ACS APPLIED MATERIALS & INTERFACES

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An Integrative Technique Based on Synergistic Coremoval and Sequential Recovery of Copper and Tetracycline with Dual-Functional Chelating Resin: Roles of Amine and Carboxyl Groups

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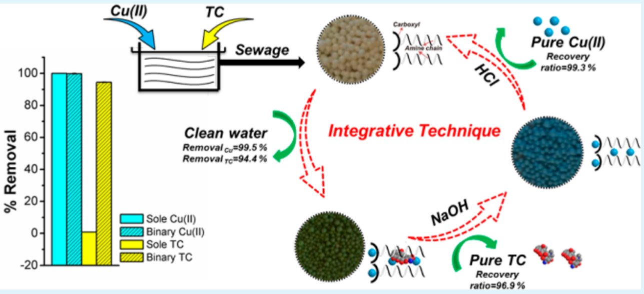
Supporting Information



ABSTRACT: A novel chelating resin (R-AC) bearing dual-functional groups (amino and carboxyl groups) was self-synthesized and it showed superior properties on synergistic coremoval of Cu(II) and tetracycline (TC) to commercial resins (amine, carboxyl, and hydrophobic types), which was deeply investigated by equilibrium and kinetic tests in binary, preloading, and saline systems. The adsorption of TC on R-AC was markedly enhanced when coexisted with Cu(II), up to 13 times of that in sole system, whereas Cu(II) uptake seldom decreased in the copresence of TC. Decomplexing-bridging, which included [Cu-TC] decomplexing and [R-Cu] bridging for TC, was demonstrated as the leading mechanism for the synergistic coremoval of Cu(II) and TC. Carboxyl groups of R-AC played a dominant role in decomplexing of [Cu-TC] complex and releasing free TC. Cu(II) coordinated with amine groups of R-AC was further proved to participate in bridging interaction with free TC, and the bridging stoichiometric ratio ([NH-Cu]: TC) possibly was 2:1. About 96.9% of TC and 99.3% of Cu could be sequentially recovered with dilute NaOH followed by HCl. Considering stable application for five cycles in simulated and practical wastewater, R-AC shows great potential in green and simple coremoval of antibiotic and heavy metal ions.

KEYWORDS: *dual-functional chelating resin, synergistic coremoval, sequential recovery, decomplexing-bridging interaction, copper, tetracycline*

1. INTRODUCTION

In recent years, combined pollution has been an increasingly hot topic in environmental field because it further reflects the real environment. Especially, combined pollution of antibiotics and heavy metal ions in soil and water was involved in many works.[1−3] Antibiotics are widely applied as human infection medicine and animal growth promoters. Poorly metabolizable and more than the half excreted to the environment as parent compounds, antibiotics are removed with low efficiency in conventional wastewater treatment plants, resulting in increasing antibiotic resistance.[4] In the meantime, heavy metals which are mostly acute toxic to human and wildlife even in trace level, are widely used in industrial and agricultural production.[5] Practices like land application of animal feces and industrial wastewater centralizing lead to their combined pollution in surface/groundwater. Various heavy metals and antibiotics have been detected in effluents of wastewater treatment plants.[6,7] Complex species were easily formed between heavy metal ions and antibiotics, making their environmental behaviors (e.g., adsorption, degradation and bioavailability) more complicated.[8−10] Growing evidence suggested that the combined toxicities of heavy metal ions (Copper, zinc and cadmium) and antibiotics (tetracyclines and quinolones) were generally larger than simple adduct of their individual toxicity.[11,12] Consequently, the effective control of the above-mentioned pollution has attracted increasing concerns, and as expected by most environmentalists, each component should be removed and recovered with high efficiency before discharging into the environment.

As a simple, green, and efficient technology, adsorption with such adsorbents as modified nature soil matters, biomaterials and polymers has been attempted to simultaneously remove heavy metals and organics (e.g., dyes, pesticides, antibiotics and their intermediate compounds).[13−15] With fewer procedures, the coadsorption method needed lower costs and space in comparison with traditional methods which combined two or more techniques such as chemical precipitation, advanced oxidation and biodegradation.[16] However, presence of heavy metal ions could either positively or negatively affect the sorption of antibiotics and vice versa, because of (1) strong complexation of solutes, (2) competition/shield of adsorption sites, or (3) formation of ternary surface complex.[3,17,18] Kang et

Received: August 20, 2013
Accepted: October 29, 2013
Published: October 29, 2013

al. found that the presence of tetracycline inhibited the adsorption of copper by competitively interacting with the same amine sites in chitosan, whereas the presence of copper improves tetracycline adsorption likely because of the formation of a ternary complex.[3] Therefore, it is of significance to explore adsorbents for synergistic coremoval of heavy metals and antibiotics, which have to date been rarely reported.

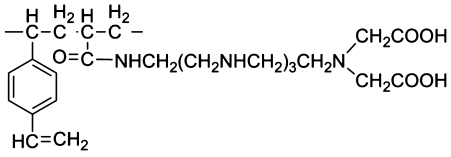
Obviously, the structure of an adsorbent always plays a key role on its properties.[19] The structure−function relationship and interaction processes during coremoval can provide more fundamental information for the proper design of adsorbents and operation of wastewater purification treatment. However, few studies have thoroughly discussed this point. Besides, almost no studies involved the sequential recovery of each pollutant and the reuse of adsorbents, which are also very important.

The object of this work is to explore a novel technique for synergistic coremoval of heavy metal ions and antibiotics. Different researches have respectively mentioned that N or O functional groups have excellent affinities to heavy metal ions by chelation or ion exchange interaction, and antibiotics by physical forces (such as electrostatic and hydrogen-bond interactions).[20,21] Thus, a chelating resin (R-AC) with dual-functional groups (amino and carboxyl groups) was newly synthesized. Tetracycline (TC) and Cu(II) was chosen as the typical pollutants because of their great production and consumption in China.[22−25] Roles of functional groups and interaction processes were further revealed by carrying out equilibrium and kinetic experiments in sole, binary, preloading, and saline systems as well as UV−vis, FTIR, XPS characterizations. Additionally, sequential recovery for TC and Cu(II) was also concerned.

2. MATERIALS AND METHODS

2.1. Materials. R-AC was newly synthesized from polystyrene-methacrylate beads by orderly reacting with amine and sodium chloroacetate in liquid phase at lab-level (the details are shown in the Supporting Information, part I). The general structure of R-AC was shown in Scheme 1. The typical properties of resins included R-AC and three commercial resins: S984 (Purolite, USA), D113 (Jiangsu Nan&Jin Environ. Technol. Co., P. R. China) and XAD-4 (Rohm & Haas, USA), were listed in Table S1-1 in the Supporting Information. Tetracycline ($C_{22}H_{24}N_2O_8$·HCl, 99% purity, as described in Scheme S1 in the Supporting Information) was purchased from Sigma-Aldrich as commercial products. Cupric chloride, hydrochloric acid, sodium hydroxide, and amine were analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China). Ultrapure water was used to prepare all solutions.

