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Journal Name

Paper

Elegant Cooperativity of Noncovalent Interactions in Effective Removal of Cu-EDTA from Water via Stepwise Addition of Polymer and Surfactant

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Removal of chelated metal ions from water remains a challenge in the treatment of industrial waste water since the chelating complex are extremely stable which can hardly be precipitated. We report the elegant cooperativity of electrostatic interaction, coordinating interaction, and hydrophobic effect allows facile flocculation of Cu-EDTA through stepwise addition of polyethylenamine (PEI) and sodium dodecyl sulphate(SDS). The electrostatic interactions are important at 'initiating' the coordination between PEI and Cu-EDTA, and the hydrophobic interaction between SDS and PEI allows cross-linking the PEI/Cu-EDTA complex to generate precipitate. With this facile protocol, 97% of the Cu-EDTA complex in the wasted water can be removed, and the residual level of Cu-EDTA can be lowered to below 2 mg/L. Such cooperativity of noncovalent interactions is of great potential interest in the removal of chelated metal complex from industrial water.

Water pollution resulted from heavy metals has severe threat to environment and the health of human beings, so that removal of them has become an urgent issue. So far, tremendous efforts have been input in this field, and a number of methods have been invented to cope with metal ions in water. Successful strategies include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment, and coagulation-flocculation.¹⁻⁷ However, these methods are usually very effective for free metal ions, but less practicable for chelated metals. It is well-known that addition of strong chelating agents, such as citrate, tartrate, and ethylenediaminetetracetic (EDTA), is very crucial for many industrial cleaning processes,⁸⁻¹⁰ where the formation of stable and highly water soluble chelating complex is utilized to generate high surface appearance of the products.

However, the chelated metals are highly soluble and extremely stable, which can hardly be precipitated.^{11, 12} Because of the difficulty in removing these chelated metals, relating industries, such as electroplating, has been prohibited in many country and area. Although electrochemical methods are effective toward them,¹³⁻¹⁵ the high energy cost has prevented them from application. Therefore, economically treatment of chelated metals has become a bottleneck that limits the development of relating industries.

Herein we report a straight-forward method of removal of Cu-EDTA complex from water by stepwise interaction with a cationic polyelectrolyte and anionic surfactant. Polymer and surfactant have been individually investigated to remove free heavy metal ions from aqueous solutions.¹⁶⁻¹⁸ Very recently, the association between polymers and surfactants were found to be able to remove free heavy metal ions from dilute solutions with high efficiency.¹⁹ In this cooperative removal strategy, polymers with binding affinity to metal ions are very crucial.²⁰ The presence of surfactant can generate precipitates of the polymer-metal complex.²¹⁻²³ However, so far, no attempt has been reported to remove chelated metal ions with polymer and surfactant. The lack of efforts in this regard is probably limited by the general consideration on chelated metal complex: in most cases, the coordinating sites of a metal ion are fully occupied by the chelating groups, so that it is not possible to bind to polymer any more.

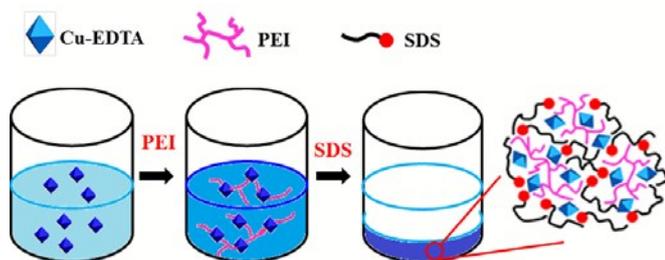
In this work, we report that with the assistance of electrostatic interaction, the negatively charged chelated metal complex Cu-EDTA can still coordinate with positively charged polyethyleimine (PEI). This results in effective binding of the Cu-EDTA to the chain of PEI. Then addition of sodium dodecyl sulphate (SDS) that carries opposite charges to the polymer can further induce precipitation of the PEI/Cu-EDTA complexes. In this way, the Cu-EDTA complexes can be successfully removed from water so that the residual copper level can be lowered to 1.8 mg/L, which is close to the safety requirements of China (1.0~1.5 mg/L)(Scheme 1). Furthermore, we expect that recycling this treated water in electroplating industry may reduce the content of chelated copper maximally.

