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Elegant cooperativity of noncovalent interactions in effective removal of Cu–EDTA from water via stepwise addition of polymer and surfactant

Yanan Zhang,^{†a} Xuedong Gao,^{†a} Yun Yan,^{*a} Jide Wang^{*a} and Jianbin Huang^{*ab}

Removal of chelated metal ions from water remains a challenge in the treatment of industrial waste water since the chelating complexes are extremely stable, which means that precipitation is difficult. We report the elegant cooperativity of electrostatic interaction, coordinating interaction, and hydrophobic effects, which allows facile flocculation of Cu–EDTA through the stepwise addition of polyethyleneimine (PEI) and sodium dodecyl sulphate (SDS). The electrostatic interactions are important in 'initiating' the coordination between PEI and Cu–EDTA, and the hydrophobic interaction between SDS and PEI allows cross-linking of the PEI/Cu–EDTA complex to generate a precipitate. With this facile protocol, 97% of the Cu–EDTA complex in the waste water can be removed, and the residual level of Cu–EDTA can be lowered to below 2 mg L⁻¹. Such cooperativity of noncovalent interactions is of great potential interest in the removal of chelated metal complexes from industrial water.

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Water pollution resulting from heavy metals poses a severe threat to the environment and the health of human beings, so removal of them has become an urgent issue. So far, tremendous efforts have been made in this field, and a number of methods have been invented to deal with metal ions in water. Successful strategies include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment, and coagulation–flocculation.^{1–7} Although these methods are usually very effective for free metal ions, they are less practicable for chelated metals. It is well-known that the addition of strong chelating agents, such as citrate, tartrate, and ethylenediaminetetraacetic (EDTA), is very crucial for many industrial cleaning processes,^{8–10} where the formation of stable and highly water soluble chelating complexes is utilized to electroplate and polish products. However, the chelated metals are highly soluble and extremely stable, which means that precipitation is difficult.^{11,12} Because of the difficulties in removing these chelated metals, related industries, such as electroplating, have been prohibited in many countries and areas. Although electrochemical methods are effective toward them,^{13–15} the high energy cost has prevented them from application. Therefore, economical treatment of chelated

metals has become a bottleneck that limits the development of related industries.

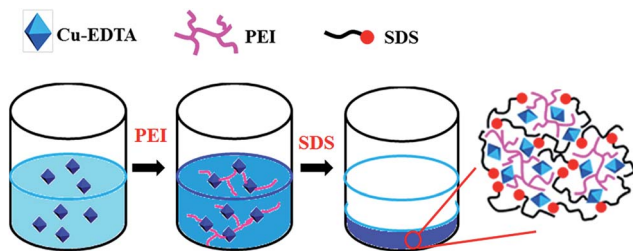
Herein we report a straight-forward method of removal of a Cu–EDTA complex from water by stepwise interaction with a cationic polyelectrolyte and an anionic surfactant. Polymers and surfactants have been individually investigated for the removal of free heavy metal ions from aqueous solutions.^{16–18} Very recently, the association between polymers and surfactants was found to be able to remove free heavy metal ions from dilute solutions with high efficiency.¹⁹ In this cooperative removal strategy, polymers with a binding affinity to metal ions are very crucial.²⁰ The presence of a surfactant can generate precipitates of a polymer–metal complex.^{21–24} However, so far, no attempt has been reported to remove chelated metal ions with a polymer and a surfactant. The lack of efforts in this regard is probably limited by the general considerations of chelated metal complexes: 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 polyethyleneimine (PEI). This results in effective binding of the Cu–EDTA to the chain of PEI. Then addition of sodium dodecyl sulphate (SDS), which 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⁻¹, which is close to the safety requirements of China (1.0–1.5 mg L⁻¹) (Scheme 1).

^aCollege of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, 830046, China. E-mail: Yunyan@pku.edu.cn; awangjd@126.com; jbhuan@pku.edu.cn

^bBeijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[†] These two authors contributed equally.



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

Furthermore, we expect that recycling this treated water in the electroplating industry may reduce the content of chelated copper greatly.

The water containing the Cu-EDTA complexes is blue and transparent, and displays strong absorption at 239 nm. Although Cu-EDTA carries negative charges, neither addition of positively charged surfactants, such as cetyltrimethylammonium bromide (CTAB), nor polycations can induce 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 a shift of the absorption to 273 nm. This indicates that coordination between Cu(II) and PEI has probably occurred. Fig. 1a shows that the colour becomes constant at a molar ratio of Cu-EDTA/PEI larger than 0.4, where the UV-vis spectra (Fig. 1b) also reach a static state. This means that the optimal interacting ratio between Cu-EDTA and PEI is 1 : 0.4.