Scheme 1. General Structure of R-AC



2.2. Batch Equilibria Adsorption and Desorption Studies. Batch equilibria adsorption experiments were carried out in triplicate by mixing 0.0500 g of resin with 50 mL of solution with presettled initial concentration in 150 mL conical flasks. The initial pH values of solutions were all adjusted to 5.0 by 0.1 mol/L HCl or NaOH. The flasks were completely sealed and rotated continuously for 24 h at room temperature (298 K) in an incubator shaker under the rotating rate 140 rpm. The residual solutes were determined.

2.2.1. Resins Comparison. Each type of resin was tested in solutions containing Cu(II) with initial concentrations ranging from 0 to 2.0 mmol/L and TC fixed at 0.2 mmol/L, or TC with initial concentrations ranging from 0 to 0.5 mmol/L and Cu(II) fixed at 1.0 mmol/L.

2.2.2. Isotherm Studies. Adsorption isotherms of TC and Cu(II) on R-AC were conducted in their sole and binary systems with the initial concentrations above-mentioned.

2.2.3. Preloading Systems. Fresh resin was first fed by sole Cu(II) solution for 24 h to obtain Cu-preloading resin (named Resin-Cu). Resin-Cu was then tested in sole TC solution with initial concentration of 0.2 mmol/L. The initial concentrations of Cu(II) ranged from 0.2 to 4.0 mmol/L and those of TC were all fixed at 0.2 mmol/L.

2.2.4. Saline Systems. To examine the influence of ionic strength, the uptake of Cu(II) and TC was also conducted in the background of various NaCl levels at 0, 20, 50, and 100 mmol/L.

2.2.5. Batch Kinetics Studies. In kinetic tests, 1.000 g of R-AC was added in 1000 mL of solution with presettled initial concentration. Cu(II) was set as 1.0 mmol/L for higher Cu(II) concentrated system and Cu(II) preloading system, or 0.2 mmol/L for lower Cu(II) concentrated system. TC was all set as 0.2 mmol/L. Samples (1 mL) were immediately withdrawn at presettled time intervals for concentration measurements.

2.2.6. Tests in Practical Water. Fresh resins were tested in mixture solutions of Cu(II) and TC prepared with ultrapure water, effluent water from sewage treatment plant (located in Xiaguan District, Nanjing, China), and river water from Tongyu river (located in Yancheng, China), respectively. The pH values of these solutions were adjusted to 5.0.

2.2.7. Sequential Recovery. After being filtered and washed with ultrapure water, the used resin were resuspended in 25 mL of different eluents at 298 K for 4 h. Concentrations of both Cu(II) and TC in eluents were determined.

2.3. Analytical Procedures. *2.3.1. Detection Methods.* The concentrations of Cu (II) and TC in the solutions were measured by the atomic adsorption spectrophotometer (AAS, THERMO, USA) and UV−vis spectrometry (Agilent 8453, USA) at absorption wavelength of 360 nm, respectively.

2.3.2. Adsorption Equations and Models. The equilibrium adsorption amount (q_e mmol/g) and adsorption efficiency (AE) was calculated by eq 1. Data of adsorption isotherms were fitted with Langmuir and Freundlich models as present in eqs 3 and 4.

$$q_e = \frac{V(C_0 - C_e)}{m}... \tag{1}$$

$$AE = \frac{C_0 - C_e}{C_0} \times 100\%... \tag{2}$$

$$q_e = \frac{bq_{max}C_e}{1 + bC_e}... \tag{3}$$

$$q_e = K_f {C_e}^{1/n}... \tag{4}$$

Where C_0 and C_e are the initial and equilibrium concentration (mmol/L), and m is the mass of resin (g), V is the volume of solution (L), b is the affinity parameter or Langmuir sorption constant (L/mmol), and q_{max} represents the capacity when the surface is fully covered with adsorbate (mmol/g). K_f and n are the Freundlich constant isotherm parameters.

Pseudo-first-order rate kinetic models and pseudo-second-order kinetic models were considered to interpret kinetic data. The nonlinear forms as eqs 5 and 6 were considered a better way to obtain the kinetic parameters.[26]

$$q_t = q_e - \frac{q_e}{e^{k_1 t}}... \tag{5}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \cdots \qquad (6)$$

Where q_e and q_t are adsorption amount during t time and at equilibrium (mmol/g). k_1 and k_2 (g/mmol/min) are the constants associated with the adsorption rate in the corresponding equation. $h = k_2 q_e^2$ is defined as the initial adsorption rate constant.

2.4. Characterization Techniques. Resin beads before and after dealt in sole and binary system (named Fresh resin, resin + Cu, and resin + Cu + TC) was characterized after the full dryness, by Fourier transform infrared spectrometer (FTIR, NEXU S870, USA) and X-ray photoelectron spectroscopy (XPS, ESCALAB-2, Great Britain). All the binding energies in the XPS referred to the neutral C1s peak at 284.6 eV to compensate for the surface charging effects and systematic errors.[27] The XPS results were analyzed with XPSPEAK41 software.

3. RESULTS AND DISCUSSION

3.1. Complexation Characteristics in Aqueous Solutions. TC shows great complexation affinities to many heavy metal ions. Its molecule has three main ionizable functional groups (see Scheme S1-1 in the Supporting Information): the tricarbonylamide group at C1−C3 (first), phenolic-*β*-diketone system at C10−C12 (second), and the dimethylamine at C4 (third), which can participate in binding metal ions depending on the pH values of the solution.[28,29] The complexation between Cu(II) and TC in aqueous solutions was investigated by theoretical calculation, cupric ion-selective electrode and UV−vis spectra analysis (details in the Supporting Information, Part II). Consistent with earlier report,[1] [Cu] and [TC] were mainly in the form of [Cu-TC] complex as $[\text{Cu-TC}]^+$ and $[\text{Cu-TC}]^0$ (>80%), and a few part of [Cu-2TC] complex and free species. Furthermore, both the first and second ionizable groups were demonstrated to participate in the complexation based on UV−vis spectra results, in line with the report by Carlotti et al.[30,31] The absorbance as a function of concentrations of Cu(II) addition was also successfully fitted by a 1:1 metal−ligand coordination model.[32] In summary, Cu(II) and TC mainly complexed with each other as the 1:1 ratio in aqueous solutions, which leads to the obvious reduction of free Cu(II) and free TC in binary systems as compared with those in sole systems.

