Efficient removal of Cu(II) and citrate complexes by combined permanent magnetic resin and its mechanistic insights

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HIGHLIGHTS

- Both permanent-magnetic MAER and MCER were synthesized in pilot scale.
- The [Cu-CA] complexes were efficiently removed by combined magnetic resins.
- Complex-adsorption of $Cu_2L_2^{2-}$ and CuL^- onto MAER greatly enhanced the Cu uptake.
- The synthetic magnetic resins exhibited superior reusability performance.
- The nanometer copper powders were recovered from the desorption liquid.

GRAPHICAL ABSTRACT
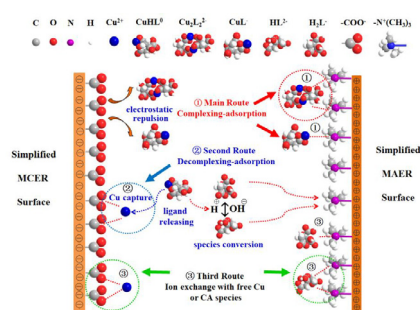
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ABSTRACT

Owing to the enormous threat from anthropogenic contamination in water resources, the effective control of heavy-metal pollution has become increasingly important. In this study, the combination of permanent magnetic anion exchange resin (MAER) and magnetic cation exchange resin (MCER) was employed to efficient removal of Cu(II) and citrate acid (CA). The removal mechanisms were systematically investigated by batch adsorption experiments, and also certificated by species distribution calculation, kinetic tests and solid-phase characterizations. The presence of CA markedly inhibited the adsorption of Cu(II) onto MCER, while the co-existing Cu(II) was beneficial for CA uptake onto MAER. With the increase of Cu(II) concentrations, the adsorption amount of CA onto MAER gradually increased and reached a plateau, with promotion rates ranging of 24.4%–47.9%. For combined magnetic resins treatment, as the MAER dosage increased from 0 to 1.50 g/L, the removal efficiencies of CA and Cu(II) were enhanced from 1.1% and 33.2% to 98.8% and 99.1%, respectively. The anionic [Cu-CA] complexes (mainly CuL^- and a small fraction of $Cu_2L_2^{2-}$) in bi-solutes system possessed higher affinity than free-CA species towards MAER, resulting in a mutual enhancement of Cu(II) and CA uptake. Both decomplexing-adsorption of Cu(II) from neutral Cu species ($CuHL_0$) by MCER and direct complex-adsorption of anionic complex species (CuL^- and $Cu_2L_2^{2-}$) by MAER were proposed as the mechanisms for synergetic removal of CA and Cu(II) in combined processes. Furthermore, nanoscale Cu powders were recovered from the desorption liquid by chemical reduction. The combined magnetic resins exhibited superior reusability over five repeated cycles, indicating their great potential in treatment of complexing heavy metal-organic acid wastewaters.

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1. Introduction

Heavy metal ions (HMIs) are widely applied in electroplating, metal finishing and mineral processing industries. Unlike organic pollutants, HMIs are highly toxic and non-degradable, and could cause serious damage to human health and the environment [1–3]. Besides, various organic acids, such as citric acid (CA), oxalic acid, ethylenediamine tetra acetic acid, and ammonia triacetic acid etc., can act as passivators or stabilizers for chelating HMIs [4,5]. The organic acids are found ubiquitously in many natural environments at levels of as high as $1 \times 10^{-5} - 1 \times 10^{-4}$ M; the concentration of oxalic acid being the highest (0.01–1 mM) [6,7]. The formed HMIs-organic complexes are highly soluble and stable over a broad pH range, which could seriously decrease the efficiency of traditional treatment processes such as chemical precipitation and coagulation, and result in increasing ecological risks of recycling wastewater [8–10]. Therefore, the effective removal of HMIs-organic acid complexes from wastewater has attracted much attention.

Typical wastewater treatment processes for these HMIs-chelating complexes involve three steps [11–13]: (1) pretreatment chemistry using oxidizers to break down complexed HMIs and precipitate metal hydroxides; (2) microfiltration of the resulting sediments; and (3) ion exchange to remove residual HMIs. However, these hybrid techniques suffer the drawbacks of secondary pollution, poor stability, and complicated operation [14–16]. By contrast, adsorption has been considered as an effective and attractive technology for removing above-mentioned pollutants due to its relatively simple, green and recyclable way. Among various adsorbents, synthetic resins have proven to have the advantages of high sorption efficiency and facile modification of functional groups, and exhibit desirable performance for complex pollutants removal [17–19]. Ling et al. [11,18] proved that the polystyrene-based polyamine resin and polyaminoacetic acid resin can efficiently remove HMIs-CA complexes from synthetic wastewater. Both complex-adsorption and surface decomplexing-bridging were proposed as the potential mechanisms. However, adsorption caused by co-ordination onto these resins is generally slow in adsorption kinetics in comparison with the electrostatic attraction process. Even worse, the regeneration of saturated resins needs high concentrations of acid solution (> 10% HCl or HNO_3), which hinders its applications in real wastewater treatment [11,20].

Adsorption by ion-exchange resin is regarded as one of the most effective separation and purification processes for its facile desorption and superior reusability [5,21]. Especially, permanent-magnetic ion exchange resin is small in particle size and can be separated easily without an external magnetic field, and can be used in a continuous process with partial resin regeneration, which obviously improves treated wastewater flux and reduces operating costs [22,23]. Generally, ion exchange resin can only target either cation or anion, not both simultaneously. Boyer et al. [23,24] tried to combine the magnetic anion exchange resin MIEX-Cl and the magnetic cation exchange resin MIEX-Na for domestic wastewater treatment, that meant, two opposite electrical magnetic resins were applied in a single fully-mixed reactor.

These combined magnetic resins could remove about 70% of dissolved organic matters and 55% of hardness. Besides, Arias-Paic et al. [25] used a gel-type strongly acidic cation exchange resin together with MIEX-Cl for domestic effluent treatment, the hardness removal efficiencies were ranging from 88% to 98%. Fu et al. [26] studied the effects of both magnetic anion- and cation-exchange resins on removal of Cu(II), Ni(II) and tannic acid complex pollutants. Under optimal conditions, the removal rates of Cu(II), Ni(II) and tannic acid were 92.1%, 94.8% and 88.4%, respectively. Therefore, the combination process of magnetic anion/cation-exchange resins may separately remove different electrical pollutants and achieve high-efficiency purification of wastewaters. The co-existence of HMIs and organic acids (with N or O electron donating groups) can form various carboxyl-complexes, which markedly suppress HMIs adsorption due to either competition or shielding of functional sites [27,28]. To date, the intrinsic mechanisms behind the adsorption of HMIs-organic acid complexes by combined resins are not well understood. Similarly, almost no studies involve the reusability of magnetic resins as well as the recovery of HMIs from desorption liquid for resource utilization.

Since Cu(II) and CA are widely detected in the wastewater of surface treatment industry, they were chosen as the model pollutants in this study. The combined magnetic anion-exchange resin (MAER) and magnetic cation-exchange resin (MCER) were applied to remove [Cu-CA] complexes in bi-solutes solutions. Both MAER and MCER used in this study were synthesized in pilot scale. The interactive behaviors and mechanisms in co-removal of [Cu-CA] complexes were systematically elucidated. The regeneration and reusability performances of combined resins were also evaluated. Additionally, the recovery of copper from the resin desorption liquid was considered.