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Scheme 1 Illustration of the removal of Cu(II)-EDTA complex from water via stepwise addition of PEI and SDS.

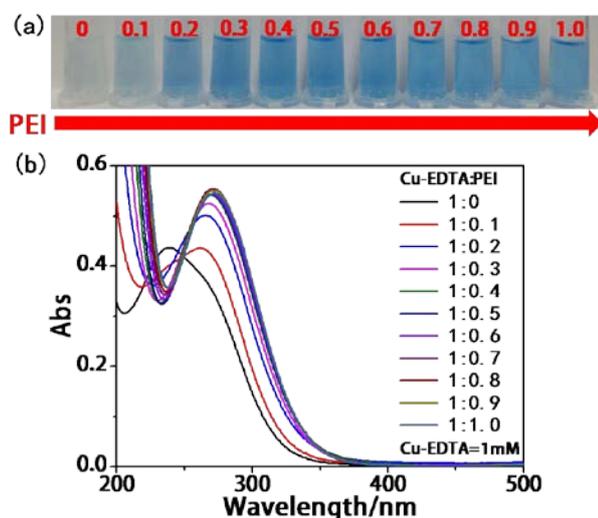


Figure 1a). Photos of the Cu-EDTA solution upon addition of PEI at various molar ratios; b). The UV-vis spectra of Cu-EDTA with variation of the ratio between Cu-EDTA/PEI. The concentration of Cu-EDTA is fixed at 1 mM.

The water containing Cu-EDTA complexes is blue and transparent, which displays strong absorption at 239 nm. Although Cu-EDTA carries negative charges, neither addition of positively charged surfactants, such as cetyltrimethylammonium bromide (CTAB), nor polycation can generate precipitation, confirming that the Cu-EDTA complex is extremely stable in water. However, upon addition of polyethyleneimine (PEI), the Cu-EDTA solution becomes dark blue but still remains transparent, which is accompanied by the shift of the absorption to 273 nm. This indicates that coordination between Cu(II) and PEI has probably occurred. Figure 1a shows that the colour becomes constant at the molar ratio of Cu-EDTA/PEI being larger than 0.4, where the UV-vis spectra (Figure 1b) also reach static state. This means that the optimal interacting ratio between Cu-EDTA and PEI is 1:0.4.

Next, anionic surfactant SDS was added to the dark blue solution of PEI/Cu-EDTA. Excitingly, blue precipitates were generated immediately, and the maximum amount of precipitation occurs at the ratio between PEI and SDS being 0.4 : 4. This simultaneously reduced the UV adsorption, indicative loss of Cu(II) from the water. Qualitative elemental analysis revealed that the residual level of copper has been lowered to 1.85 mg/L from the initial concentration of Cu(II) of 63.5 mg/L. That means 97% of the Cu-EDTA has been removed from water. This is in clear contrast with the nearly zero removal efficiency obtained by simple addition of NaOH or PEI to the aqueous solution of Cu-EDTA, strongly indicating