3.2. Mutual Effect in Cu(II) and TC Uptake. Three kinds of commercial resins as S984, D113, XAD-4, were selected to compare with R-AC. S984 and D113 are similar to R-AC in matrix but contain single type amine and carboxyl group, respectively.[33] Besides, XAD-4 was maturely applied in removing organic pollutants.[34,35] The mutual influence of copresence on the adsorption of Cu(II) and TC were shown in Figure 1. On one hand, when TC coexisted, the uptake of Cu(II) on R-AC and D113 just a little varied, whereas that on S984 significantly dropped. It suggested R-AC and D113 could keep holding a higher affinity to Cu(II) and capture Cu(II) from binary solution where Cu(II) was mostly chelated with TC. The results could be explained as the bonding affinities between Cu(II) and solid/aqueous ligands are in the order of carboxyl group ≫ TC ionic groups ≥ amino group.[36] On the other hand, TC adsorption on S984 and XAD-4 was also much suppressed by the coexistence of Cu(II). The reduction was probably attributed to the fact that physical interactions such as electrostatic or hydrophobic force between TC and resins were negatively influenced since [Cu-TC] complex was more positive and hydrophilic than free TC.[21,37] With much difference, although TC uptake on R-AC was approaching zero in sole systems, it kept rising with the increasing of Cu(II) copresence. Considering there was slight change of TC adsorption onto D113 with or without Cu(II) presence, it suggested that amino chain must help facilitate TC uptake onto R-AC instead of carboxyl group. Compared with commercial resins which take single type amine or carboxyl group, R-AC not only had steady uptake of Cu(II) but also enhanced removal of TC from their copolluted media, because of its dual-functional groups involving tail carboxyl group and long amine chain. The adsorption capacities to Cu(II) on R-AC were consistently highest among those on three commercial resins in all cases. The loading of TC on R-AC finally became the highest when coexisted with Cu(II) in concentration higher than 0.5 mmol/L. These observations proved the superior properties of R-AC in the synergistic coremoval of Cu(II) and TC from their combined wastewaters.

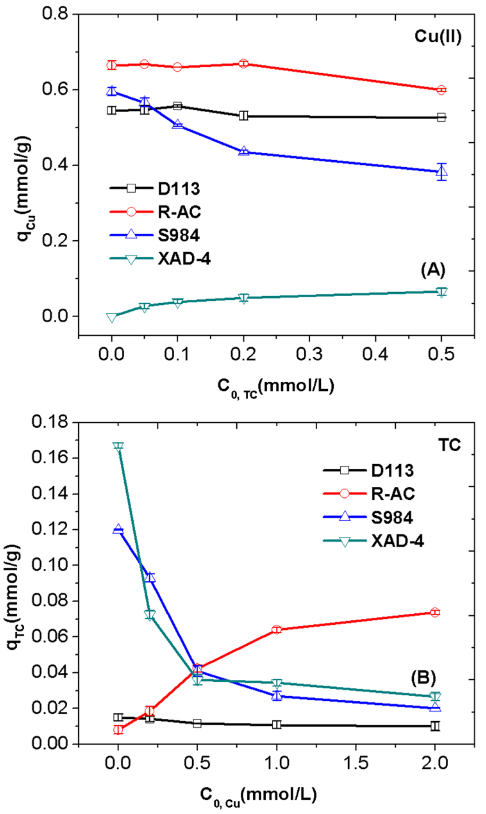


Figure 1. (A) Effect of TC coexistence on the adsorption of Cu(II) and (B) effect of Cu(II) copresence on the adsorption of TC: comparisons among R-AC and commercial resins (resin dosage = 1.0 g/L; $C_{0,\,\text{Cu}}$ was fixed at 1.0 mmol/L, $C_{0,\,\text{TC}}$ ranged from 0 to 0.5 mmol/L for A and $C_{0,\,\text{TC}}$ was fixed at 0.2 mmol/L, $C_{0,\,\text{Cu}}$ ranged from 0 to 2.0 mmol/L for B; pH 5.0; 298 K).

The adsorption isotherms of Cu(II) and TC onto R-AC in sole and binary systems were intensively studied and shown in Figure 2. As for wide range of TC concentrations, the uptake of TC was generally enhanced along with the increasing of coexistent concentrations of Cu(II). The values of q_e in binary systems were around 2−13 times of those in sole systems as shown in Figure S3-1 in the Supporting Information. The presence of TC put a negative effect on Cu(II) uptake when initial concentrations of Cu(II) were lower than 2.0 mmol/L, yet a little positive influence when higher than 2.0 mmol/L. As were shown in Table 1, the adsorption isotherms date were all better described by Langmuir equation ($R^2 > 0.99$) than by Freundlich equation, which indicated the adsorption on R-AC

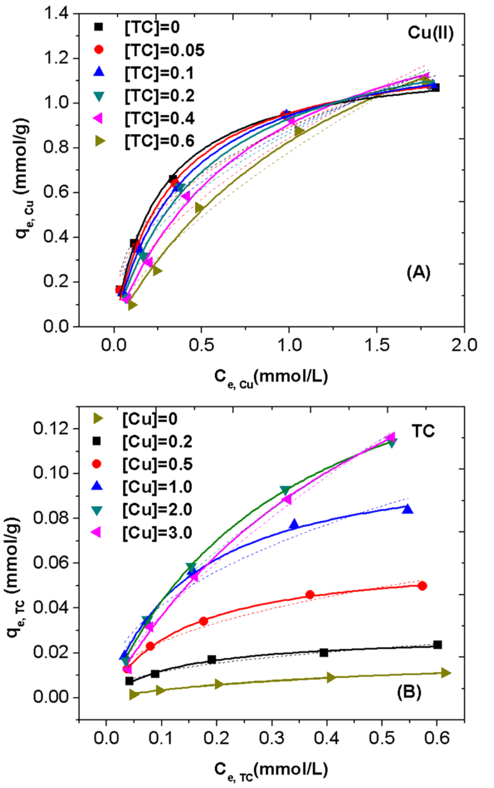


Figure 2. Adsorption isotherms of (A) Cu(II) and (B) TC in sole and binary systems fitted by Freundlich model (dashed lines) and Langmuir model (solid lines) (Resin dosage = 1.0 g/L; the initial concentrations of Cu(II) and TC were 0–3.0 and 0–0.6 mmol/L, respectively; pH 5.0; 298 K).

was likely monolayer.[38] Ultimately, the fitted values of q_{max} for TC or Cu(II) showed a positive correlation with the concentration of coexistent Cu(II) or TC, again indicating a synergistic coremoval of them onto R-AC. Similar phenomena were reported onto chitosan by Kang et al.[3] and tire powder/char by Lian et al.[39] Besides, the equilibrium pH values in Cu(II) sole or binary solutions dropped to around 3.3–4.2, probably resulting from H^+ release after Cu(II) interacted with carboxyl group.[40] Further, adsorption behaviors and surface zeta potential of R-AC as affected by pH values were investigated and are shown in Figure S3-2 in the Supporting Information. TC in sole system was hardly adsorbed onto R-AC at a wide range of pH values (2.0–8.0), which could be attributed to electrostatic repulsion between TC and R-AC.[41] However, with the presence of Cu(II), the enhancement of TC uptake occurred at various pH values, which was more obvious at pH value less than 6.0. Therefore, the change of pH value was not the reason for the enhanced adsorption toward TC.

