thus destabilizing the system. Chen *et al.*[23] have observed larger particle sizes and better sedimentation at higher polymer/cation concentrations than at lower ones. In **Figure 4a**, the PEI solution is visually clear at low SDS concentrations, and the solution then becomes cloudy and precipitates eventually form as the SDS concentration increases, but an excess concentration of SDS renders the solution transparent again. The possible explanation for this is as follows. Low concentrations of SDS associate with PEI, but the remaining positive charges of the PEI at the new equilibrium keep the system stable; as SDS concentration increases, the protonation of the PEI/SDS complexes decreases and they do not have enough mutual repulsion for each other to remain dispersed, and they form precipitates; however, excess SDS monomers associate with PEI/SDS aggregates via intermolecular forces due to their hydrophobic tail groups, and contribute a negative charge to the PEI/SDS complex, so that the PEI/SDS aggregates are dispersed again. This result also indicates that the

electrostatic forces between branched PEI-H<sup>+</sup> and DS<sup>-</sup> are stronger than the hydrophobic interactions between tail group and the PEI/SDS complex. Wang *et al.* [28] have reported findings based on conductivity and turbidity measurements, which are largely consistent with this study. Sakar-Deliormanli [36] reported similar observations for 6 mM SDS and PEI with varying concentrations. Mészáros *et al.* [30] suggested a similar explanation in that the DS<sup>-</sup> ions neutralized the excess positive charge of the PEI and increased the hydrophobicity of the PEI/SDS complex, collapsing the complex eventually into precipitates. Further increase of SDS concentration resulted in the hydrophobic adsorption of SDS onto the collapsed PEI/SDS complexes, reversing the charge. Other previous studies [36, 37] have also indicated that the stable dispersed polymer/surfactant aggregates could be attributed to a high net charge, while flocculation or sedimentation was ascribed to their low charge.

The solid circles with a red circumference in **Figure 4** demonstrate the best precipitate points, meaning that the turbidity of the PEI/SDS permeate following coarse filtration is close to zero. The best SDS/PEI molar ratio increased as the initial solution pH value decreased. Because a lower pH causes a higher protonation fraction, more SDS is needed to neutralize the charge of PEI and cause precipitation of the PEI-H-DS complexes. For example, when the concentration of PEI was 10 mM, 0.7 mM SDS was needed to cause precipitation at pH 6, while the required SDS concentration decreased to 0.3 mM when the pH went up to 9.5. Therefore, the optimum precipitation ratio depends on the pH value, and -for the optimal application of PSAs to metal ion removal, the required ratio should be determined - according to the conditions (such as pH) of the effluent solutions.

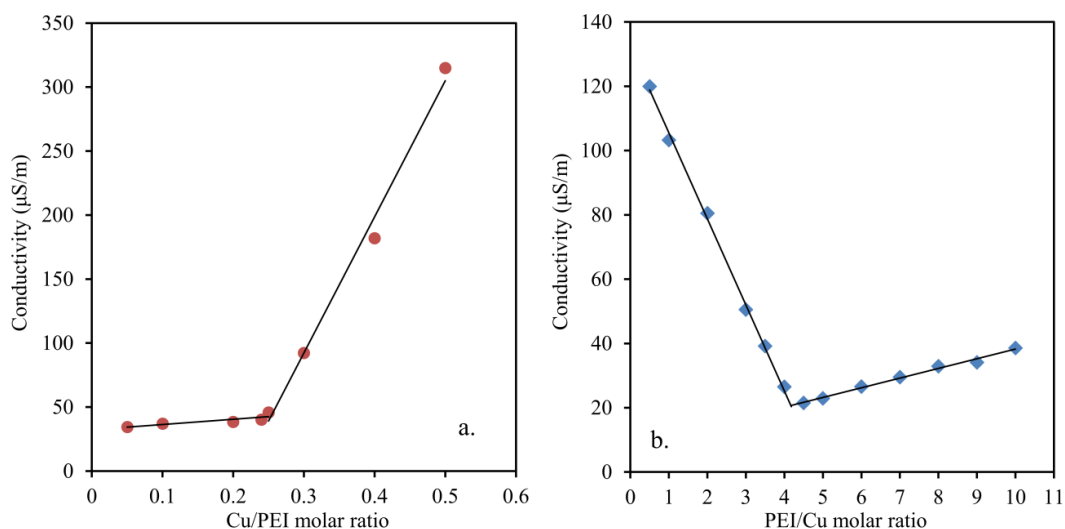
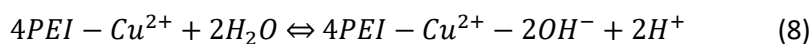


**Figure 4.** pH change of branched PEI solutions upon addition of SDS (solid circles indicate visible cloudiness or precipitates; open circles indicate visually clear solutions with turbidity < 30 NTU): (a) 1 mM PEI; (b) 10 mM PEI.