2. Materials and methods

2.1. Materials

Glycidyl methacrylate, methylacrylate (MA, > 99%), benzoyl peroxide (BPO), divinylbenzene (DVB, 63.3 wt%), γ-Fe_2O_3, thiourea dioxide (TD) and trimethylamine hydrochloride etc., used in this work were of analytical grade. The coupling agents (TEOS and DMDES) were obtained by Nanjing Capture Chemical Co., Ltd. Sodium citrate, Cu $(NO_3)_2$, NaOH, HCl, HNO_3, $Ca(NO_3)_2$, Na_2SO_4, K_3PO_4, NaCl and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Diallyl itaconate (DAI), as a hydrophilic crosslinker, was synthesized and purified according to our previous study (see Text S1) [29]. The commercial anion-exchange resin D201 and cation-exchange resins D001 were supported by Jiangsu Jinkai Resin Chemical Co. Ltd (China).

The synthesis routes and general structures of MAER and MCER were shown in Supplementary Text S2, and were similar to our previous literatures [29,30]. Both MAER and MCER were synthesized at pilot-level using a 50 L reactor (Fig. S1). The physicochemical characteristics of tested resins including MAER, MCER, D201 and D001 were tabulated in Table 1. All resins had relatively low surface area and small pore

Table 1
Physicochemical characteristics of four tested resins.

Parameters	MAER	MCER	D201	D001
Matrix structure	Polyacrylate	Polyacrylate	Polystyrene	Polystyrene
Functional groups	$-CH_2N^+(CH_3)_3 \cdot Cl^-$	$-CH_2COO^- \cdot Na^+$	$-CH_2N^+(CH_3)_3 \cdot Cl^-$	$-CH_2SO_3^- \cdot Na^+$
Anionic exchange capacity (mmol/g)	2.62	–	3.80	–
Cationic exchange capacity (mmol/g)	–	8.70	–	4.40
Water content (%)	55–60	45–50	50–55	45–55
Diameter (μm)	80–250	80–200	250–600	250–600
Average pore size (nm)	26.40	8.60	ND[a]	ND
BET specific surface area(m^2/g)	0.78	2.54	ND	ND

[a] "ND" in Table 1 means not determined.

volume but high contents of functional groups, suggesting that the adsorption processes were mainly driven by surface chemical interactions. Detailed characterizations of both MAER and MCER resins were performed and displayed in supplementary Figs. S1–S5 and Text S3.

2.2. Batch adsorption study

2.2.1. Single resin adsorption

The adsorption equilibrium experiments were conducted by mixing 0.100 g of MAER or 0.025 g of MCER with 100 mL of different molar ratios of Cu(II) and CA solutions in 250 mL conical flasks, and shaking in a thermostatic oscillator at 293 K, 150 rpm for 24 h to reach equilibrium. The initial pH of the solutions was adjusted to constant value of 5.0. All experiments were performed in triplicates. The concentrations of Cu(II) were measured with an atomic adsorption spectrophotometer (AAS, THERMO, USA). The concentrations of CA were analyzed by ion chromatography (ICS-1100, DIONEX, USA) with an IonPac AS11-HC (4 mm × 250 mm) column. The 35 mM KOH solution was used as eluent at a flow rate of 1.0 mL/min. All water samples were filtered through the 0.22 μm membrane before testing. For CA determination, the samples were pretreated by the Na-Column (Dionex Onguard II) with the flow rate about 2.0 mL/min to remove the Cu(II) from [Cu-CA] complexes.

The amount of adsorbate on resin q_e (mmol/g) was estimated according to the Eq. (1).

$$q_e = (C_o - C_e) \cdot V / W \qquad (1)$$

where, V and W are the solution volume (mL) and dried resin mass (g), respectively. C_o and C_e are the adsorbate concentration (mmol/g) at initial and equilibrium, respectively.

2.2.2. Combined resin adsorption

Different amounts of MAER and MCER were introduced into conical flasks with 100 mL of various concentrations of mixed Cu/CA solution (molar ratio of 1:1). One set of experiments was fixing the MCER amount at 0.025 g, along with the amount of MAER increasing from 0 to 0.160 g. The other set of experiments was fixing the MAER amount at 0.025 g or 0.050 g, while the MCER amount increased from 0 to 0.100 g. The flasks were shaken at identical conditions (initial pH 5.0, 293 K, 150 rpm) for 24 h. All experiments were carried out in triplicates and the adsorption amount was calculated by the Eq. (1).

2.2.3. Adsorption kinetics

For adsorption kinetic experiments, 1.000 g of MAER or 0.250 g of MCER, together with 1000 mL of different metal to ligand molar ratio of Cu(II) and CA solution, were mixed in 2 L conical flasks. The flasks were shaken at identical conditions (initial pH 5.0, 293 K, 150 rpm) for 24 h. At different time intervals, 2 mL of supernate was withdrawn for residual Cu(II) and CA concentration measurements.

2.2.4. Effect of pH and salinity

The effects of solution pH on Cu(II) and CA adsorption were examined by varying the pH from 2.5 to 7.0. For each pH condition, 0.100 g of MAER or 0.025 g of MCER was mixed with 100 mL of Cu/CA solution (molar ratio of 1:1) in a series of conical flasks, respectively. The solution pH was adjusted with 1 M HNO$_3$ or NaOH solution. The influences of ionic strength on Cu(II) adsorption in binary Cu/CA system were determined in the background of NaCl (20 mmol/L), Ca$_2$(NO$_3$)$_2$ (10 mmol/L), Na$_2$SO$_4$ (10 mmol/L) or K$_3$PO$_4$ (2 mmol/L). Other conditions were similar as the pH-series experiments except for the pH change. All flasks were shaken in an orbital shaker at initial pH 5.0, 293 K for 24 h.

2.2.5. Reusability study

Five adsorption-desorption cycles were repeated to investigate the reusability of combined magnetic resins. 0.100 g of MAER and 0.025 g

of MCER were added in a 250 mL conical flask, together with 100 mL of Cu/CA solution (1.0/1.0 mmol/L). The above mixture was shaken at identical condition (initial pH 5.0, 293 K and 150 rpm) for 24 h. The saturated resins after adsorption equilibrium were then regenerated by acid-alkali-salt three-stage desorption, which were first regenerated by 5 mL of 0.015 M HCl solution for 10 min, then followed by 5 mL of 1% NaOH solution and 5 mL 1% NaCl solution for another 10 min, respectively. The regenerated resins were used for next operation run thereafter.