All the results inferred that Cu(II) must participate in the enhanced adsorption of TC, acting as a bridge linking TC and R-AC. According to earlier literatures about synergistic coadsorption of heavy metal ions and organics on soils and CNTs etc., two possible bridging routes were illustrated as (I) directly adsorption of [Cu-TC] complex as a new adsorbate onto R-AC,[17,42] and (II) surface coordination between TC and Cu sites which was newly provided after Cu(II) preloading.[1,14,36] From Figure 3, it was noteworthy that the molar ratios of q_{TC}:q_{Cu} in various binary systems were all less than 0.25, far less than the complexation ratio value (1.0) of Cu(II) and TC in the aqueous phase. Therefore, TC uptake was more likely to be bridged through route II versus route I. For route II, the b[Cu-TC] complex was decomplexed along with the capture of Cu(II) by R-AC, and then a part of free TC was subsequently bridged adsorption by interaction with the newly created Cu sites on solid phase.

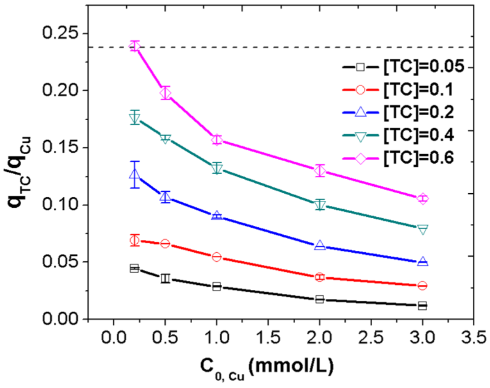


Figure 3. Value of q_{TC}/q_{Cu} in binary systems with different initial concentrations of Cu(II) and TC (resin dosage = 1.0 g/L;the initial concentrations of Cu(II) and TC were 0.25–3.0 and 0.05–0.6 mmol/L, respectively; pH 5.0; 298 K).

Table 1. Isotherm Parameters of Langmuir and Freundlich Models for Cu(II) and TC Adsorption onto R-AC in Copresence of TC and Cu(II) with Various Concentrations

		Langmuir model			Freundlich model		
target	conditions	q_{max} (mmol/g)	b (L/mmol)	R^2	K_f (mmol^{1-n}L^n/g)	$1/n$	R^2
TC	[Cu] = 0	0.011	2.07	0.995	0.012	0.390	0.987
	[Cu] = 0.2	0.029	7.128	0.993	0.029	0.404	0.960
	[Cu] = 0.5	0.063	6.999	0.998	0.067	0.428	0.953
	[Cu] = 1.0	0.109	6.520	0.995	0.117	0.455	0.948
	[Cu] = 2.0	0.189	2.951	0.999	0.177	0.617	0.981
	[Cu] = 3.0	0.241	1.792	0.997	0.189	0.711	0.988
Cu(II)	[TC] = 0	1.208	3.788	0.997	0.379	0.893	0.957
	[TC] = 0.05	1.270	3.034	0.995	0.407	0.894	0.966
	[TC] = 0.1	1.320	2.513	0.999	0.438	0.878	0.957
	[TC] = 0.2	1.418	1.911	0.994	0.488	0.865	0.945
	[TC] = 0.4	1.642	1.231	0.994	0.565	0.846	0.957
	[TC] = 0.6	2.020	0.696	0.992	0.669	0.782	0.967

3.3. Mechanisms Behind Synergistic Coremoval.

To further reveal roles of functional groups and interaction processes, both equilibrium and kinetic adsorption of Cu(II) and TC onto R-AC were comparatively investigated from sole/binary/preloading and saline systems.

3.3.1. Effect of Cu(II) Preloading. TC uptake as affected by Cu(II) in preloading and coaddition modes were studied at the same initial concentrations. From Figure 4, a markedly enhanced removal of TC appeared likewise on Resin-Cu without obvious release of Cu(II), indicative of a stronger affinity of Resin-Cu than fresh resin toward TC. Similar phenomena were obtained for the enhanced uptake of dye or atrazine onto metal coated adsorbents.[43−45] Resin-Cu could be regarded as a kind of metal−ligand resin, where the immobilized Cu kept coordination capacity to interact with TC in the solution.[44]

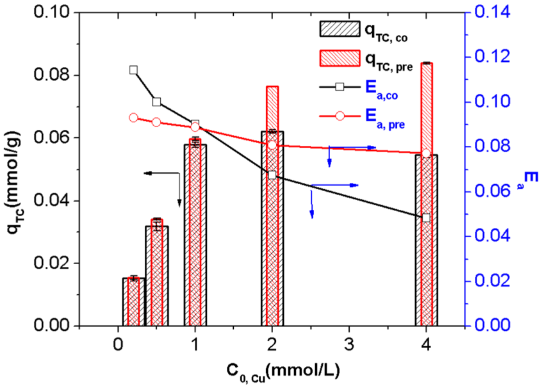


Figure 4. Adsorption amount of TC onto R-AC and E_a values as affected by Cu(II) initial concentrations in preloading (pre) and coaddition (co) mode (resin dosage = 1.0 g/L; $C_{0,\ TC}$ was fixed at 0.2 mmol/L, $C_{0,\ Cu}$ ranged from 0.2 to 4.0 mmol/L; 50 mL; pH 5.0; 298 K).

Moreover, although there was almost no difference in Cu(II) uptake in the two adsorption modes, the amount TC removal was found to be larger in Cu preloading mode than that in coaddition mode with the same initial concentration of Cu(II), especially at Cu(II) concentration higher than 1.0 mmol/L. The values of E_a which described the enhanced amount contributed by per mole Cu in the resin were calculated as eq 7.

$$E_{\mathrm{a,co}} = \frac{q_{\mathrm{TC,co}} - q_{\mathrm{TC,cont}}}{q_{\mathrm{Cu,co}}},\ \text{or}\ E_{\mathrm{a,pre}} = \frac{q_{\mathrm{TC,pre}} - q_{\mathrm{TC,cont}}}{q_{\mathrm{Cu,co}}}\ldots \tag{7}$$

Where co, pre, and cont refer to coaddition mode, preloading mode, and non-Cu mode, respectively.

With the increase in Cu(II) concentration, values of $E_{\mathrm{a,\ co}}$ gradually dropped to lower values than those of $E_{\mathrm{a\ pre}}$. It suggested there was more efficient utilization of Cu sites in preloading mode than in coaddition mode when TC coexisted with higher concentration Cu(II). Obviously, although the total initial concentration of each adsorbate in aqueous solutions was the same in the two modes, most TC existed as the form of [Cu-TC] complex in coaddition mode.[1] As described in the mechanistic equations (eqs 8−11):

$$\text{free Cu(II) (part a)} + \overline{\text{resin}} \Leftrightarrow \overline{\text{resin}-\text{Cu}}\ldots \tag{8}$$

$$[\text{Cu}-\text{TC}] \overset{\overline{\text{resin}}}{\Longleftrightarrow} \text{free Cu(II) (part b)} + \text{free TC}\ldots \tag{9}$$

$$\text{free Cu(II) (part b)} + \overline{\text{resin}} \Leftrightarrow \overline{\text{resin}-\text{Cu}}\ldots \tag{10}$$

$$\overline{\text{resin}-\text{Cu}} + \text{free TC} \Leftrightarrow \overline{\text{resin}-\text{Cu}-\text{TC}}\ldots \tag{11}$$

R-AC owned high affinity to free Cu(II), which were divided into "part a" from initial solutions and "part b" fm decomplexing of [Cu-TC] complex (eqs 8−10). Under the same TC condition, with the increase in coexistent Cu(II), more free Cu(II) in solutions (part a) competitively interacted with R-AC (eq 8) and suppressed the decomplexation of [Cu-TC] complex (eq 9). Less TC was released from the complex, adverse to the bridging interaction between TC and Cu sites (eq 11).