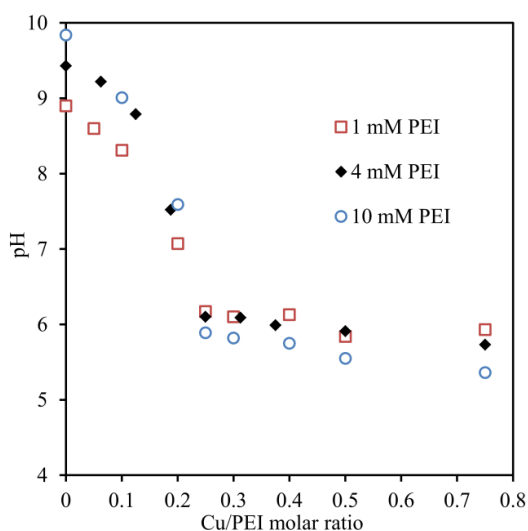
### 3.3 Copper complex with branched PEI

**Figure 5** shows the conductivity change of PEI/ $\text{Cu}^{2+}$  solutions at different molar ratios, demonstrated by maintaining PEI or Cu concentration constant, respectively, at a pH above 4. Because of the amino groups, PEI is able to undergo chelation with metal ions. Once metal ions chelate with PEI, they lose the ability of to move freely in the solution, which is indicated by changes in the conductivity. In **Figure 5a**, with increasing  $\text{Cu}^{2+}$  concentration in 10 mM PEI solution until all of the chelation sites were occupied, free  $\text{Cu}^{2+}$  increased the conductivity of the solution markedly; on the other hand, in **Figure 5b**, increasing PEI concentration decreased the conductivity of 1 mM  $\text{CuSO}_4$  solution until all of the  $\text{Cu}^{2+}$  was bound. In both cases, the point where the curve slope changes can be used to determine the chelation ratio/number between PEI amino groups and Cu, as 0.25 for Cu/PEI ratio or 4 as PEI/Cu number. Therefore, four amino groups of PEI undergo the most stable chelation with one Cu ion, which can be expressed by **eq 7**; this ratio is also the same for linear PEI chelating with Cu, as observed by analyzing visible light absorbance of PEI/Cu solutions at 630 nm and pH 5.3 [38]. Because of the consumption of

unprotonated amino groups by  $\text{Cu}^{2+}$ , the reaction shown in **eq 4** moves to the left hand side, decreasing the pH (as shown in **Figure 6**), and because of the positive charges, the PEI/Cu complex has the potential to attract anions (e.g.,  $\text{OH}^-$ , shown in **eq 8**).

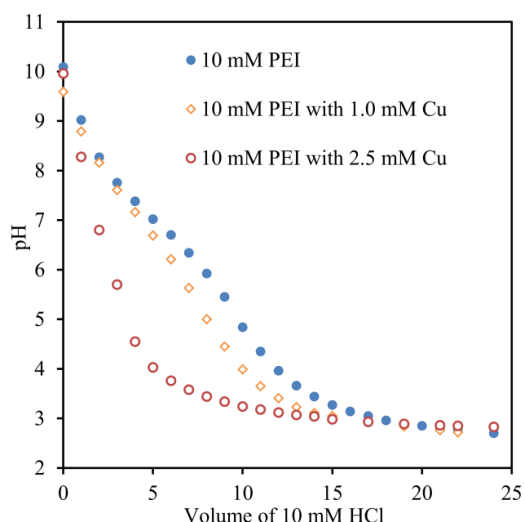


**Figure 5.** Conductivity of Cu/PEI solutions at various molar ratios: (a) PEI concentration constant at 10 mM; (b)  $\text{Cu}^{2+}$  concentration constant at 1 mM.