Next, the 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 occurred at a ratio between PEI and SDS of 0.4 : 4 (Fig. 2).

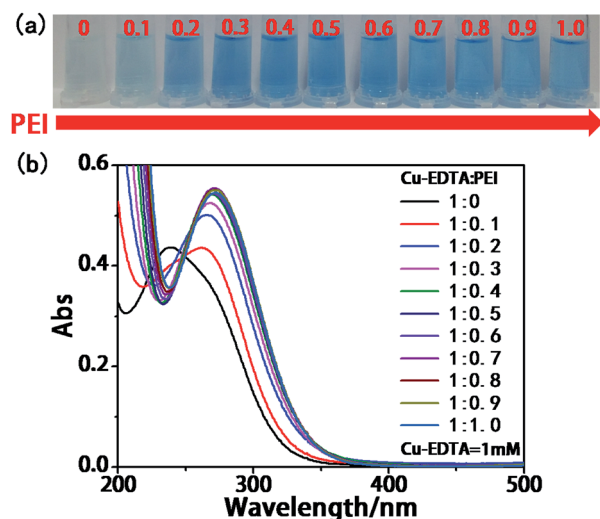


Fig. 1 (a) Photos of the Cu-EDTA solution upon addition of PEI at various molar ratios; (b) the UV-vis spectra of Cu-EDTA with variation of the ratio between Cu-EDTA/PEI. The concentration of Cu-EDTA was fixed at 1 mM.

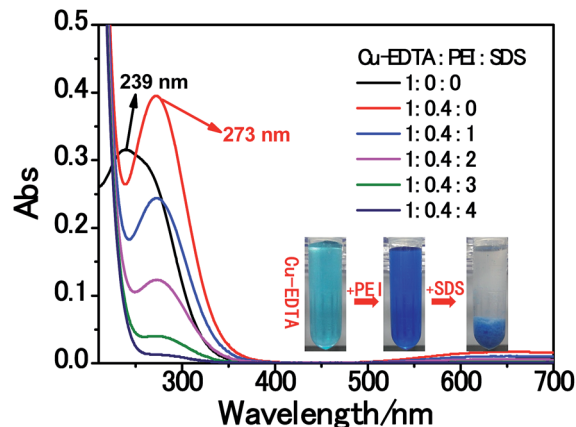


Fig. 2 Changes of the absorption spectra with addition of SDS (a fixed molar ratio of Cu-EDTA to PEI at the optimal value of 1/0.4, [Cu-EDTA] = 1 mM). The inset shows the change of color and phase behaviour upon stepwise addition of PEI to the Cu-EDTA solution.

This simultaneously reduced the UV adsorption, indicative of the loss of Cu(II) from the water. Qualitative elemental analysis revealed that the residual level of copper had been lowered to 1.85 mg L^{-1} from the initial concentration of Cu(II) of 63.5 mg L^{-1} . That means that 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 the removal of Cu-EDTA. It is worth noting that all of these operations were carried out in neutral water, which avoided polluting the 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+}),²⁵ this approach of the removal of Cu-EDTA is both benign to the environment and highly efficient. Ferrous sulphate can acidify the water body, and the addition of excess inorganic salts can harden the soil. In contrast, SDS and low molecular weight PEI would not be poisonous to water if their concentration is controlled.²⁶ In the 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^{-1} , respectively. Although these levels may also do harm to the 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.²⁷ Furthermore, upon addition of supplementary SDS and PEI of a desired amount, the supernatant water can be recycled in the treatment of 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 applications.

In order to examine the components of the precipitates, FT-IR spectra measurements were carried out (Fig. 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.²⁸ Moreover, extremely strong bands at 2927 and

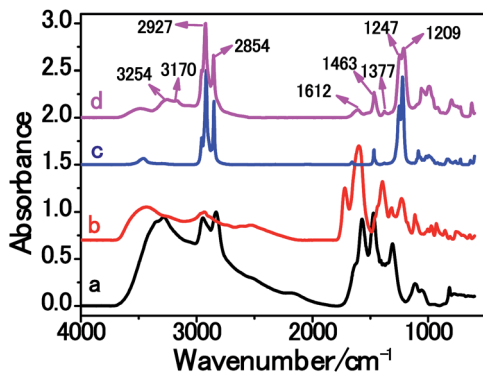


Fig. 3 FTIR spectra of (a) PEI, (b) Cu-EDTA, (c) SDS and (d) blue precipitates.