3.3.2. Kinetic Processes. Kinetic studies can help describe the whole interaction processes.[46] As shown in Figure 5, the kinetic data were described with pseudo-first-order model and pseudo-second-order model. The kinetic parameters were listed in Table 2. In all cases, the pseudo-second-order model fit better with higher correlative coefficients (R^2 > 0.99). At the initial stage (0−30 min), TC concentration remained almost unchanged, whereas Cu(II) was quickly adsorbed with a higher initial adsorption rate ($h_{\mathrm{Cu}} = 2{-}5h_{\mathrm{TC}}$), suggesting that Cu(II) was adsorbed prior to TC. Cu (II) uptake was much tardier in binary system in comparison with the corresponding sole system. The adsorption rate constant K_2 kept in the order of sole system > binary system. Moreover, TC adsorption in preloading mode took much less time to reach equilibration than that in coaddition mode (800 min earlier). The values of K_2 and h in the preloading system were about 2 times those in the binary system. These observations could also be explained

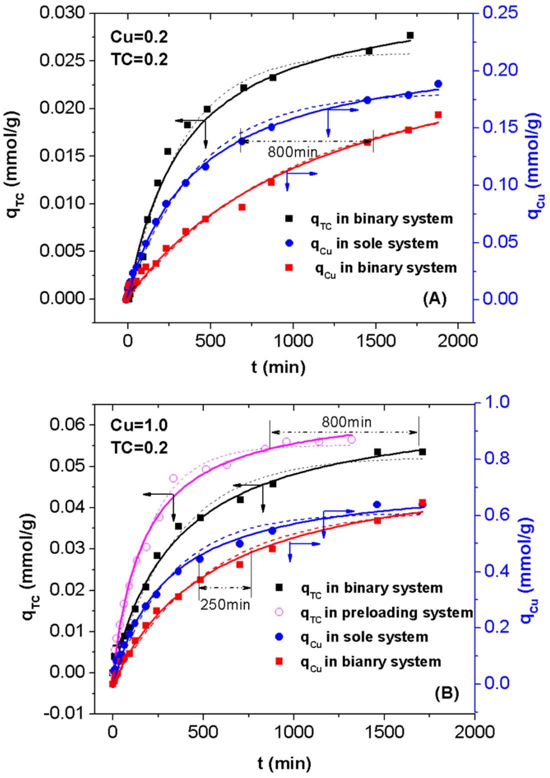


Figure 5. Kinetic curves of Cu(II) and TC adsorption on R-AC in different systems fitted by first-order kinetic equation (dashed lines) and second-order kinetic equation (solid lines) (dosage = 1.0 g/L; $C_{0,\ \mathrm{Cu(II)}}$ in each system was (A) 0.2 and (B) 1.0 mmol/L; $C_{0,\ TC}$ was all set as 0.2 mmol/L in systems containing TC; pH 5.0; 298 K).

Table 2. Kinetic Parameters for the Adsorption of Cu(II) and TC on R-AC[a]

systems[b]		pseudo-first-order model			pseudo-second-order model			
	targets	$q_{e,\text{ fit}}$	k_1	R^2	$q_{e,\text{ fit}}$	k_2	h	R^2
(a)	Cu in SS	0.181	0.024	0.993	0.225	0.01	0.0005	0.998
	Cu in BS	0.180	0.001	0.984	0.252	0.003	0.0002	0.991
	TC in BS	0.026	0.003	0.982	0.0325	0.091	0.0001	0.990
(b)	Cu in SS	0.609	0.003	0.977	0.737	0.005	0.0028	0.990
	Cu in BS	0.625	0.002	0.988	0.816	0.002	0.0013	0.995
	TC in BS	0.0523	0.003	0.988	0.0653	0.043	0.0002	0.992
(c)	TC in PS	0.055	0.005	0.990	0.0655	0.085	0.0004	0.993

[a] The initial concentrations of Cu (II) and TC were 0.2 and (a) 0.2 and (b, c) 1.0 and 0.2 mmol/L, respectively. [b] SS, BS, and PS are abbreviation of sole system, binary system, and preloading system.

as eqs 9−11. [Cu-TC] decomplexing instead of [Cu-TC] adsorption occurred in binary systems, which slowed down the adsorption of Cu(II) as well as the bridging interaction toward TC.

3.3.3. Effect of Ionic Strength. High ionic strength would shield carboxyl sites in a certain degree, since the strong competition of high concentrated cations with target pollutant ions.[47,48] Various levels of NaCl were coadded with Cu(II) and TC to alter the ionic strength of solutions in saline systems. The adsorption performance of R-AC and commercial resins in saline systems was shown in Figure 6 and Figure S3-3 in the Supporting Information. As expected, Cu(II) adsorption onto D113 obviously decreased at high ionic strength. However, the adsorption of Cu(II) onto R-AC kept increasing with the increase of NaCl levels independent of the presence of TC, maximum by 20%. As similar trend was found for Cu adsorption onto S984 and R-NH_2 (precursor amine resin in the former synthetic step), the novel phenomenon was only related to amine sites (−NH−/−NH_2) in R-AC, S984 and R-NH_2. Based on HSAB theory, coordination could be easily formed between Cu(II) and amino group, in which N atom shares its lone pair of electrons with Cu(II) to form a bond.[20,49] The hydrogen bonding interaction among amine unites and water molecular could be weakened in high ionic strength, creating more available amine sites for Cu(II).[50] Yet, Liu et al. found the increase in ionic strengths lowered the positive zeta potentials of amine-modified adsorbents and regarded it as the reason for the enhancement of Cu(II) adsorption.[51]