the powerfulness of the stepwise addition of PEI and SDS in removal of Cu-EDTA. It is worth noting that all these operations were carried out in neutral water, which avoided polluting water with acid or base. Compared with the conventional procedure which requires sequential addition of excess ferrous sulphate (to destabilize the chelated Cu-EDTA) and sodium phosphate (to precipitate the destabilized Cu^{2+}),²⁴ this approach of removal of Cu-EDTA is both benign to environment and high efficiency. The ferrous sulphate can acidify water body, and the addition of excess inorganic salt can harden the soil. In contrast, SDS and low molecular weight PEI would not be poisonous to water if their concentration is under control.²⁵ In present study, the molecular weight of PEI seems to have no effect on the removal efficiency of Cu-EDTA (data not shown). The residual concentration of SDS and PEI is 12.6 and 21.6 mg/L, respectively. Although these levels may also do harm to water body, they can be efficiently lowered by biodegradation of these two organic compounds. There are many organisms in nature that can degrade amphiphilic organic compounds.²⁶ Furthermore, upon addition of supplementary SDS and PEI at desired amount, the supernatant water can be recycled in treating more industrial waste water. This means that the cooperative application of PEI and SDS in the removal of chelated copper has great potential in practical application.

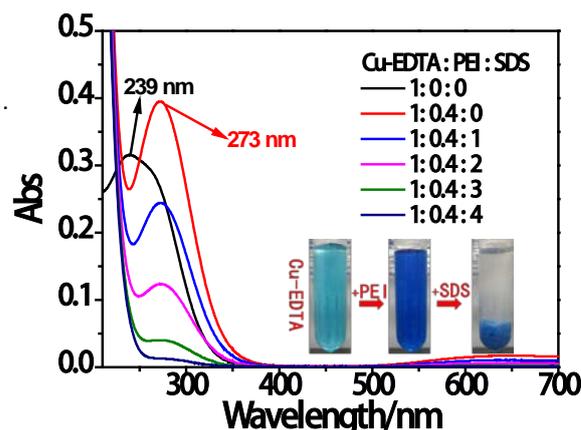


Figure 2 Changes of absorption spectra with the addition of SDS (fixed molar ratio of Cu-EDTA to PEI at the optimal value of 1/0.4, [Cu-EDTA] = 1 mM). The inset shows the change of color and phase behaviour upon stepwise addition of PEI to the Cu-EDTA solution.

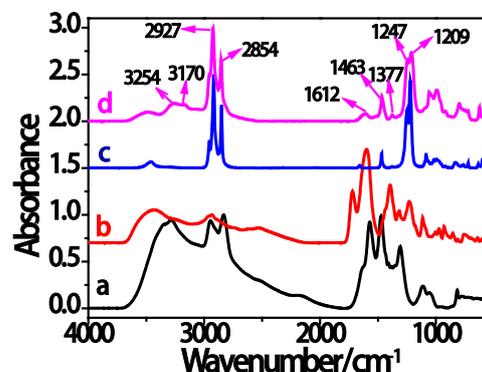


Figure 3 FTIR spectra of (a) PEI, (b) Cu-EDTA, (c) SDS and (d) blue precipitates

In order to examine the components in the precipitates, FT-IR spectra measurements were carried out (Figure 3). A couple of broad bands corresponding to the N-H stretching vibrations occurred around 3254 and 3170 cm^{-1} , which signifies the presence of PEI.²⁷ Moreover, extremely strong bands at 2927 and 2854 cm^{-1} were observed, indicative of long alkyl chains.^{28, 29} Meanwhile, the vibrational bands at 1247 and 1209 cm^{-1} can be attributed to the stretching vibrations of O=S=O of sulphate.¹⁷ The above information clearly points to the presence of SDS in the precipitates. Furthermore, EDTA can also be recognized by the C=O symmetric vibration at 1377 cm^{-1} .^{30, 31} The occurrence of mono peak of C=O in the precipitates suggests that EDTA binds to Cu^{2+} in a monodentate mode, namely, only one oxygen from COO bind with Cu(II).^{30, 32, 33} So far, it is obvious that the precipitates are composed of PEI, Cu-EDTA, and SDS.