2854 cm^{-1} were observed, which is indicative of long alkyl chains.^{29,30} 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} .^{31,32} The occurrence of a single peak of C=O in the precipitates suggests that EDTA binds to Cu^{2+} in a monodentate mode, namely, only one oxygen from COO binds with $\text{Cu}(\text{II})$.^{31,33,34} So far, it is obvious that the precipitates are composed of PEI, Cu-EDTA, and SDS.

Next, we determined the composition of the precipitates qualitatively by combining the ICP and element analysis results.³⁵ 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 that the precipitates are formed at a stoichiometric ratio of $(\text{Cu-EDTA})(\text{PEI})_{0.4}(\text{SDS})_4$. According to the residual concentrations that remained in the supernatant ($[\text{SDS}] = 12.6 \text{ mg L}^{-1}$ and $[\text{PEI}] = 21.6 \text{ mg L}^{-1}$), the estimated K_{sp} is about 6.37×10^{-26} . This extremely small K_{sp} means that the precipitation is almost complete, suggesting that this stepwise precipitation process is quite practicable.

Since it has been inferred that PEI interacts with Cu-EDTA through coordinating interaction in the previous text, XPS measurements were performed to characterize the change of binding energy. Both the N1s electrons in PEI (Fig. 4a) and the O1s in EDTA (Fig. 4b) were examined, which allows an understanding of the overall coordinating states of $\text{Cu}(\text{II})$. Fig. 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 $\text{Cu}(\text{II})$ and the nitrogen of PEI.^{29,36,37} This is because the N atom donated a lone pair of electrons to $\text{Cu}(\text{II})$, resulting in a reduction of the electron cloud density of N so that a higher binding energy is found. Meanwhile, the O1s electron binding energy in EDTA was found to be lowered from 531.79 eV in Cu-EDTA to 530.20 eV in PEI/Cu-EDTA (Fig. 4b), suggesting that the coordination between EDTA and $\text{Cu}(\text{II})$ has been weakened in the presence of PEI. This means that competitive coordination

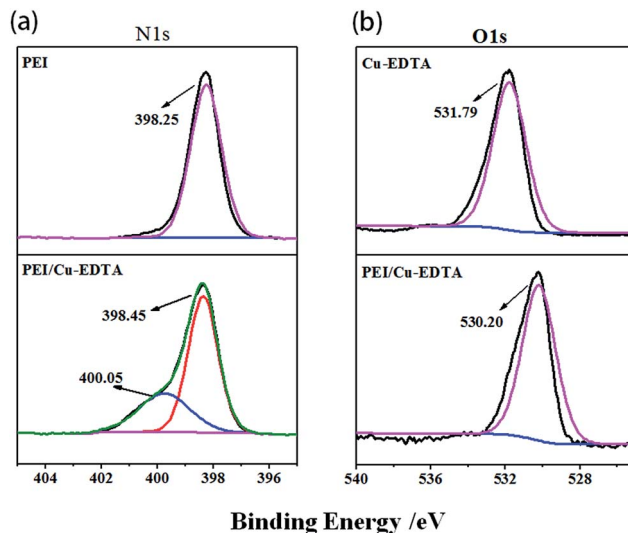
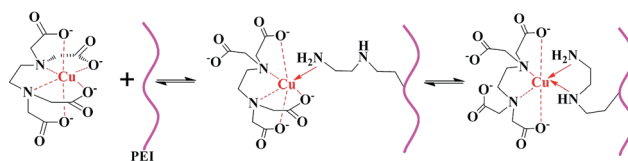


Fig. 4 XPS spectra of (a) N1s and (b) O1s in PEI, Cu-EDTA and the PEI/Cu-EDTA complex.

between PEI and EDTA to $\text{Cu}(\text{II})$ has occurred, so that $\text{Cu}(\text{II})$ coordinates both with PEI and with EDTA in the $(\text{Cu-EDTA})(\text{PEI})_{0.4}(\text{SDS})_4$ complex. As a result, a mixed-ligand has been formed, as illustrated in Scheme 2. Mixed ligand formation of Cu with other compounds has been reported in the literature,^{38,39} while this is the first time that the occurrence of mixed-ligand coordination of Cu with EDTA and PEI has been revealed.