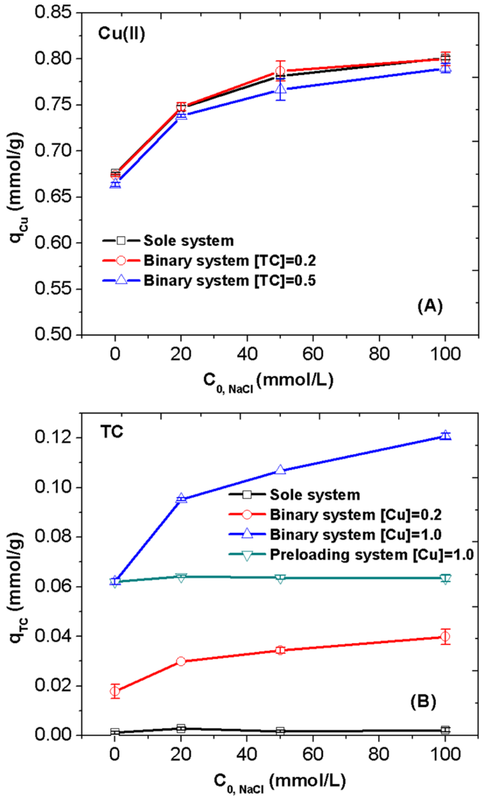


Figure 6. Influence of ionic strength on the adsorption of (A) Cu(II) and (B) TC onto R-AC in different systems (resin dosage = 1.0 g/L; (A) $C_{0,\text{ Cu}}$ was fixed at 1.0 mmol/L, $C_{0,\text{ TC}}$ was 0, 0.2, and 0.5 mmol/L for; and (B) $C_{0,\text{ TC}}$ was fixed at 0.2 mmol/L, $C_{0,\text{ Cu}}$ ranged from 0, 0.2, and 1.0 mmol/L; NaCl levels ranged from 0 to 100 mmol/L; pH 5.0; 298 K).

The impact of ionic strength on TC adsorption was very different in sole, binary and preloading systems. Ionic strength exerted little influence on TC uptake in sole system and Cu(II) preloading systems, but a remarkable positive effect in binary system where Cu(II) and TC coexisted in aqueous phase. The adsorption amount of TC in binary system at 100 mmol/L NaCl had reached a maximum of 2 times that in the binary system without addition of NaCl. It meant that the great increase in TC adsorption in saline system was just attributed to the increase in [NH-Cu] solid interaction at higher ionic strength. Therefore, [NH-Cu] site was directly proved as the leading Cu-site for bridging interaction with TC. Furthermore, the mole ratio of increment of Cu and TC uptake (Δq_{Cu}:Δq_{TC}) in various saline systems compared with corresponding none salt systems was calculated as 2.1−2.5. It could be deduced that the possible bridging stoichiometric ratio ([NH-Cu]:TC) was 2:1 in view of sites effectiveness.[52] Besides, the investigation above also proved the application feasibility of R-AC in coremoval of Cu(II) and TC, even from high saline wastewaters.

3.3.4. Confirmation with FTIR and XPS. (1). FTIR Spectra. FTIR spectra of R-AC dealt with Cu(II) and Cu+TC solutions were present together with that of fresh resin in the Supporting Information (part I, Figure S1-1). After the loading of Cu(II), the vibration of −NH group at 1562.4 cm^{-1} was weakened and peak at 1161.0 cm^{-1} has shifted to 1172.2 cm^{-1}, indicative of the interaction between Cu(II) and −NH−.[38,53] Moreover, the stretching bands of −C−O, −C=O and δOH associated with carboxyl group at 1437.1, 1389.5, and 604.9 cm^{-1} exhibited a clear shift to 1455.1, 1385.9, and 609.9 cm^{-1}.[49] Except for the above changes, a new peak was located at 1103.0 cm^{-1} in sample resin + Cu, most likely due to the formation of new bond between Cu(II) and amine or carboxyl. As for resin + Cu + TC, the FTIR curve was closely similar to that of R + Cu. Yet

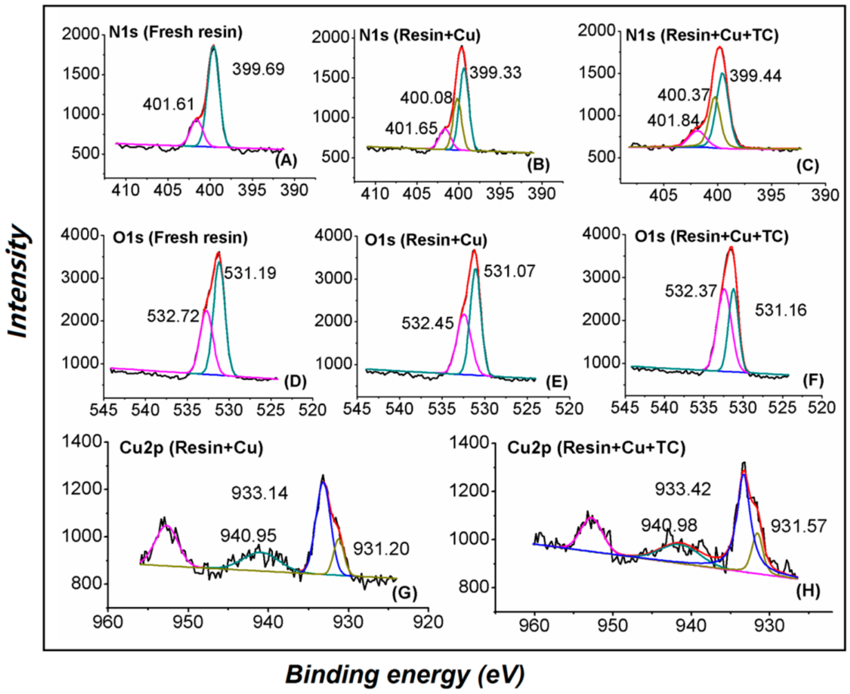


Figure 7. XPS spectra of O1s, N1s, and Cu2p in the samples of fresh resin, resin + Cu, and resin + Cu + TC.

there was a red shift of the new band from 1103.0 to 1108.6 cm^{-1}, proving a bridging interaction between TC and Cu-sites.

(2). XPS Spectra. XPS characterization of the resin samples was also conducted to check state changes of N, O and Cu element in each sample. The high-resolution O1s, N1s, Cu2p spectra as well as the wide scans of fresh resin, resin + Cu and resin + Cu + TC are shown in Figure 7.

The XPS spectra of N1s (Figure 7A–C) were deconvoluted as two peaks with binding energy of 399.69 and 401.61 eV, corresponding to the N atom in secondary amine (−NH−) and imine (C−N−C), respectively.[54] After Cu(II) uptake, the peak of secondary amine shifted to 399.33 eV and a new peak at 400.08 eV appeared, without obvious change of imine peak. It directly proved the adsorption interaction between Cu(II) and long amine chain (−NH−), in which N atom donated a lone pair electrons to form the covalent bond N−Cu, causing the reduction of electron cloud density and locating at a higher binding energy.[54,55] Furthermore, as the sample of resin + Cu + TC, similar change occurred for peak of −NH−. However, the new peak for N1s in [NH-Cu] was located at a higher binding energy (400.37 eV) than that of resin + Cu sample, confirming the conclusion that [NH-Cu] site participated in bridging interaction with TC. Additionally, peak at 401.84 eV may result from the overlying of tertiary amine in TC and the resin.