Next, we determined the composition in the precipitates qualitatively by combining the ICP and element analysis results.³⁴ The molar ratio of Cu-EDTA:SDS:PEI is 1:4.03:0.39, which is nearly equal to the initial preparation ratio of 1:4:0.4, suggesting the precipitates are formed at a stoichiometric ratio of $(\text{Cu-EDTA})(\text{SDS})_{0.4}(\text{PEI})_4$. According to the residual concentrations remained in the supernatant ($[\text{SDS}] = 12.6\text{ mg/L}$, $[\text{PEI}] = 21.6\text{ mg/L}$), the estimated K_{sp} is about 6.37×10^{-26} . This extremely small K_{sp} means the precipitation is rather complete, suggesting this stepwise precipitation process is quite practicable.

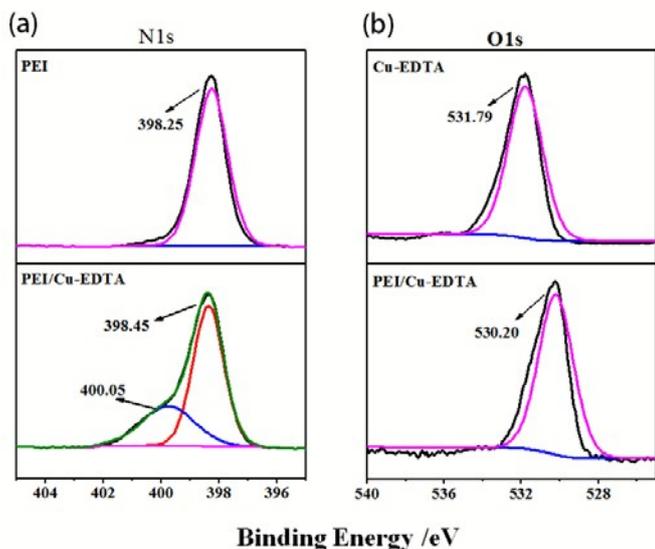
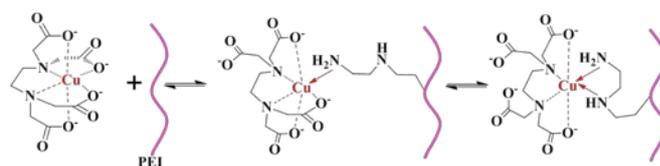


Figure 4 XPS spectra of (a) N1s and (b) O1s in PEI, Cu-EDTA and PEI/Cu-EDTA complex.

Since PEI has been inferred to interact with Cu-EDTA through coordinating interaction in the previous text, XPS measurement was performed to characterize the change of binding energy. Both the N1s electrons in PEI (Figure 4a) and the O1s in EDTA (Figure 4b) were examined, which allows to understand the overall coordinating states of Cu(II). Figure 4a shows that the binding energy for the N1s electrons in PEI is 398.25 eV before interaction with Cu-EDTA. It is noticed that a

new peak for the N1s appears at 400.05 eV in the PEI/Cu-EDTA precipitates, indicating the occurrence of strong coordination between Cu (II) and the nitrogen of PEI.^{28, 35, 36} This is because the N atom donated a lone pair electrons to Cu(II), resulting in the reduction of electron cloud density of N so that a higher binding energy occurs. Meanwhile, the O1s electron binding energy in EDTA was found lowered from 531.79 eV in Cu-EDTA to 530.20 eV in PEI/Cu-EDTA (Figure 4b), suggesting the coordination between EDTA and Cu(II) has been weakened in the presence of PEI. This means that competitive coordination between PEI and EDTA to Cu(II) has occurred, so that Cu(II) coordinates both with PEI and with EDTA in the $(\text{Cu-EDTA})(\text{SDS})_{0.4}(\text{PEI})_4$ complex. As a result, mixed-ligand has been formed, as illustrated in Scheme 2. Mixed ligand formation of Cu with other compounds have been reported in literature,^{37, 38} while it is for the first time to reveal the occurrence of mixed-ligand coordination of Cu with EDTA and PEI.



Scheme 2. The possible binding mode of PEI with Cu-EDTA.