**Figure 6.** pH change after addition of  $\text{CuSO}_4$  into PEI solutions

**Figure 7** shows the plots of pH change against volume of HCl titrated into PEI and PEI/Cu solutions. As shown in the figure, when 10 mM PEI complexed with 1 mM  $\text{Cu}^{2+}$ , the PEI/Cu solution still showed a proton buffering capacity, but lower than that of the pure PEI solution, because the PEI still had partially unprotonated amino groups. However, when PEI was fully chelated with  $\text{Cu}^{2+}$  (2.5 mM), the pH decreased quickly after titration with HCl, indicating complexation with  $\text{Cu}^{2+}$  decreases the proton buffering capacity of PEI, and  $\text{Cu}^{2+}$  has a higher affinity for the PEI than  $\text{H}^+$  in a non-acid solution; yet, when the pH went down to below 4 in this case, the proton buffering capacity of PEI was restored, for which  $\text{H}^+$  now exchanged with the  $\text{Cu}^{2+}$  chelated on the PEI. Therefore, acidification is a possible way to release bound metal ions from PEI.

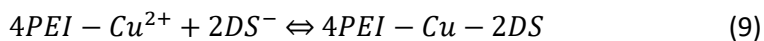


**Figure 7.** Titration of PEI and PEI/Cu complex solutions using 10 mM HCl

### 3.4 Interaction between PEI/ $\text{Cu}^{2+}$ complex and surfactant

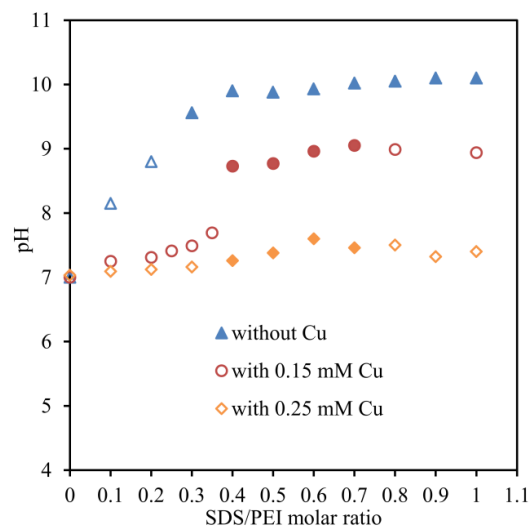
**Figure 8** demonstrates the pH changes of PEI or PEI/Cu solutions after the addition of SDS. Without complexation with  $\text{Cu}^{2+}$ , the pH increased markedly after addition of SDS, which has been explained previously in **section 3.2**. However, the pH remains almost constant when the PEI is fully complexed with  $\text{Cu}^{2+}$ , and the slight increase of pH is possibly due to  $\text{DS}^-$  exchange with  $\text{OH}^-$ , which is absorbed onto the PEI/ $\text{Cu}^{2+}$  complex. When PEI is partially complexed with  $\text{Cu}^{2+}$ , as shown for 1 mM PEI with 0.15 mM

$\text{Cu}^{2+}$  (i.e. 0.6 mM amino groups are complexed with  $\text{Cu}^{2+}$  and 0.4 mM amino groups are free), the pH increases slowly before an SDS/PEI ratio of 0.35, and jumps to ~8.7 when the ratio reaches 0.4, because  $\text{DS}^-$  associates with  $4\text{PEI}-\text{Cu}^{2+}$  (**eq 9**) first before being attracted to  $\text{PEI}-\text{H}^+$  (**eq 6**). The solid circles indicate solution turbidity or precipitation, and it can be deduced that complexation with copper shrinks the SDS/PEI molar ratio range of precipitation, because complexation with copper decreases the amount of PEI positive charge for every four amine groups from 4 (four  $\text{PEI}-\text{H}^+$ ) to 2 ( $4\text{PEI}-\text{Cu}^{2+}$ ). For example, 0.15 mM  $\text{Cu}^{2+}$  chelated with 0.6 mM amino groups of PEI, reducing the charges of this segment from 0.6 to 0.3 mM. The remained 0.4 mM amino groups of PEI were free and their protonation depended on pH, yet the total charge of the complex was less than that of 1 mM PEI without  $\text{Cu}^{2+}$ . Therefore, the SDS needed for PSAs precipitation varies.