The O1s spectra of the resin (Figure 7D–F) were dissected into two kind of O1s at 531.19 and 532.72 eV, mainly associated with C═O and −OH of carboxyl.[56] After Cu(II) adsorption, the bonding energy of them has decreased by 0.12 and 0.27 eV. Compared with the changes of amine, smaller shift of carboxyl peaks suggested that the interaction between Cu(II) and carboxyl was probably a kind of ionic exchange.[48] No obvious shift of O1s appears in resin + Cu + TC relative to resin + Cu, except that the loading of TC molecules containing many −OH groups strengthened the intensity of peak at 532.37 eV.

As expected, Cu2p peaks were newly added at 925−945 eV in the wide scan of R + Cu and R + Cu + TC samples compared with fresh resin (see Figure S3-4 in the Supporting Information, Part III).[57] For the resin + Cu sample, there was one main peak for Cu $2p_{3/2}$ at 933.14 eV and a shakeup satellite for Cu $2p_{1/2}$ at 940.95 eV, which were representative of the oxidation state (+2) of copper, especially for copper chloride (the copper salt used in this study).[3,58] After TC adsorption, the two branch peaks in Cu $2p_{3/2}$ have shifted by 0.28 and 0.37 eV, directly proving the interaction between Cu(II) and TC. As discussed above, Cu(II) captured by the amine site of resin maintained the coordination ability to TC from aqueous solution as a bridge in the [NH-Cu-TC] ternary complex.

3.4. Mechanistic Simulation. The above investigations in preloading, kinetic and saline studies suggested that decomplexing-bridging was revealed as the leading mechanism for the enhancement in TC uptake from the binary system, orderly including [Cu-TC] decomplexing (step I) and Cu-sites bridging for TC (step II). Tail carboxyl group and long amine chain in R-AC played different roles during the whole synergistic coremoval. Step I was key to offering free Cu and free TC. Carboxyl group (−COOH) played an important role on decomplexing of [Cu-TC] as it has higher bonding affinities than TC ionic groups toward Cu(II) through ion exchange. Although both carboxyl and amine group were involved in Cu(II) uptake as proved by FTIR and XPS, only Cu(II) that interacted with amine group ([NH-Cu]) remained coordination ability to TC from aqueous solution as a bridge in [NH-Cu-TC] ternary complex. The bridging stoichiometric ratio ([NH-Cu]: TC) possibly was 2:1. The proposed interaction processes behind synergetic coremoval was illustrated in Figure 8A. According to earlier reports, Cu could adopt three, four, five, and six coordination geometry.[59] Per unit of the [NH-Cu] site is likely to be centered by three or four amine ligands and one ionizable group of TC. Thus, several possible bridging configurations were proposed in Figure 8B.

3.5. Sequential Recovery and Resin Regeneration. The regeneration of the adsorbent is important for lowering the cost of the adsorption process and reutilization of toxics in

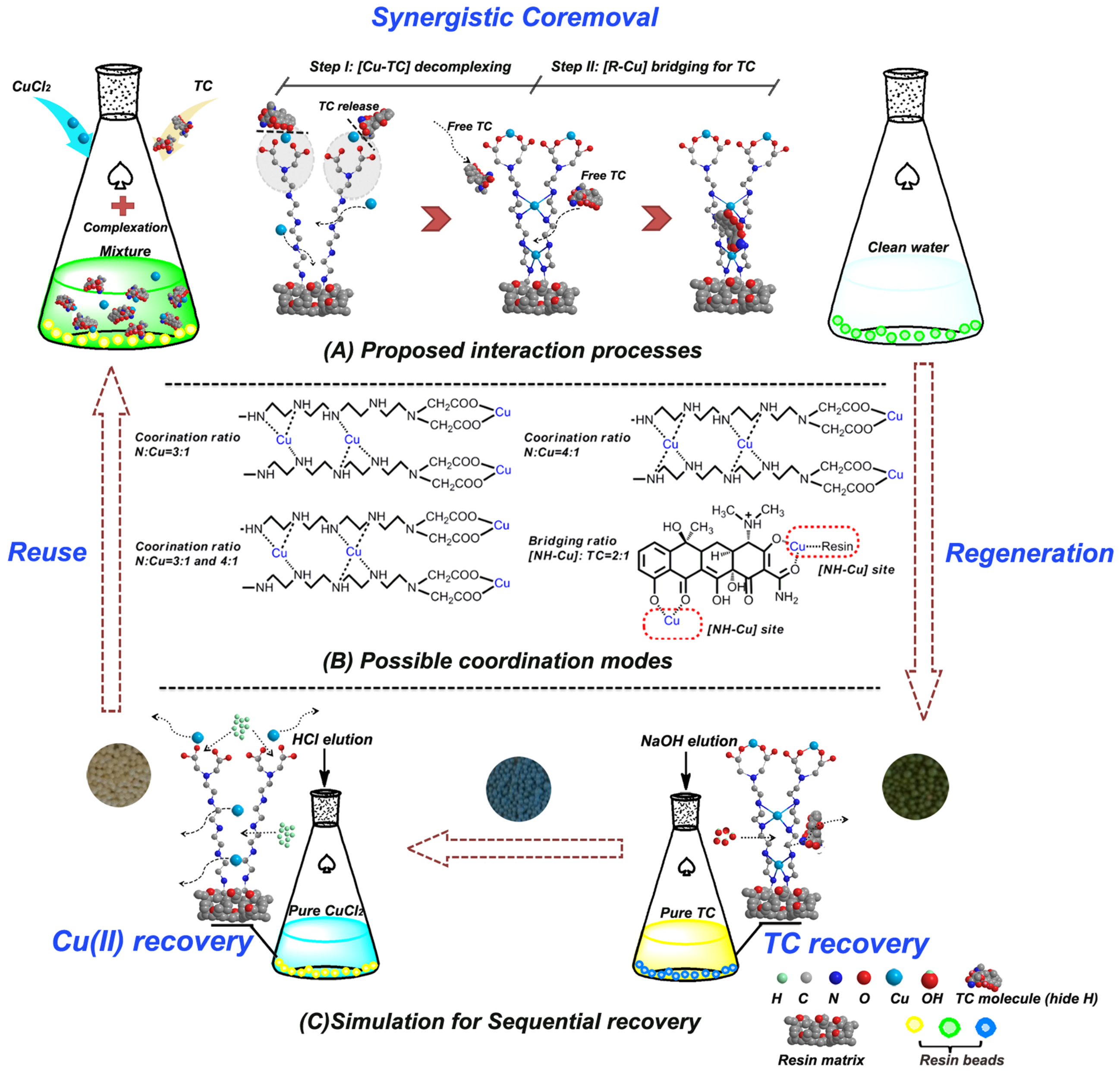


Figure 8. Mechanistic simulations (including (A) interaction processes in synergistic coremoval, (B) possible coordination modes, and (C) sequential recovery).