3. Results and discussion

3.1. Effects of solution pH and salinity

It is well known that species distribution of adsorbates and surface charge of adsorbents would be affected by the solution pH, and further the extent of adsorption capacity [13,30]. CA is an aliphatic triprotic a-hydroxy carboxylic acid, which shows high affinity for HMIs and readily forms stable complexes with most divalent HMIs in a 1:1 M ratio [28]. In this study, the distribution information of possible species was obtained by MINTEQ calculations. Fig. S6 showed the distribution of major species under different pH-values for equimolar Cu(II) and CA. The formation constants (logK$_f$) of the species were summarized in Table S1 [11,28]. It can be found that the values of logK$_f$ increased with the number of hydrogens in [Cu-CA] complexes. For single CA system, the CA species dissociated into different anionic forms (H$_2$L$^-$, HL^{2-} and L^{3-}, L means CA ligand) as pH increased. For bi-solutes systems, with the increase of pH values, the ligands-free Cu species progressively disappeared and formed various [Cu-CA] complexes including CuHL^0, CuL$^-$ and Cu$_2$L$_2$$^{2-}$, while the proportion of H$_2$L$^-$, HL^{2-} and L^{3-} in solution was obviously reduced.

The adsorption of Cu(II) and CA by MCER or MAER under various pH conditions were investigated and depicted in Fig. 1. In the presence of CA ligands, the chelated-Cu species were soluble at all tested pHs. For single Cu and binary Cu/CA systems, the adsorption amount of Cu(II) by MCER increased with the increase of solution pH and gradually reached a plateau, which was directly related to the dissociation of carboxyl functional groups of MCER, as demonstrated by the variations of zeta potentials. In most cases, the Cu(II) uptake in single Cu system was higher than that in binary Cu/CA system, and particularly, the Cu(II) uptake onto MCER in bi-solutes system attained its maximum value at pH 5.0 and then declined a little, which may be due to the fact that free-Cu(II) was gradually changed into anionic chelating species at higher pH values, resulting in the electrostatic repulsion towards negatively charged MCER.

On the other hand, as the solution pH increased from 2.5 to 7.0, the zeta potentials of MAER maintained stable and positively charged (25–30 mV), while the CA uptake onto MAER greatly enhanced from 0.060 to 0.970 mmol/g for single CA system, and from 0.053 to 1.010 mmol/g for bi-solutes system. At acidic conditions (such as pH 2.5), most of CA existed in the molecular state, hence the adsorption amount of CA by MAER was negligible. It should be noted that an obvious increase of CA uptake was observed in the presence of Cu(II) at pH above 5.0. Since CA molecules gradually dissociated with the pH increase, the adsorption of CA species in single CA system would occupy more active sites of MAER. However, the dominant species in mixed Cu/CA solution were CuL$^-$ and Cu$_2$L$_2$$^{2-}$ at higher pH, which would save the adsorption sites of MAER resin. Furthermore, according to Kabra and Francis et al. [1,31], two carboxylic and one hydroxyl groups were involved in the mononuclear complexes (CuHL$_0$ and CuL$^-$). The long spatial distance between hydroxyl groups and Cu(II) made it difficult for hydroxyl groups to participate in the coordination reaction. By contrast, in the binuclear complexes, one Cu(II) ion was quadridentate-coordinated with two carboxylic groups and two hydroxyl groups, while the other Cu(II) ion was bidentate-coordinated with only two carboxylic groups, resulting in a steadier geometrical
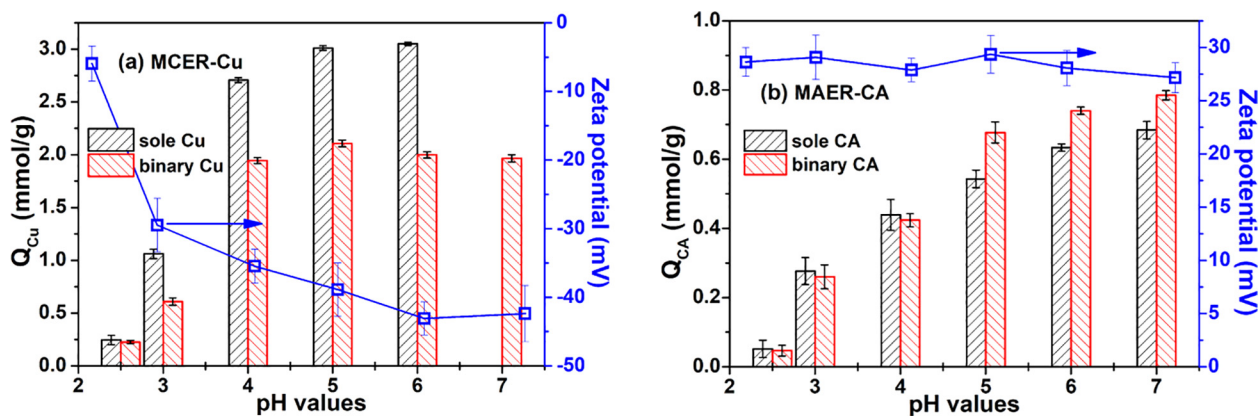
Fig. 1. The adsorption capacity of (a) Cu(II) onto MCER and (b) CA onto MAER and their zeta potentials at different pH values (MCER 0.25 g/L, MAER 1.0 g/L, $C_{0,Cu(II)} = C_{0,CA} = 1.0$ mmol/L, additional CA and Cu(II) was 0.5 mmol/L, 293 K).
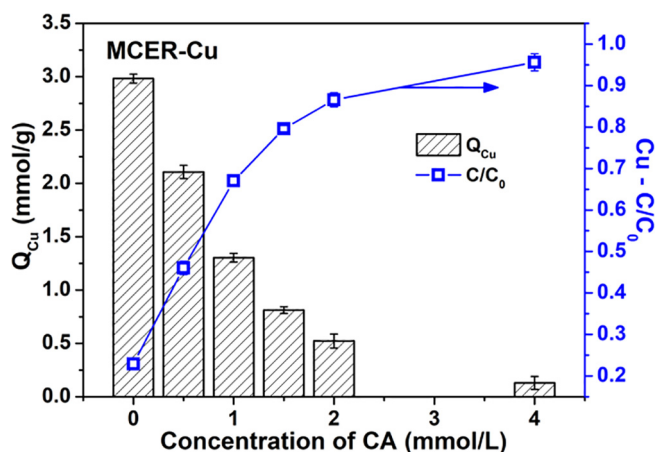

Fig. 2. Effect of CA concentration on Cu(II) adsorption by MCER resin (resin dosage 0.25 g/L, $C_{0,Cu(II)} = 1.0$ mmol/L, initial pH 5.0, 293 K).

configuration. This structure of $Cu_2L_2^{2-}$ complexes could reduce the electrostatic rejection within CA species and exhibit higher affinity toward MAER, which markedly facilitate the removal of CA from mixed solutions.

Considering that abundant foreign salt additives often present in wastewaters, the effects of coexisting inorganic salts on Cu(II) uptake by both magnetic resins were studied, and the salinity was set according to the real wastewaters [6,7,11]. It was shown in Fig. S7 that the presence of inorganic salts in binary Cu/CA solution markedly suppressed the adsorption amount of Cu(II) onto MCER and MAER. The higher ion

charges resulted in more obvious suppression, indicating that the role of coexisting salts was to compete for adsorption sites via electrostatic interaction. For example, the Cu(II) uptake onto MCER was reduced by 27.3% and 28.9% at 20 mmol/L of NaCl and 10 mmol/L of Na_2SO_4 respectively, which was because the monovalent ion had low affinity towards carboxylic groups. By contrast, in the presence of 10 mmol/L of $Ca(NO_3)_2$, the adsorption amount of Cu(II) onto MCER dropped to 23.1% of its initial capacity due to the higher affinity of Ca(II) toward MCER.