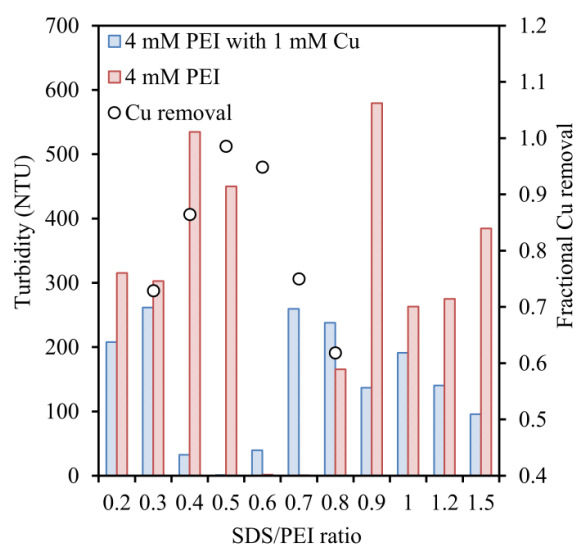


**Figure 9** shows the turbidities of PEI/SDS and PEI/Cu/SDS solutions at a pH of 6. The optimum ratio (i.e. lowest final turbidity) of SDS to PEI occurred at 0.5 for 4 mM PEI together with 1 mM  $\text{Cu}^{2+}$ , where the highest Cu removal was observed, because all of the positive charges of  $\text{Cu}^{2+}$  were associated with  $\text{DS}^-$  (1 mole of Cu complex with 2 moles of SDS) at this point. However, the best ratio of SDS to PEI shifted up to 0.6 and 0.7 when only PEI was present at pH 6, since the polymer has a higher charge (as discussed above). The turbidities of the PEI/SDS solutions were in general higher than those of the PEI/Cu/SDS solutions, possibly because complexation with Cu caused collapsing or shrinking of PEI backbones so that the particle sizes of the complexes were smaller than those of the PEI/SDS (alone) complexes.





**Figure 8.** pH changes of PEI (1 mM) and PEI/Cu solutions after addition of SDS (solid symbol indicates precipitate)



**Figure 9.** Turbidity of PEI and PEI/Cu solution after adding SDS and then filtering using filter paper at constant pH 6

### 3.5 Application of PEI/SDS aggregates to remove and recover $\text{Cu}^{2+}$

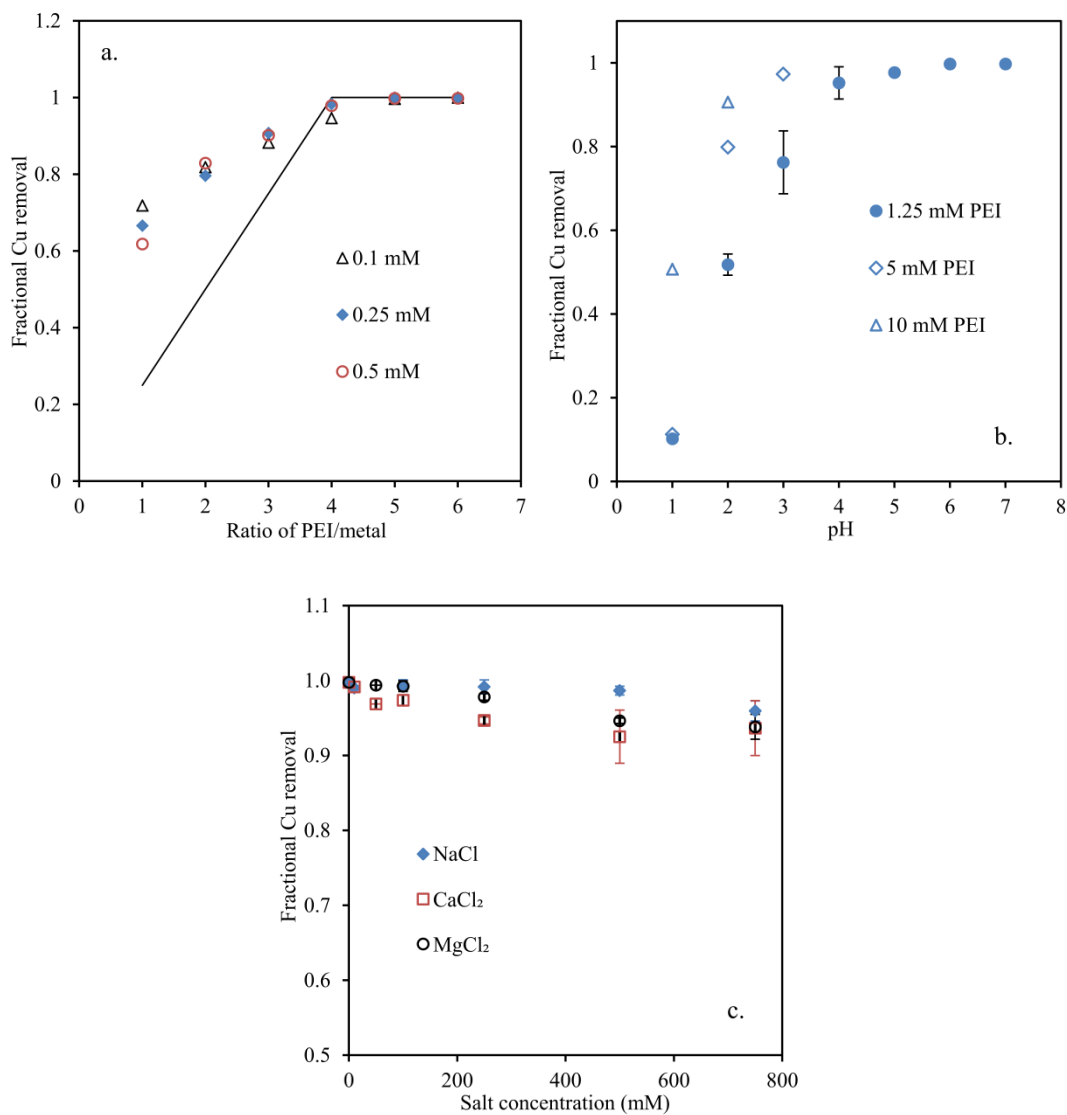
Due to the interaction among PEI, SDS and copper ions, the aggregates formed can be used to remove  $\text{Cu}^{2+}$  from aqueous solutions and effluents, and because the properties of the aggregate depend