Furthermore, effect of pH on the removal efficiency is examined because it affects the coordination of PEI with Cu-EDTA. For the branched PEI employed in this study, it contains amido groups with pKa ranging between 8 and 11.8.³⁹ In Figure 5 we show that optimal removal efficiency can be achieved in the pH range of 8~11. This pH range is in good agreement with the pKa of the PEI, suggesting both protonated and unprotonated amino are essential in the interaction between PEI and Cu-EDTA. We expect that the charged protonated N attracts the oppositely charged Cu-EDTA to the PEI chain, which simultaneously promotes the coordination of Cu-EDTA with the unprotonated N. These two kinds of N atoms function cooperatively to ensure sufficient coordination with Cu-EDTA. In the following step of SDS triggered precipitation, the protonated N can also offer enough electrostatic interaction with the SDS. This can be inferred from Figure 5. At low pH ($\text{pH} < 5$), where most the amine are protonated thus lose the ability of coordination with copper, the removal efficiency dramatically decreases although the electrostatic interaction between PEI and SDS is much stronger. This means that the coordination interaction between PEI and Cu-EDTA is very crucial for efficient removal of Cu-EDTA from water. It also confirms that electrostatic interaction between Cu-EDTA and PEI is not sufficient to bind Cu-EDTA to the PEI chain. As a result, at low pH, the increased ionic density of PEI only promotes the interaction between PEI and SDS, leading to the formation of white PEI-SDS precipitates. In contrast, at the extremely higher pH ($\text{pH} > 11$) where PEI is fully deprotonated, the lack of electrostatic attraction between SDS and PEI prevents the formation of bulk aggregates.

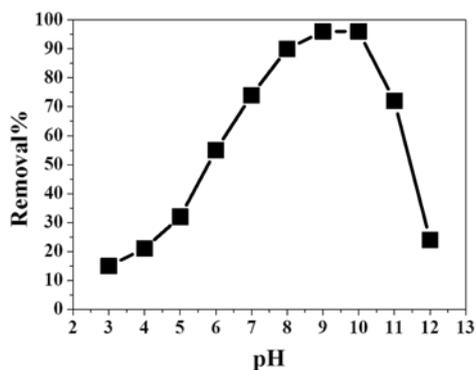


Figure 5 Cu-EDTA removal efficiency at different pHs ([Cu-EDTA = 1 mM], fixed molar ratio of Cu-EDTA/PEI/SDS at 1/0.4/4)

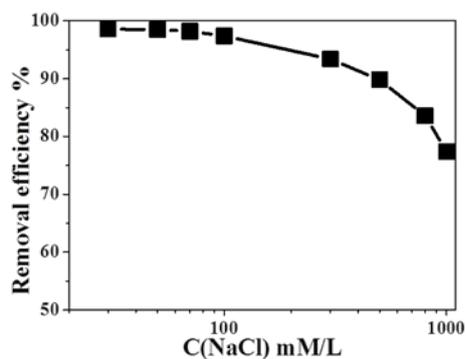


Figure 6 Cu-EDTA removal efficiency in the presence of different NaCl concentrations ([Cu-EDTA = 1 mM], fixed molar ratio of Cu-EDTA/PEI/SDS at 1/0.4/4)

Finally, the efficiency of removing Cu-EDTA from water was also tested in the presence of excess EDTA. In practical applications, excess EDTA is usually employed to efficiently remove the adsorbed Cu^{2+} in the electroplating industry. Both ICP and UV-vis measurements reveal that even in the presence of double amount of EDTA, the removal efficiency is not influenced (data not shown). Moreover, the removal efficiency was also not affected by the presence of interfering ion of Pb-EDTA , which often exists in industrial waste water. However, the amount of SDS between should be increased for an efficient removal. ICP measurements in the presence of 1 mM Pb^{2+} demonstrate that the residual concentration of Cu(II) in water still keeps around 1.85 mg/L, suggesting the stepwise protocol is selectively effective to removal of Cu-EDTA.