3.2. Batch adsorption study

3.2.1. Effect of CA concentration on Cu(II) adsorption by MCER resin

The adsorption of Cu(II) onto MCER with the addition of citric acid (CA), tannic acid (TA) and gallic acid (GA) was investigated. The adsorption amount and removal efficiencies of Cu(II) were shown in Figs. S8 and 2. All these organic acids exerted negative influences on Cu(II) uptake. With the addition of 4.0 mmol/L organic acids, the inhibition rates on Cu(II) adsorption of CA, TA and GA were 96.4%, 60.3% and 55.0%, respectively. The more obvious suppression by CA could be attributed to the stronger electrostatic repulsion between negatively charged CA-chelated Cu(II) species and resin surface. These results were consistent with the lower pH variation in the presence of high concentrations of CA, as illustrated in Table S2. The released [H+] was also in accordance with the ion exchange mechanism of the adsorption process. On the other hand, under different CA concentrations, nearly no CA was adsorbed onto MCER in binary solutions, which indicated that the adsorption of Cu(II) by MCER in the bi-solutes system needed to decompose Cu(II) from [Cu-CA] complex firstly and then adsorbed free-Cu(II). Overall, the removal of various carboxylated Cu(II)-organic
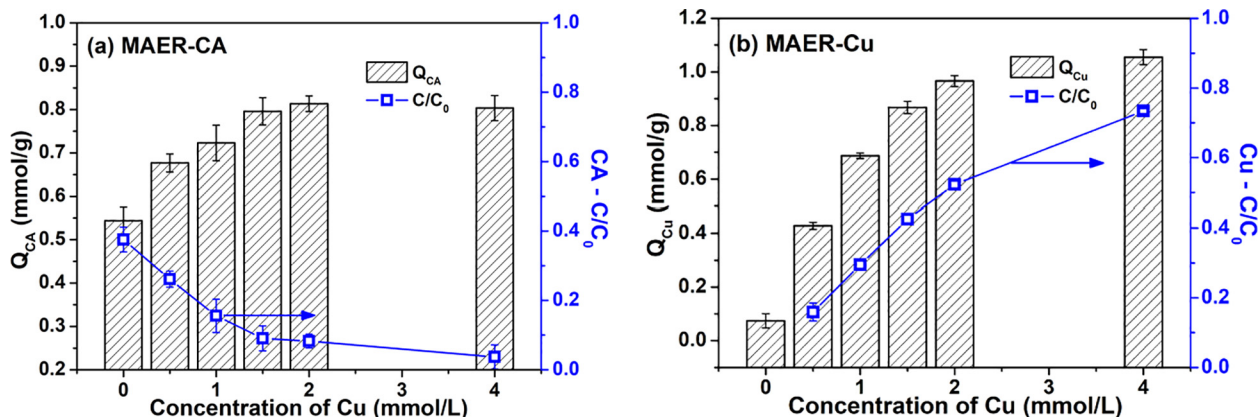

Fig. 3. Effect of Cu(II) concentration on (a) CA and (b) Cu(II) adsorption by MAER resin (1.0 g/L MAER, $C_{0,CA} = 1.0$ mmol/L, initial pH 5.0, 293 K).
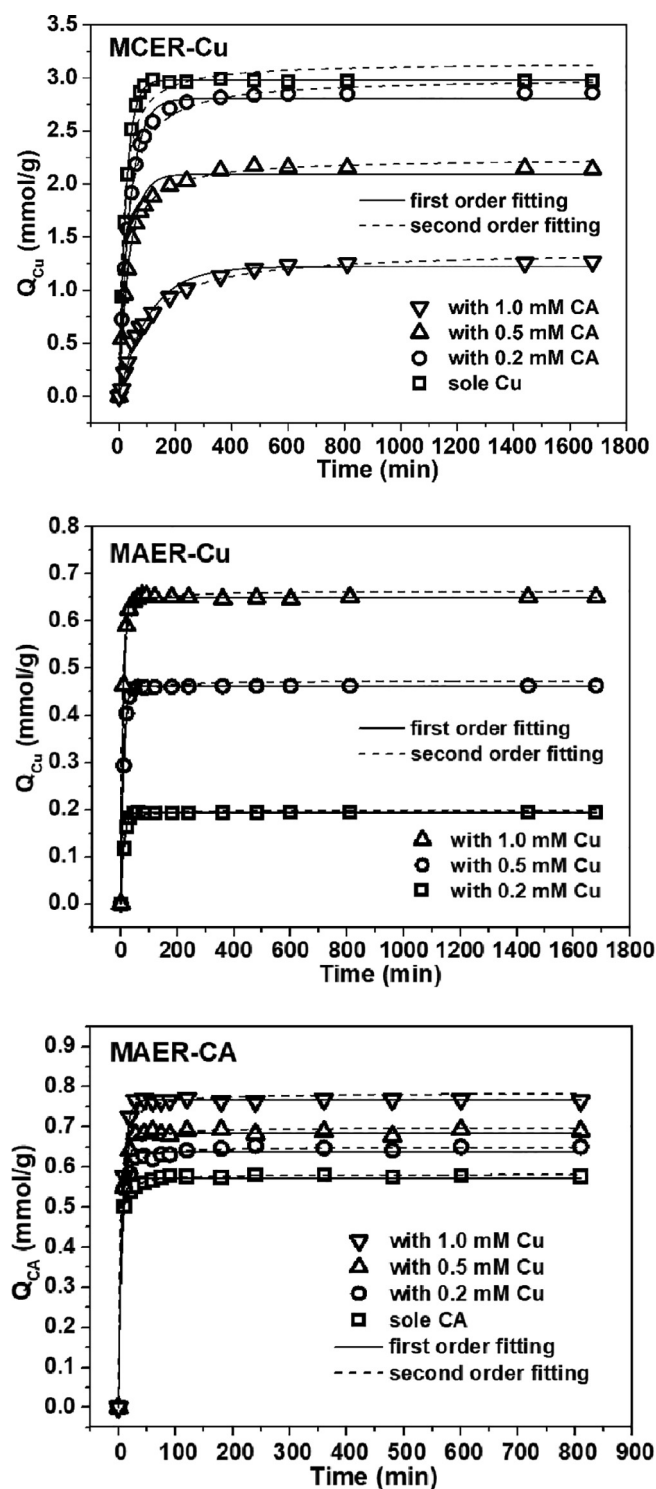
Fig. 4. The adsorption kinetic curves of Cu(II) and CA by MAER or MCER (0.25 g/L MCER, 1.0 g/L MAER, $C_{0,CA} = C_{0,Cu(II)} = 1.0$ mmol/L, initial pH 5.0, 293 K).

acid complexes onto MCER was undesirable.