on pH,  $\text{Cu}^{2+}$  can be released by acidification, and the PEI and SDS can then be reused after the release of  $\text{Cu}^{2+}$  by alkalization.

### 3.5.1 Copper removal using PEI/SDS aggregates

**Figure 10** shows the removal of copper ions under varying conditions using PEI/SDS aggregates. **Figure 10a** shows fractional  $\text{Cu}^{2+}$  removal at different PEI/Cu molar ratios, where the optimal SDS concentrations are then applied to precipitate the complex. Cu removal increases with increasing PEI/Cu ratio, and when this is above the ideal PEI/Cu chelation ratio of 4, the Cu removal is close to 1, for varying initial  $\text{Cu}^{2+}$  concentrations. It can also be noted that when PEI/Cu ratios are below the chelation number of 4, higher Cu removals are observed than those expected for a model based on chelation alone (indicated by the straight line). The possible reasons for this are; (1) some  $\text{Cu}^{2+}$  interacts with the PEI by weak chelation (lower than a chelation number of 4), and (2) because of the “sweep out” function of PEI/Cu/SDS flocculates. **Figure 10b** shows the  $\text{Cu}^{2+}$  removal at varying pH values.  $\text{Cu}^{2+}$  removal is close to 1 when 1.25 mM PEI and 0.25 mM  $\text{Cu}^{2+}$  is used and the pH is higher than 4 ( i.e. a ratio of 5, slightly above the chelation ratio of 4), but the removal decreases markedly as pH decreases from 3 to 1, due to the loss of available unprotonated amino groups and the weak chelation of  $\text{Cu}^{2+}$  at low pH values [38]. It should be noted that the consumption of SDS for the best precipitation of PSAs was the same above pH 4, at an SDS/PEI ratio of  $\sim 0.55$ ; while when pH decreased from 3 to 1, the SDS/PEI ratio increased from 0.8 to 1, because more charged amino groups needed to be neutralized after the  $\text{Cu}^{2+}$  release at low pH values. Increasing the concentration of PEI increased the  $\text{Cu}^{2+}$  removal at low pH, because more chelation sites are available for the  $\text{Cu}^{2+}$  removal. **Figure 10c** shows the influence of varying salinity and hardness on  $\text{Cu}^{2+}$  removal. As can be seen, a high ionic strength has no marked effect on  $\text{Cu}^{2+}$  removal, as observed with the high concentration of NaCl (up to 750 mM). Calcium and magnesium have a slightly higher influence than sodium, but Cu removal is still higher than 90% when  $\text{CaCl}_2$  or  $\text{MgCl}_2$  concentration is 750 mM, indicating the much higher affinity of  $\text{Cu}^{2+}$  to PEI than that of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , and also implying

that the PSAs process can still be used effectively for metal removal in high salinity solutions (e.g. from seawater and oil/gas produced water).