Furthermore, the effect of pH on the removal efficiency is examined because it affects the coordination of PEI with Cu-EDTA. The branched PEI employed in this study contains amido groups with a pK_{a} ranging between 8 and 11.8.⁴⁰ In Fig. 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 pK_{a} of the PEI, suggesting that both protonated and unprotonated amido groups 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 the SDS triggered precipitation, the protonated N can also offer enough electrostatic interaction with the SDS. This can be inferred from Fig. 5. At low pH ($\text{pH} < 5$), where most of the amines are protonated and thus lose the ability of coordination with copper, the removal efficiency dramatically decreases although the electrostatic interaction between PEI



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

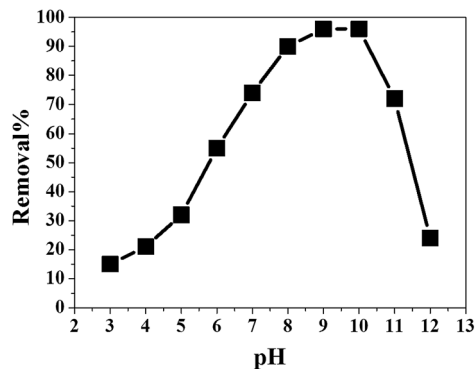


Fig. 5 Cu-EDTA removal efficiency at different pHs ([Cu-EDTA = 1 mM], a fixed molar ratio of Cu-EDTA/PEI/SDS at 1/0.4/4).

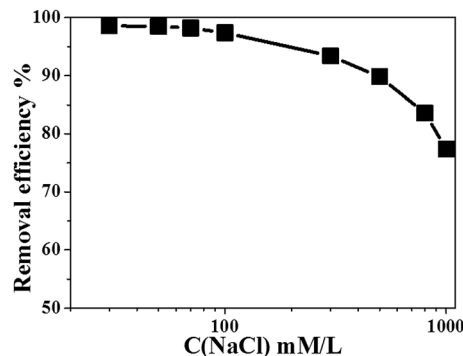


Fig. 6 Cu-EDTA removal efficiency in the presence of different NaCl concentrations ([Cu-EDTA = 1 mM], a fixed molar ratio of Cu-EDTA/PEI/SDS at 1/0.4/4).

and SDS is much stronger. This means that the coordination interaction between PEI and Cu-EDTA is very crucial for the efficient removal of Cu-EDTA from water. This 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 a much higher pH (pH > 11) where PEI is fully deprotonated, the lack of electrostatic attraction between SDS and PEI prevents the formation of bulk aggregates.

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 Cu²⁺ in the electroplating industry. Both ICP and UV-vis measurements reveal that, even in the presence of double the 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 ions of Pb-EDTA, which often exist in industrial waste water. However, the amount of SDS present should be increased for efficient removal. ICP measurements in the presence of 1 mM Pb²⁺ demonstrate that the residual concentration of Cu(II) in water still remains around 1.85 mg L⁻¹, suggesting that the stepwise protocol is selectively effective for the 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. Fig. 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 1 M NaCl. Since the electrostatic interactions have been considerably suppressed by such a high NaCl concentration,^{28,41} this means that the precipitates are not solely driven by the electrostatic interaction between SDS and PEI, and hydrophobic interaction should also play an important role. It is possible that the hydrocarbon tail of the SDS binds to the uncharged hydrophobic segments of PEI (the ethylene groups) through the hydrophobic effect.⁴²

In summary, we realized effective removal of a Cu-EDTA complex from water by the stepwise employment of

polyethyleneimine (PEI) and sodium dodecyl sulphate (SDS). The residual concentration of copper can be lowered to below 2 mg L⁻¹. 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 the 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 the effective removal of Cu-EDTA from water. We expect that upon careful control of the cooperativity between a number of noncovalent interactions, it will be possible to develop a general approach leading to the effective removal of chelated metal complexes from water.

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 and used without further purification. Ultrapure water was used throughout the work.

Sample preparation

The solution of Cu-EDTA was prepared by weighing the desired amount of CuCl₂·2H₂O and EDTA·2Na, where the molar ratio between Cu²⁺ and EDTA was 1 : 1, into a 50 mL vial, and then adding water to prepare a stock solution of 15 mM. Stock solutions of 15 mM PEI and 50 mM SDS were prepared. In the Cu-EDTA removal experiments, the desired amounts of the PEI and SDS stock solutions were 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 was estimated according to the following equation:

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

where C_0 is the initial concentration of Cu-EDTA in mg L^{-1} and 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 carried out 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 the liquid phase was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (PROFILE SPEC, Leeman).

Elemental analysis was performed on an Elementar Bario EL, Germany, in order to analyse the organic composition in the precipitates and supernatant. The average composition of 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 that the molar ratio of Cu and EDTA remains at 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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