In addition, different metal to ligand molar ratio of Cu/CA solutions were treated by MCER, MAER and commercial resins (D001 and D201) respectively, and the results were presented in Fig. S9. In the absence of CA, the cation exchange resin D001 (containing sulfonic groups -SO3$^-$) and MCER showed a high adsorption amount of Cu(II), while anion exchange resin D201 (containing quaternary ammonium groups -NR3$^+$) and MAER nearly cannot absorb Cu(II). As CA concentrations increased,

the Cu(II) uptake by D001 and MCER was markedly declined. When CA concentration was 2.0 mmol/L, the adsorption amount of Cu(II) onto D001 and MCER dropped by 71.1% and 82.8%, respectively. Since most Cu species were in anionic forms in the presence of high content of CA, the [Cu-CA] complexes could hinder the adsorption of Cu species onto MCER, but greatly facilitate the Cu uptake onto D201 and MAER. These observations confirmed the superior performance of anion-exchange resin for highly efficient removal of [Cu-CA] complexes from binary solutions.

3.2.2. Effects of Cu(II) concentration on CA adsorption by MAER resin

The effects of different concentrations of Cu(II) on the removal of [Cu-CA] complexes by MAER were shown in Fig. 3. Clearly, the presence of Cu(II) was advantageous for CA uptake onto MAER. As the concentration of Cu(II) increased from 0 to 4.0 mmol/L, the adsorption amount of CA gradually enhanced and reached a plateau value, along with the promotion rate about 24.4%-47.9%. The chelated [Cu-CA] complexes in bi-solutes system could save the adsorption sites and promote the CA removal efficiency onto MAER. Therefore, the [Cu-CA] complexes seemed more preferred than free-CA species in binary solution. On the other hand, with the Cu(II) concentration increasing from 0.5 to 4.0 mmol/L, the removal efficiency of Cu(II) by MAER resin dropped from 84.1% to 26.6%, although the adsorption amount was obviously enhanced. Taken together, the overall enhancement in adsorption amount of Cu(II) and CA could be considered as the Cu-bridging effect in solid-phase through offering new active sites to CA with the formation of surface complexes.

3.2.3. Adsorption kinetics

The adsorption kinetics of CA and Cu(II) in single or bi-solutes solutions onto MAER or MCER were evaluated. As can be seen in Fig. 4, the adsorption amount of both Cu(II) and CA on magnetic resins increased rapidly over time at initial stage and then attained equilibrium. As CA concentrations increased, the maximum Cu(II) uptake onto MCER was significantly reduced, along with the much tardier adsorption processes. On the other hand, the adsorption of Cu(II) and CA onto MAER was rapid in all cases, and attained equilibrium within 30 min. The presence of Cu(II) can significantly promote the uptake of CA by MAER resin. The adsorption kinetic data was fitted by both pseudo first-order and pseudo second-order kinetic models (see supplementary Text S4). The fitting kinetic parameters under different conditions were listed in Table 2.

According to the high correlation coefficients (R^2), both pseudo first-order and pseudo second-order kinetic equations can fit the adsorption data well, which were consistent with their chemisorption nature. For Cu(II) adsorption by MCER, the theoretical adsorption amount q_e and the initial adsorption rate h were steadily decreased. As CA concentration increased from 0 to 1.0 mmol/L, the adsorption amount of Cu(II) by MCER dropped from 2.97 to 1.27 mmol/g, with the inhibiting rate reaching about 57.2%. On the other hand, the adsorption of CA and Cu(II) by MAER was in an opposite trend. CA and Cu (II) could be simultaneously adsorbed onto MAER with comparable adsorption rate (k_1 and k_2) and equilibrium time. Hence, the [Cu-CA] complexes possessed higher affinities than free-CA species towards MAER, which also demonstrated the direct complex-adsorption of negatively charged [Cu-CA] complexes instead of surface complex-interaction (CA-bridging) in bi-solutes systems. However, the kinetic parameters k_1, k_2 and h for CA adsorption onto MAER were all decreased with increasing Cu(II) concentration, indicating a slower adsorption rate in bi-solutes systems. Although [Cu-CA] complexes saved the adsorption sites of MAER resin, the mass transfer rates decreased due to the increasing steric hindrance. Given that the CA removal was much efficient in both single or bi-solutes systems, the obvious enhancement in CA uptake should be driven by the mechanism of direct ion exchange with anionic complexes.

Table 2
Kinetic constants for CA and Cu(II) adsorption onto MAER or MCER.

| Code	Cu (mM)	CA (mM)	Pseudo-first-order model			Pseudo-second-order model			
			$k_1/10^{-2}$ (min^{-1})	q_e (mmol/g)	R^2	$k_2/10^{-2}$ (g/mmol·min)	q_e (mmol/g)	$h/10^{-2}$ (mmol/(g·min))	R^2
MCER-Cu	1.0	0	4.03	2.98	0.999	2.16	3.15	21.42	0.963
	1.0	0.2	2.60	2.80	0.997	1.33	3.00	11.97	0.990
	1.0	0.5	2.64	2.09	0.987	1.80	2.24	9.04	0.995
	1.0	1.0	0.93	1.22	0.989	0.83	1.38	1.58	0.994
MAER-Cu	1.0	0.2	9.46	0.19	0.999	104.9	0.20	4.20	0.979
	1.0	0.5	10.22	0.46	0.999	49.07	0.48	11.07	0.981
	1.0	1.0	12.30	0.65	0.999	46.83	0.66	20.65	0.968
MAER-CA	0	1.0	20.07	0.57	0.996	109.3	0.58	37.02	0.999
	0.2	1.0	18.31	0.64	0.992	79.93	0.65	33.87	0.998
	0.5	1.0	15.71	0.69	0.999	65.69	0.70	32.19	0.993
	1.0	1.0	14.15	0.77	0.999	50.01	0.79	30.82	0.987
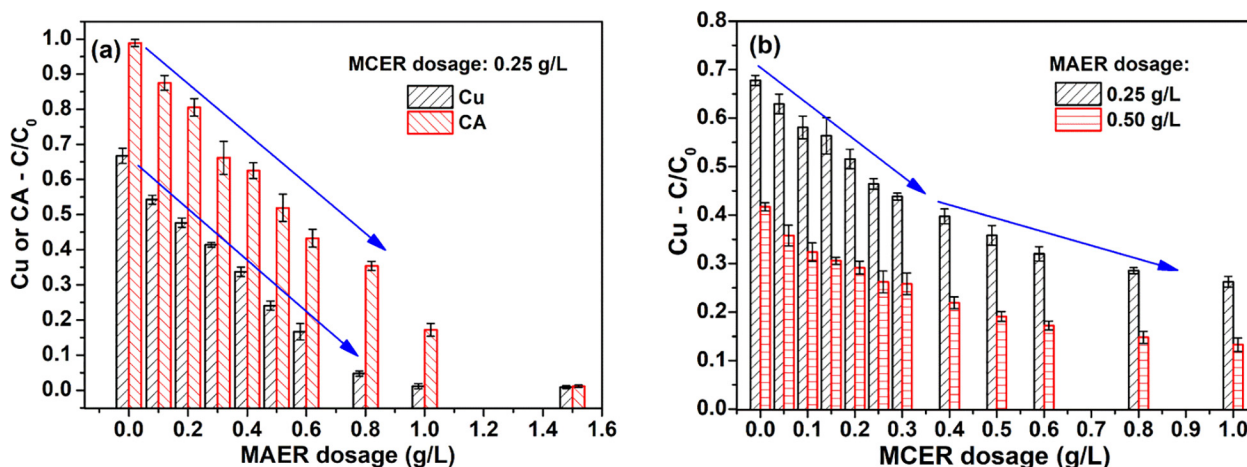
Fig. 5. The removal of [Cu-CA] complexes by combined magnetic resins ($C_{Cu(II),CA}$ = 1.0/1.0 mmol/L, initial pH 5.0, 293 K).