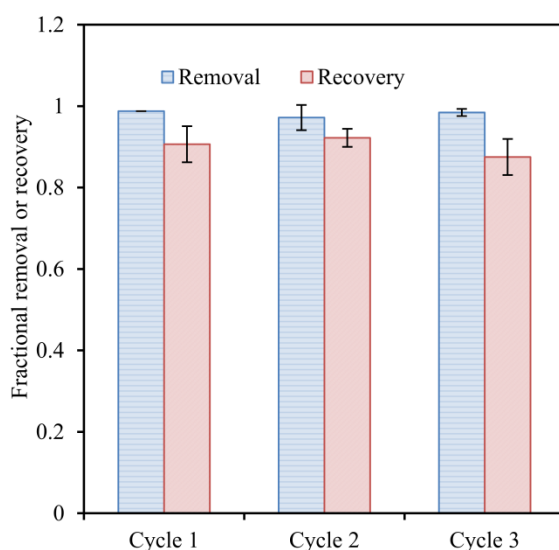


**Figure 10.** Copper removal under varying conditions using PSAs: (a) Varying PEI/Cu molar ratios; (b) Varying pH values; (c) Impact of salinity/hardness.

### 3.5.2 Copper release and PEI/SDS reuse

According to the process shown in **Figure 2**, blue precipitates formed after adding PEI (2.5 mM) and SDS (1.25 mM) into a 0.5 mM Cu<sup>2+</sup> solution and stirring for a short time. The precipitates and the aqueous phase free of Cu<sup>2+</sup> were separated using sedimentation or coarse filtration (filter papers with

15  $\mu\text{m}$  pores were used in this study). 5 mL  $\text{H}_2\text{SO}_4$  (0.1 M) was used to rinse the PEI/Cu/SDS precipitates in order to release the  $\text{Cu}^{2+}$ , and the recovery of  $\text{Cu}^{2+}$  into a concentrated copper sulphate solution can be above 90% of that present in the effluent feed solution. After release of  $\text{Cu}^{2+}$ , white PEI/SDS precipitates were dissolved using 2.5 mL NaOH (0.2 M), to reuse in a new treatment cycle. **Figure 11** shows the results of  $\text{Cu}^{2+}$  removal and recovery in the above example solutions, in which the PEI/SDS materials were reused for three cycles. After three cycles,  $\text{Cu}^{2+}$  removal was still up to 98%, and the copper recovery from precipitates can be 87.5% (the  $\text{Cu}^{2+}$  released into 5 mL  $\text{H}_2\text{SO}_4$  was  $\sim 280$  mg/L). A previous study has similarly shown that the recovery of Cd (II) can still be up to around 90% using PEI/SDS aggregates after seven cycles [15].



**Figure 11.** Copper removal and recovery for three cycles using the PSAs process

#### 4. Conclusions

In previous work, a novel metallic ions removal and recovery process has been developed by application of polymer–surfactant aggregates (PSAs). To understand the mechanism of the treatment process, branched polyethylenimine (PEI) and sodium dodecyl sulfate (SDS) were selected as the polymer and the surfactant to form PSAs, and copper sulphate was chosen as the source of metal ions; the interaction among them was investigated in this study. Branched PEI showed a proton buffer

capacity, and a higher PEI concentration showed a higher trend to resist protonation at low pH, indicating that increasing the PEI concentration at low pH provides more available amino groups to complex with metal ions and provides the possibility of removing metal ions from highly acidic solutions, such as acid mine drainage. SDS formed PSAs with branched PEI due to electrostatic association, and precipitated at certain molar ratios, but re-dispersal of PSAs could be achieved via an increase of pH; this latter was due to a hydrophobic, intermolecular interaction between SDS and PEI. Precipitation of PSAs depended on the SDS/PEI concentration ratio and the best SDS/PEI ratio decreased with increasing pH; higher concentrations of PEI showed a greater potential to precipitate. PEI showed a strong chelation with  $\text{Cu}^{2+}$  at a molar ratio of 4, but acidification decreased the complex capacity between PEI and  $\text{Cu}^{2+}$ , which in turn provided the strategy for metal release from PSAs. Copper removal increased with increasing PEI concentration below the chelation ratio of 4, and with increasing pH from 1 to above 4. Additionally, above 99.5% removal of  $\text{Cu}^{2+}$  was achieved when the best PEI/SDS concentrations were employed. Ionic strength and hardness (up to 750 mM  $\text{CaCl}_2$  or  $\text{MgCl}_2$ ) had no marked effect on  $\text{Cu}^{2+}$  removal using the PSAs process. Based on the interactions among them,  $\text{Cu}^{2+}$  could be released from PSAs by acidification and the PSAs materials could be reused following alkalization. Copper removal and recovery were still up to 98% and 88% after three cycles of reuse, respectively.