It should be pointed out that although ionic interaction occurs between SDS and PEI, the hydrophobic effect is very helpful in triggering the precipitates formation. Figure 6 shows that the removal efficiency only decreases 1.4 % in the presence of 100 mM NaCl, and the removal efficiency still remains above 60% even in 1M NaCl. Since the electrostatic interactions have been considerably suppressed by such high NaCl concentration,^{27,40} it means that the precipitates are not solely driven by the electrostatic interaction between SDS and PEI, hydrophobic interaction should also play an important role. It is possible that the hydrocarbon tail of the SDS bind to the

uncharged hydrophobic segments of PEI (the ethylene groups) through hydrophobic effect.⁴¹

In summary, we realized effective removal of Cu-EDTA complex from water by stepwise employment of polyethyleneamine (PEI) and sodium dodecyl sulphate (SDS). The residual concentration of copper can be lowered to below 2 mg/L. It is found that PEI interacted with Cu-EDTA with coordinating and electrostatic interactions, while SDS probably cross-linked the PEI-Cu-EDTA complex through hydrophobic effect. The most important discovery of this work is that the role of electrostatic interaction is mainly to enrich or drag Cu-EDTA and SDS to the PEI chain, which then facilitates the coordination between PEI and Cu-EDTA and the hydrophobic interaction between PEI and SDS. This delicate cooperation of noncovalent interaction is very crucial in achieving effective removal of Cu-EDTA from water. We expect that upon carefully control the cooperativity between a number of noncovalent interactions, it is possible to develop a general approach leading to effective removal of chelated metal complexes from water.

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Experimental

Materials

Ethylene imine polymer (PEI, $M_w=1800$, 99%) was purchased from Aladdin and used as received. sodium Dodecyl sulphate (SDS, 99%) was purchased from Acros Organics Co. and used as received. Other reagents were of analytical grade used without further purification. Ultrapure water was used throughout the work.

Sample preparation

The solution of Cu-EDTA was prepared by weighting desired amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{EDTA} \cdot 2\text{Na}$ where the molar ratio between Cu^{2+} and EDTA is 1:1 into a 50 mL vial, then water was added to prepare stock solution of 15 mM. The stock solutions of 15 mM PEI and 50 mM SDS were prepared, respectively. In Cu-EDTA removal experiments, desired amount of PEI and SDS stock solutions was added to a 3 mL Cu-EDTA stock solution. Then the mixed solution was diluted to 1 mM for UV-vis measurements. For other measurements, no dilution was conducted.

The removal efficiency (Re) of Cu-EDTA is estimated according to the following equation:

$$\text{Re} = \frac{C_0 - C_e}{C_0} \times 100\%$$

where C_0 is the initial concentration of Cu-EDTA in mg/L, C_e is the concentration after treatment with PEI/SDS. Ten parallel measurements were made to obtain one Re value.

Characterization

Ultraviolet-visible (UV-vis) spectral measurements were performed on a Shimadzu UV-1800 spectrophotometer in the range of 200-700 nm. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS-Ultra Imaging Photoelectron

Spectrometer from Kratos Analytical Ltd, using monochromatic Al-K α radiation in a vacuum of 2×10^{-8} Pa. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Vector-22 spectrophotometer in the range of 4000 to 650 cm^{-1} . The concentration of Cu^{2+} in liquid phase was determined by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (PROFILE SPEC, Leeman).

Elemental analysis was performed on Elementar Bario EL, Germany, to analyse the organic composition in the precipitates and supernatant, respectively. The average composition in the precipitates was found to be C:51.66%, H:9.84%, N:7.22%, and S:3.52% after measuring ten groups of samples in parallel. The amount of SDS can be simply obtained by the ratio of S, whereas we assumed the molar ratio of Cu and EDTA remains 1:1 both in the precipitates and in the supernatant. Then the N in EDTA can be obtained from the amount of Cu obtained from ICP. Consequently, the N contributed by PEI can be determined by subtracting the amount of N contributed by EDTA from the total N composition.

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