3.2.4. Removal of [Cu-CA] complexes by combined magnetic resins

The co-removal performances of CA and Cu(II) from bi-solutes solutions onto combined MCER and MAER were considered. Initially, the binary Cu/CA solutions with the equimolar ratio of Cu(II) and CA were treated with fixed amount of MCER and varying amount of MAER. The final pH values after adsorption equilibrium were illustrated in Table S3. It was shown in Fig. 5a that about 35% of Cu(II) was removed with single MCER, while the CA removal was negligible. With the increase of MAER dosage, a noteworthy enhancement in both Cu(II) and CA adsorption was observed. The removal efficiencies of CA and Cu(II) enhanced linearly from 1.1% and 33.2% to 98.8% and 99.1%. Since MAER can directly adsorb the electronegative CuL$^-$ and Cu$_2$L$_2^{2-}$ species, the magnetic resin combination process can greatly enhance the removal performances of [Cu-CA] complexes. As the functional groups (carboxyl groups and quaternary ammonium groups) of combined magnetic resins have different charges, the combined resins can efficiently remove CA and Cu(II) from bi-solutes systems.

The other set of experiments was fixing the amount of MAER at 0.25 or 0.50 g/L, along with the different amount of MCER. The results illustrated in Fig. 5b showed that the removal efficiencies of Cu(II) were increased with the increasing amount of MAER. However, even if 1.0 g/L of MCER was added, the removal efficiencies of Cu(II) by combined magnetic resins were about 30–40% higher than that without MCER, while there were almost no effects for CA removal (not shown). The final pH values shown in Table S4 were also increased with the increasing MCER dosage, which was because the cation exchange resin had higher affinity to the hydrion. Since most Cu-species were in the complexed forms at tested pH, the adsorption of Cu(II) by MCER may initially dissociate Cu(II) from CuHL$_0$ complexes and then capture free-Cu(II) by its carboxylic groups. Due to the existence of free or neutral-

Cu species in wastewater, the addition of MCER is necessary in practical applications.

Based on above discussions, the removal of [Cu-CA] complexes by combined magnetic resins is mainly through decomplexation-competitive adsorption of CuHL$_0$ onto MCER and complex-adsorption of CuL$^-$ and Cu$_2$L$_2^{2-}$ onto MAER. According to the hard and soft acids and bases theory (HSAB), hard acids-hard bases/junction bases and soft acids-soft bases/junction bases appear strong complexing ability [11,20]. Since HMIs commonly found in wastewaters, such as Pb(II), Cd(II) and Ni(II), can act as boundary acids and have strong affinities to common organic acids like CA, oxalate and tartrate etc., the fully-mixed magnetic resin combination processes are supposed to possess attractive application prospects for removal of HMIs-organic acid complex pollutants.

3.3. Verification of interaction mechanisms

In order to illuminate the interaction mechanisms for co-adsorption of Cu(II) and CA on the solid phase, the resin samples were determined by FTIR and XPS characterizations, and were illustrated in Fig. 6. For FITR spectra of MAER samples presented in Fig. 6a, an absorption peak belonging to the C=O of resin skeleton at 1567.9 cm^{-1} was observed. After the loading of CA, two sharp absorption peaks appeared at 1577.5 and 1390.4 cm^{-1}, which were attributed to the symmetrical stretching vibration of carboxyl groups of CA species. In addition, the C-N stretching vibration absorption peaks at 1400–1500 cm^{-1} were obviously weakened, which indicated the variations in the electron cloud density of quaternary ammonium groups. With the co-existence of Cu(II) in solution, the stretching vibration peak of carboxyl groups at 1577.5 cm^{-1} gradually blue-shifted to 1581.4, 1583.3 and
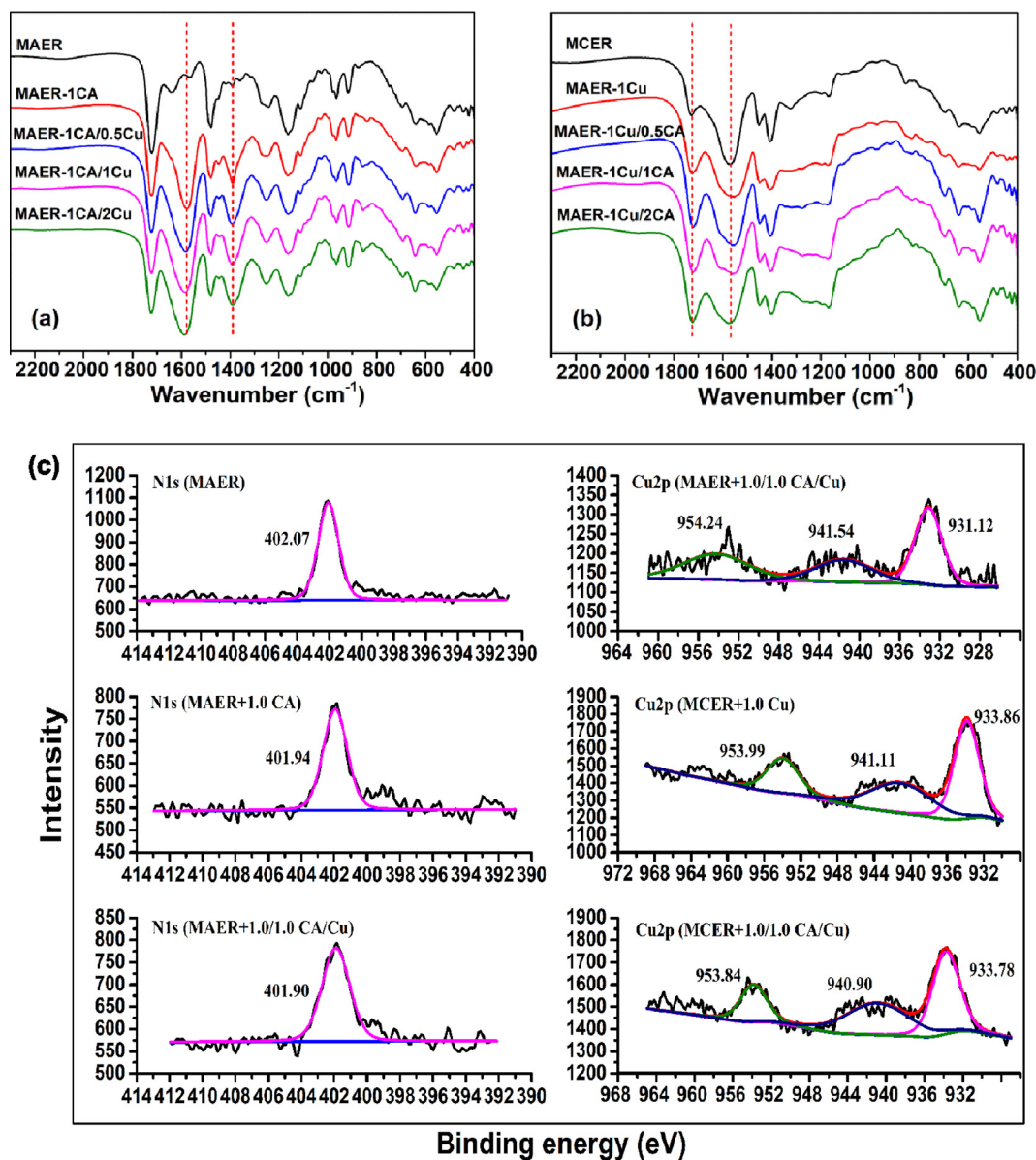
Fig. 6. The FTIR spectra of (a) MAER and (b) MCER and (c) the N1s and Cu2p XPS spectra before and after the adsorption of Cu(II) and/or CA complexes.