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## References

- [1] Y. Lu, S. Song, R. Wang, Z. Liu, J. Meng, A.J. Sweetman, A. Jenkins, R.C. Ferrier, H. Li, W. Luo, Impacts of soil and water pollution on food safety and health risks in China. *Environ. Int.* 77 (2015) 5-15.

- [2] F. Wang, X. Lu, X.-y. Li, Selective removals of heavy metals ( $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$ ) from wastewater by gelation with alginate for effective metal recovery. *J. Hazard. Mater.* 308 (2016) 75-83.
- [3] L. Ling, X.Y. Huang, W.X. Zhang, Enrichment of precious metals from wastewater with core-shell nanoparticles of iron. *Adv. Mater.* 30 (2018) 1705703.
- [4] J.-J.S. Huang, S.-C. Lin, L. Löwemark, S.Y.H. Liou, Q. Chang, T.-K. Chang, K.-Y. Wei, I.W. Croudace, Rapid assessment of heavy metal pollution using ion-exchange resin sachets and micro-XRF core-scanning. *Sci. Rep.* 9 (2019) 6601.
- [5] Y. Ge, Z. Li, Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. *ACS Sustain. Chem. Eng.* 6 (2018) 7181-7192.
- [6] M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M.R. Qtaishat, M. Alkasrawi, Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance. *Chem. Eng. J.* 260 (2015) 749-756.
- [7] Y. Zhang, S. Zhang, T.-S. Chung, Nanometric graphene oxide framework membranes with enhanced heavy metal removal via nanofiltration. *Environ. Sci. Technol.* 49 (2015) 10235-10242.
- [8] G.M. Kirkelund, P.E. Jensen, L.M. Ottosen, K.B. Pedersen, Comparison of two-and three-compartment cells for electrodialytic removal of heavy metals from contaminated material suspensions. *J. Hazard. Mater.* 367 (2019) 68-76.
- [9] M. Schwarze, M. Groß, M. Moritz, G. Buchner, L. Kapitzki, L. Chiappisi, M. Gradzielski, Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylthoxycarboxylate. *J. Membr. Sci.* 478 (2015) 140-147.
- [10] M. Chen, Y. Wu, C.T. Jafvert, Synthesis of cross-linked cationic surfactant nanoparticles for removing anions from water. *Environ. Sci. Nano* 4 (2017) 1534-1543.
- [11] M. Chen, K. Shafer-Peltier, S.J. Randtke, E. Peltier, Competitive association of cations with poly(sodium 4-styrenesulfonate)(PSS) and heavy metal removal from water by PSS-assisted ultrafiltration. *Chem. Eng. J.* 344 (2018) 155-164.
- [12] M. Chen, C.T. Jafvert, Anion recovery from water by cross-linked cationic surfactant nanoparticles across dialysis membranes. *Environ. Sci. Nano* 5 (2018) 1350-1360.
- [13] K. Shafer-Peltier, C. Kenner, E. Albertson, M. Chen, S. Randtke, E. Peltier, Removing Scale-Forming Cations from Produced Waters. *Environ. Sci. Water Res. Technol.* (2019).
- [14] L.-C. Shen, X.-T. Nguyen, N.P. Hankins, Removal of heavy metal ions from dilute aqueous solutions by polymer-surfactant aggregates: A novel effluent treatment process. *Sep. Purif. Technol.* 152 (2015) 101-107.
- [15] L. Shen, A. Lo, X. Nguyen, N. Hankins, Recovery of heavy metal ions and recycle of removal agent in the polymer-surfactant aggregate process. *Sep. Purif. Technol.* 159 (2016) 169-176.
- [16] L. Shen, N.P. Hankins, Removal of metallic ions at the parts per billion level from aqueous solutions using the polymer-surfactant aggregate process. *J. Water Process Eng.* (2017).
- [17] L. Shen, J. Wu, S. Singh, N. Hankins, Removal of metallic anions from dilute aqueous solutions by polymer-surfactant aggregates. *Desalination* 406 (2017) 109-118.
- [18] L. Shen, N. Hankins, Metallic anion removal from dilute aqueous solutions using polymer-surfactant aggregate process: Effect of surfactant chain length. *J. Water Process Eng.* 20 (2017) 243-248.
- [19] L. Shen, N. Hankins, Metallic anion recovery from aqueous streams and removal agent recycle in the polymer-surfactant aggregate process. *Desalination* 406 (2017) 67-73.
- [20] E.D. Goddard, Polymer-surfactant interaction part II. Polymer and surfactant of opposite charge. *Colloid Surface* 19 (1986) 301-329.
- [21] E. Staples, I. Tucker, J. Penfold, N. Warren, R. Thomas, D. Taylor, Organization of polymer-surfactant mixtures at the air-water interface: sodium dodecyl sulfate and poly(dimethyldiallylammonium chloride). *Langmuir* 18 (2002) 5147-5153.