wastewaters. HCl and NaOH solutions were usually applied to recovery adsorbates and regenerate adsorbents. The recovery ratios of Cu(II) and TC using different eluents are listed in Table S3-1 in the Supporting Information. Only with dilute NaOH solution (0.01 mol/L) was one kind of adsorbate recovered with high efficiency without any release of the other one. Thus, the novel technique, in which 0.01 mol/L NaOH was first used to recover TC and then 1 mol/L HCl was applied to recover Cu(II), has been successfully implemented to sequentially obtain both pure resources and regenerate all resin beads. Desorption mechanisms were illustrated in eqs 12 and 13 and Figure 8C. In the alkali stage, with 0.01 mol/L NaOH (pH ∼12), TC binding to R-Cu would be replaced by a large amount of OH^- without release of Cu. As shown earlier in Figure S2-1 in the Supporting Information, the dominant species in mixture aqueous solution were $Cu_3(OH)_4^{2-}$, $Cu(OH)_2$ (aq), $Cu(OH)_3^-$, TC^- at pH 12. However, once pH value above 12, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ sprung up, leading to the shift of Cu(II) from resin-phase to liquid-phase because of the electrostatic repulsion between R-AC and Cu species. More than 96.9% of TC in resin was recovered and thus pure TC was obtained. Subsequently, in acid stage, high concentrated proton quickly replaced Cu(II) for protonating both carboxyl site and amine site.[40] More than 99.3% of Cu (II) in solid phase was desorbed. Ultimately, R-AC was regenerated and reusable. From Table 3, it was indicated that R-AC had stable excellent performance for coremoval and sequentially recovery Cu(II) and TC after five cycles of adsorption and desorption procedures.

$$\overline{\text{resin}-\text{Cu}-\text{TC}} + \text{NaOH} \Rightarrow \overline{\text{resin}-\text{Cu}-\text{OH}} + \text{TC}-\text{Na}... \tag{12}$$

$$\overline{\text{resin}-\text{Cu}-\text{OH}} + 2\text{HCl} \Rightarrow \overline{\text{resin}-\text{H}} + \text{CuCl}_2 + \text{H}_2\text{O}... \tag{13}$$

Table 3. Coremoval and Sequential Recovery of Cu(II) and TC on/from R-AC

	coremoval (mmol/g)		alkali stage (%)		acid stage (%)	
cycle	Cu(II)	TC	TC	Cu(II)	Cu(II)	TC
I	0.671	0.061	96.8	[a]	98.8	
II	0.680	0.059	96.9		99.3	
III	0.657	0.056	95.8		98.9	
IV	0.648	0.054	96.2		99.2	
V	0.631	0.053	96.0		99.1	

[a] Empty entries means the value was below the limit detection.

3.6. Practical application of R-AC. Concerning its practicability, R-AC was used to remove real combined pollutants of Cu(II) and TC in ultrapure water, effluent water (from sewage treatment plant), and river water. The corresponding results are tabulated in Table 4. It could be found that the adsorption amounts of both pollutants were in the order of effluent water > river water > ultrapure water, which may be attributed to high ionic strength from chlorate and sulfate in real waters, as consistent with the results of the above saline experiments. Moreover, TC owned stronger affinity than nature organic matters for Cu bridging interaction.[60] The maximum adsorption efficiency could reach 99.5% for Cu(II) and 94.4% for TC from effluent water when the initial concentrations of Cu(II) and TC were 32 and 4.9 mg/L, respectively. These results indicated that R-AC was suitable to be applied to coremoval of Cu(II) and TC from real samples.

4. CONCLUSION

Synergistic coremoval and sequential recovery toward Cu(II) and TC was obtained with the novel chelating resin R-AC. Owning dual-functional groups (tail carboxyl group and long amine chain), R-AC had steady uptake toward Cu(II) from solutions containing TC, whereas the removal of TC on R-AC was markedly strengthened (~13 times) in the copresence of Cu(II). Decomplexing-bridging was the leading mechanism for synergetic removal: carboxyl group played an important role in [Cu-TC] decomplexing; then [NH-Cu] sites made a bridging interaction with free TC with a 2:1 bridging mole ratio ([NH-Cu]: TC). Finally, about 96.9% of TC and 99.3% of Cu(II) were sequentially recovered with 0.01 mol/L NaOH followed by 1.0 mol/L HCl. The excellent trends in this work imply an attractive applicative potential of R-AC in an green, simple, low-cost, and integrated treatment technology for wastewater containing Cu(II) and TC.

ASSOCIATED CONTENT

Supporting Information

Additional methods, description, and figures/tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge generous support provided by the National Natural Science Foundation of P.R. China (Grant 51078178), the Resources Key Subject of National High Technology Research & Development Project (863 Project, Grants 2009AA06Z315 and SQ2009AA06XK1482331) of P.R. China, the State Key Program of National Natural Science (Grant 50938004), and the Discipline Crossing Foundation of Nanjing University.

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Table 4. Practical Application of R-AC in Coremoval of Cu(II) and TC in Different Waters[a]

solutions (mmol/L) (mg/L)[b]		1 g/L dosage				3 g/L dosage			
		$C_{e,\,Cu}$	AE_{Cu}	$C_{e,\,TC}$	AE_{TC}	$C_{e,\,Cu}$	AE_{Cu}	$C_{e,\,TC}$	AE_{TC}
$C_{0,Cu}$ = 0.25 (16) $C_{0,TC}$ = 0.01 (4.9)	UW	4.1	71.2	2.5	46.0	0.3	97.8	1.4	70.6
	EW	1.5	89.3	1.8	69.2	0.1	99.3	0.5	91.7
	RW	1.4	89.9	2.1	63.1	0.1	99.2	0.6	89.5
$C_{0,Cu}$ = 0.5 (32) $C_{0,TC}$ = 0.01 (4.9)	UW	10.2	63.2	2.2	54.2	0.4	98.6	1.1	78.1
	EW	6.8	75.5	1.4	76.4	0.1	99.5	0.3	94.4
	RW	7.0	74.6	1.6	70.6	0.2	99.4	0.4	93.2
$C_{0,Cu}$ = 0.5 (32) $C_{0,TC}$ = 0.02 (9.8)	UW	10.7	61.0	5.2	45.2	1.4	94.9	3.8	59.7
	EW	7.5	73.0	4.2	62.7	0.4	98.4	2.3	79.6
	RW	7.4	73.3	4.5	57.6	0.4	98.6	2.4	77.5
$C_{0,Cu}$ = 1.0 (64) $C_{0,TC}$ = 0.05 (24)	UW	29.3	47.6	14.7	40.5	3.9	93.0	12.9	47.8
	EW	24.1	55.6	12.9	51.2	1.2	97.9	5.9	77.4
	RW	25.7	53.6	14.1	45.1	0.8	98.5	6.1	76.4

[a] The units of C_e and AE are mg/L and %, respectively. [b] UW, EW, and RW are ultrapure water, effluent water, and river water, respectively; their total organic matter (TOC) was ~0, ~2.967, and ~5.892 mg/L for water in UW, EW, and RW, respectively. Conductivity was 10.1, 4023, and 4950 μS/cm for water a, b, c respectively.

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