$1587.2\,cm^{-1}$, confirming the complexation of Cu(II) and CA species. On the other hand, the FTIR spectra of different MCER samples were presented in Fig. 6b. After the loading Cu(II), the peak at $1573.7\,cm^{-1}$ was red-shifted to $1552.4\,cm^{-1}$, demonstrating that the carboxylic groups of MCER participated in the Cu(II) uptake. The FTIR spectra of MCER after adsorption of [Cu-CA] complexes were similar to that of Cu(II) adsorption, which reinforced our suspicion that the decomplexing-adsorption of Cu(II) was the mechanism for Cu(II) uptake onto MCER in bi-solutes system.

The high-resolution N1s and Cu2p spectra of different resin samples were shown in Fig. 6c. From the N1s spectra of MAER before and after adsorption of CA or [Cu-CA] complexes, a unique energy peak appeared at $402.07\,eV$, which corresponded to quaternary ammonium functional groups of MAER resin. Slight changes were observed among different MAER samples, confirming that the adsorption of CA or [Cu-CA] complexes by MAER was mainly through ion exchange. For Cu2p spectra of MAER and MCER after the loading of [Cu-CA] complexes, the Cu2p spectra of MCER-Cu samples at $933.86\,eV$ and $941.11\,eV$ were attributed to the Cu2p$_{3/2}$ and Cu2p$_{1/2}$ peak, respectively. For single Cu(II) and bi-solutes systems, the Cu2p peaks of MCER remained

unchanged ($933.78\,eV$ and $940.90\,eV$), which was mainly due to the adsorption of chelated-Cu species by MCER needed to decompose Cu(II) from CA ligands firstly and was similar to the free-Cu(II) adsorption. By contrast, the peaks of Cu2p$_{3/2}$ and Cu2p$_{1/2}$ for MAER samples appeared at $931.12\,eV$ and $941.54\,eV$ respectively and were significantly different from that of MCER samples, which were consistent with the direct adsorption of electronegative complexes ($Cu_2L_2^{2-}$ and CuL^-) in bi-solutes systems.

Herein, the interaction mechanisms behind synergistic removal processes are proposed in Fig. 7. In the bi-solutes system with equimolar Cu(II) and CA, the main species in solution are free-Cu(II), free-CA, $CuHL^0$, CuL^- and $Cu_2L_2^{2-}$, respectively. The mixtures can be removed by the combination of magnetic resins through following mechanisms. (1) Complex-adsorption of $Cu_2L_2^{2-}$ and CuL^- species by MAER. Compared with free-CA species, MAER resin can adsorb $Cu_2L_2^{2-}$ and CuL^- more efficiently, which is mainly due to the complexed $Cu_2L_2^{2-}$ and CuL^- save the active sites of MAER and thus facilitate the adsorption of both CA and Cu species onto MAER; (2) Decomplexing-adsorption of Cu(II) from $CuHL_0$ by MCER. The decomplexation of the neutral complex ($CuHL_0$) and concurrent Cu(II)
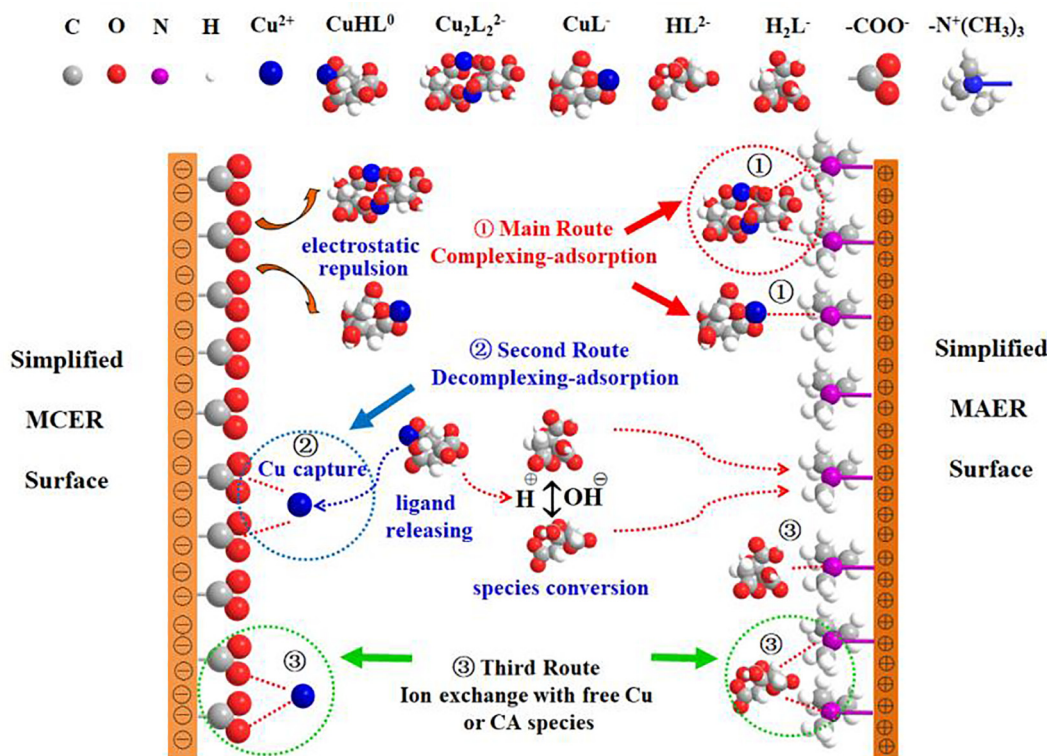
Fig. 7. Proposed mechanisms for synergetic removal of Cu(II) and CA by combined magnetic resins in bi-solutes system.
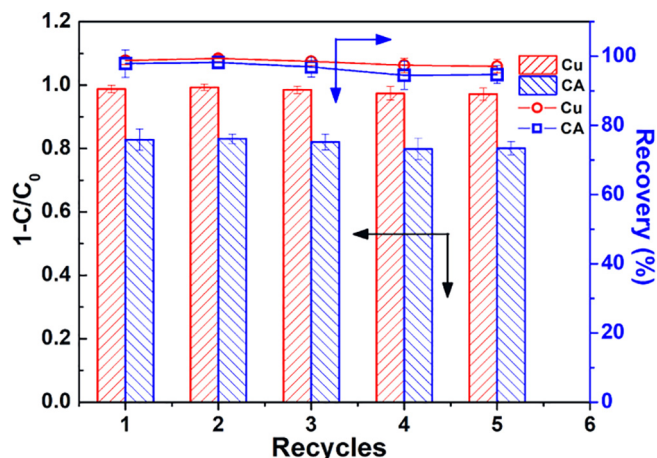