- [22] J. Penfold, I. Tucker, R. Thomas, J. Zhang, Adsorption of polyelectrolyte/surfactant mixtures at the air– solution interface: poly (ethyleneimine)/sodium dodecyl sulfate. *Langmuir* 21 (2005) 10061-10073.
- [23] M. Chen, K. Shafer-Peltier, M. Veisi, S. Randtke, E. Peltier, Complexation and precipitation of scale-forming cations in oilfield produced water with polyelectrolytes. *Sep. Purif. Technol.* 222 (2019) 1-10.
- [24] M. Chen, C.T. Jafvert, Anion exchange on cationic surfactant micelles, and a speciation model for estimating anion removal on micelles during ultrafiltration of water. *Langmuir* 33 (2017) 6540-6549.
- [25] M. Chen, K. Shafer-Peltier, S.J. Randtke, E. Peltier, Modeling arsenic (V) removal from water by micellar enhanced ultrafiltration in the presence of competing anions. *Chemosphere* 213 (2018) 285-294.
- [26] M. Chen, C.T. Jafvert, Application of cross-linked stearic acid nanoparticles with dialysis membranes for methylene blue recovery. *Sep. Purif. Technol.* 204 (2018) 21-29.
- [27] M. Taseidifar, M. Ziaee, R.M. Pashley, B.W. Ninham, Ion flotation removal of a range of contaminant ions from drinking water. *J. Environ. Chem. Eng.* 7 (2019) 103263.
- [28] H. Wang, Y. Wang, H. Yan, J. Zhang, R.K. Thomas, Binding of sodium dodecyl sulfate with linear and branched polyethyleneimines in aqueous solution at different pH values. *Langmuir* 22 (2006) 1526-1533.
- [29] M. Veisi, S. Johnson, K. Shafer - Peltier, J.T. Liang, C. Berkland, M. Chen, R. Barati, Controlled release of poly (vinyl sulfonate) scale inhibitor to extend reservoir treatment lifetime. *J. Appl. Polym. Sci.* 136 (2019) 47225.
- [30] R. Mészáros, L. Thompson, M. Bos, I. Varga, T. Gilányi, Interaction of sodium dodecyl sulfate with polyethyleneimine: surfactant-induced polymer solution colloid dispersion transition. *Langmuir* 19 (2003) 609-615.
- [31] F. Qu, N.B. Li, H.Q. Luo, Highly sensitive fluorescent and colorimetric pH sensor based on polyethylenimine-capped silver nanoclusters. *Langmuir* 29 (2013) 1199-1205.
- [32] J. Suh, H.J. Paik, B.K. Hwang, Ionization of Poly(ethylenimine) and Poly(allylamine) at Various pH's. *Bioorg. Chem.* 22 (1994) 318-327.
- [33] T. Tomida, K. Hamaguchi, S. Tunashima, M. Katoh, S. Masuda, Binding properties of a water-soluble chelating polymer with divalent metal ions measured by ultrafiltration. *Poly (acrylic acid). Ind. Eng. Chem. Res.* 40 (2001) 3557-3562.
- [34] E. Kokufuta, Colloid titration behavior of poly (ethyleneimine). *Macromolecules* 12 (1979) 350-351.
- [35] J. Nagaya, M. Homma, A. Tanioka, A. Minakata, Relationship between protonation and ion condensation for branched poly(ethylenimine). *Biophys. Chem.* 60 (1996) 45-51.
- [36] A. Şakar-Deliormanlı, Interaction of sodium dodecyl sulfate with poly (ethyleneimine) in bulk solution and at the air-solution interface. *J. Disper. Sci. Technol.* 31 (2009) 23-30.
- [37] P.M. Claesson, M. Bergström, A. Dedinaite, M. Kjellin, J.-F. Legrand, I. Grillo, Mixtures of Cationic Polyelectrolyte and Anionic Surfactant Studied with Small-Angle Neutron Scattering. *J. Phys. Chem. B* 104 (2000) 11689-11694.
- [38] S. Kobayashi, K. Hiroishi, M. Tokunoh, T. Saegusa, Chelating properties of linear and branched poly (ethylenimines). *Macromolecules* 20 (1987) 1496-1500.