Fig. 8. The reusability of combined magnetic resins for removal of [Cu-CA] complexes (0.25 g/L MCER, 1.0 g/L MAER, initial pH 5.0, $C_{Cu(II),CA}$ = 1.0/1.0 mmol/L, 293 K).

adsorption is achieved by the competition of carboxylic groups of MCER. The releasing anionic CA ligands can be simultaneously removed by MAER; (3) Ion exchange of free CA or Cu species. MCER and MAER can directly ion-exchange these species through carboxylic groups and quaternary ammonium groups of each resin. Each above adsorption mechanism can be confirmed by other literatures. However, some other adsorbents such as modified carbon and carbon nanotubes, grapheme oxide and chitosan-like materials were mainly targeted with certain adsorption route due to their simplicity in functional groups [32–35].

3.4. Regeneration and reusability

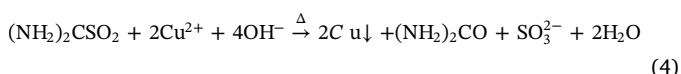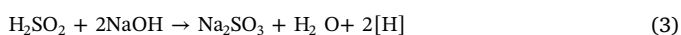Due to the different composition of magnetic resins, it is of vital importance to regenerate the combined resins for reducing operating costs and prolonging working life of the resins [2]. Depending on our previous studies, 0.01 M HCl could effectively regenerate the Cu-saturated MCER [30]. Since the selectivity of [H$^+$] to MCER is much higher than common HMIs like Cu(II) and Ni(II), the hydrogen-form MCER after regeneration is slow in kinetics for Cu(II) uptake, and thus should be converted into Na-form by NaOH solution. Next, the alkali-form MAER (MAER-OH) should be further transformed into chlorine-form (MAER-Cl) to prevent precipitation of HMIs. Accordingly, the exhausted combined magnetic resins were regenerated by acid (0.015 M HCl)-base (1% NaOH)-salt (1% NaCl) three-stage desorption in this study.

Importantly, the stability of both resins under acidic conditions was evaluated. It can be observed in Fig. S10 that the leaching concentrations of Fe increased with the decline of solution pH. The overall Fe leaching was not obvious at pH higher than 2.0, indicating the excellent acid-resistance of self-prepared magnetic resins due to the modification of inorganic γ-Fe$_2$O$_3$ particles within resin matrix. The step-by-step desorption efficiencies were shown in Table S5. In acid-desorption stage, 97.4% of Cu(II) and 93.4% of CA were desorbed by applying 5 mL of 0.015 M of HCl solution. In alkali-desorption stage, the residual Cu on MAER was converted to Cu(OH)$_3$$^-$ and Cu(OH)$_4$$^{2-}$ from resin phase to strongly basic liquid-phase. The cumulative desorption rates of Cu(II) and CA in first two stages were 99.7% and 98.6%, respectively. Moreover, another 1% NaCl solution was indispensable to completely desorb the Cu and CA species in resin and convert the combined resins to initial ionic-form (MAER-Cl and MCER-Na).

The reusability of combined magnetic resins for co-removal of [Cu-CA] complexes in the equimolar bi-solutes system was assessed by repeating the adsorption-desorption cycle for 5 times (Fig. 8). At the 5th cycle, the removal of Cu(II) and CA by combined resins declined to approximately 97.1% and 94.7% of their initial efficiency, respectively. Taken together, the fully-mixed magnetic resin combination processes exhibited superior reusability in removal of [Cu-CA] complexes, indicating great potential applications for removing HMIs-organic acid complex pollutants from wastewaters.

3.5. Copper recovery

As discussed above, the desorption liquid of combined magnetic resins was complicated in composition and in strongly alkaline pH, which was highly toxic and would threaten the environment if it was not effectively disposed. On the other hand, the recovery of copper can not only reduce the toxicity of desorption liquid, but also achieve recycling and utilization of heavy metals. In our previous research, the waste electroless nickel plating bath was treated by chemical reduction with a green reducing agent, thiourea dioxide (TD), for its cheaper price and greater reducing ability than thiourea and sodium borohydride [36]. The nanometer nickel powders with narrow distribution and high purity were obtained. For the treatment of resin desorption liquid in this study, the optimal experimental conditions were temperature 80 °C, pH13.5 for 10 min, and the mole ratio of TD and Cu(II) was 1:1.8. The reaction mechanisms were proposed as the following equations:

$$NH_2C(:SO_2)NH_2 \xrightarrow{\Delta} NH:C(SO_2H)NH_2 \xrightarrow{OH^-} NH_2CONH_2 + H_2SO_2 \quad (2)$$

$$H_2SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O + 2[H] \quad (3)$$

$$(NH_2)_2CSO_2 + 2Cu^{2+} + 4OH^- \xrightarrow{\Delta} 2Cu\downarrow + (NH_2)_2CO + SO_3^{2-} + 2H_2O \quad (4)$$

The Cu species in desorption liquid were completely removed and converted into Cu powder, and TD was oxidized to sodium sulfate and urea, which also increased the biodegradability of desorption liquid. The SEM micrographs in Fig. S11 showed that the obtained copper powders were about 15–25 nm in highly uniform spherical shape. Taken together, this method could take advantage of the alkaline condition of desorption liquid without neutralization treatment, which greatly reduced the toxicity of desorption liquid, along with the recovery of nanometer heavy metals.

4. Conclusions

In this study, the combination of permanent magnetic anion-exchange resin MAER and cation-exchange resin MCER were employed to efficient removal of Cu(II) and CA species from bi-solutes solutions. As Cu(II) concentrations increased, the adsorption amount of CA onto MAER increased gradually, with the promotion rates ranging from 24.4% to 47.9%. With the amount of MAER increasing from 0 to 1.5 g/L, the removal efficiencies of CA and Cu(II) dramatically increased from 1.1% and 33.2% to 98.8% and 99.1%, respectively. Both complex-adsorption of anionic $Cu_2L_2^{2-}$ and CuL^- by MAER and decomplexing-adsorption of Cu(II) from neutral $CuHL_0$ by MCER were proposed as the mechanisms for the synergetic removal of CA and Cu(II) by combined magnetic resins. Especially, the anionic [Cu-CA] species had higher affinity towards MAER than free-CA ligands, resulting in an enhancement of both Cu(II) and CA uptake onto MAER. The combined resins could be completely regenerated by the three-stages desorption, and maintained most of their initial removal efficiency during 5 repeated cycles. Moreover, nanometer copper powders were recovered through the chemical reduction of resin desorption liquid, which rendered it an attractive potential for resource utilization of HMIs-organic acid complex pollutants.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.02.070.

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