

Highly efficient co-removal of copper (II) and phthalic acid with self-synthesized polyamine resin

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ABSTRACT

A novel method was proposed for efficient co-removal of Cu (II) and phthalic acid (PA) using self-synthesized polyamine resin (R-NH₂). The adsorption properties of R-NH₂ were thoroughly investigated by equilibrium, kinetic and dynamic tests in sole and binary systems at pH 5.0. The Freundlich model was a good fit for all the isotherm data, showing higher K_f values in the binary system than the sole system. The pseudo-second-order kinetic equation showed a better correlation to the experimental data in all cases and PA uptake was much faster than that of Cu (II). R-NH₂ showed highest adsorption capacities to both Cu (II) and PA among the five tested resins. Moreover, the presence of PA markedly enhanced the adsorption of Cu (II), being around 3.5 times of that of the sole system. The adsorption of PA was also slightly increased when Cu (II) was coexistent. Furthermore, using Fourier transform infrared spectrometry (FTIR) and species calculations, possible mechanisms were proposed that Cu (II) coordinated with -NH₂ and negative PA species interacted with -NH₃⁺ by electrostatic attraction. [Cu-PA] complex in the binary system possessed a much higher affinity than free Cu (II) to chelating with -NH₂, resulting in mutual enhancement.

Key words | coordination, copper (II), co-removal, phthalic acid, polyamine resin

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INTRODUCTION

Heavy metal ions (HMI) in water always cause much concern and are strictly controlled due to their toxicity and persistence (Repo *et al.* 2013). Low molecular weight organic acids (LMWOA), which are ubiquitous in water/soil media at total concentrations ranging from 0.01 to 5 mmol/L, often exert much negative influence on the removal of HMI (Hwang & Lenhart 2010; Méndez-Díaz *et al.* 2012). Moreover, growing evidence suggests that the combined toxicities of binary systems of HMI and LMWOA are generally more complicated than the sole system (Qian *et al.* 2012). Consequently, the effective control of the above-mentioned pollutants has attracted increasing interest. Both HMI and LMWOA should be removed and recovered with high efficiency before wastewaters are discharged into the environment.

Traditionally, the combined technologies of coagulation, chemical precipitation and biotechnology, advanced oxidation, adsorption, etc. (Qian *et al.* 2012) have been applied to successively remove HMI and LMWOA. However, the technologies have suffered from drawbacks like secondary pollution, long processes and complex

regulations. The co-adsorption method with low-cost adsorbents, modified activated carbon and other carbonaceous materials has been reported to simultaneously remove HMI and organics including LMWOA, and are relative simple, green, recyclable and widely applicable. Sreejalekshmi *et al.* (Sreejalekshmi *et al.* 2009) reported sawdust-activated carbon simultaneously removed Pb (II) and Pb (II)-citric acid. Kang *et al.* (Kang *et al.* 2010) found that chitosan has high adsorption capacities to both tetracycline and copper. Furthermore, synthetic polymers are generally superior to soil adsorbents or bio-materials in regeneration properties and mechanical strength (Zhou *et al.* 2010). However, the presence of LMWOA could mostly negatively affect the sorption of HMI and vice versa, because of strong complexation of mixed pollutants, competition and/or shielding of adsorption sites (Huang *et al.* 2010; Repo *et al.* 2011). Therefore, it is important to explore adsorbents for the synergistic co-adsorption of HMI and LMWOA, which have yet been rarely reported.

Different researchers have mentioned that adsorbents with amine groups have excellent affinities with HMI by

chelation, and LMWOA by physical forces (such as electrostatic forces and hydrogen-bond interactions) in their sole-component system (Kampalanonwat & Supaphol 2010; Huang *et al.* 2012). Therefore, the object of this work is to explore the application of a self-synthesized polyamine resin in the co-removal of HMI and LMWOA from their combined wastewaters. Cu (II) and phthalic acid (PA) were chosen as the model pollutants as they are commonly present in wastewaters. Interaction behaviours and mechanisms of the two pollutants were thoroughly investigated by carrying out equilibrium, kinetic and dynamic experiments in sole and binary systems as well as by Fourier transform infrared spectrometry (FTIR).

MATERIALS AND METHODS

Materials

The resin with polyamine functional groups (R-NH₂) was synthesized in the laboratory. The physicochemical characteristics of tested resins, including R-NH₂, are presented in Table 1. D001 and D201 were commonly used to remove cations and anions, respectively, from water through ion exchange. Also, XAD-4 was applied to remove organic pollutants, mainly due to its hydrophobic effect (Xiao & Long 2012). Similar to R-NH₂, S984 was also grafted onto polyamine groups and reported to remove many kinds of HMI highly efficiently. All reagents, including cupric chloride, PA, hydrochloric acid and sodium hydroxide, were used as analytical reagents and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China). Deionized water was used to prepare all solutions.

Adsorption equilibria studies

The adsorption equilibria studies were all performed by taking 0.025 g resin in 150 mL conical flasks with 100 mL adsorbate solutions. For the experiments to compare resins, each type of resin was tested in sole-component or binary-components solutions of 0.5 mmol/L for Cu (II) and 1.0 mmol/L for PA. For Cu (II)/PA adsorption isotherms, the initial concentration of Cu (II)/PA were 0.2–2.0 mmol/L in the co-presence of 0, 0.5 and 1.0 mmol/L PA/Cu (II). The initial pH values of the solutions were all adjusted to 5.0 with HCl (0.1 mol/L) or NaOH (0.1 mol/L). The flasks were completely sealed and agitated in an incubator shaker at 303 K and 140 rpm. The tests were conducted continuously for 36 hours to attain the adsorption equilibria.

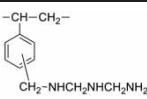
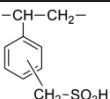
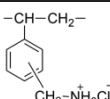
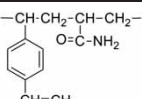
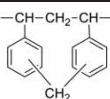
Adsorption kinetics studies

A batch of 1,000 mL consisting of sole or binary solutions with the settled concentrations of 0.5 mmol/L for Cu (II) and 1.0 mmol/L for PA was adjusted to the initial pH value of 5.0 and then mixed with 0.250 g resin, stirred at 303 K and 140 rpm. The samples (1 mL) were taken out at pre-determined time intervals for concentration measurements.

Adsorption dynamics studies

The fixed-bed dynamic experiments were carried out in a water-jacketed glass column (Φ10 × 240 mm). An aliquot of fresh resin particles (0.500 g) was put into the column. Sole or binary solutions with settled concentrations of 0.5 mmol/L for Cu (II) and 1.0 mmol/L for PA were adjusted to the initial pH value of 5.0 and then pumped at

Table 1 | Physicochemical characteristics of resins

Properties	R-NH ₂	D001	D201	S984	XAD-4
General structure					
BET surface area (m ² /g)	9.78	27.91	25.08	4.17	905.10
Average pore diameter (nm) (cm ³ /g)	20.88	13.34	12.22	19.22	5.80
Pore volume	0.007	0.18	0.26	0.004	0.283
Manufacturer	Self-synthesized	Zhengguang Industrial Co., Ltd, China		Purolite, USA	Rohm and Haas, USA

the desired flow rate of 10 bed volume per hour (BV/h), and the temperature was maintained at 303 K in each system. The concentrations of pollutants in the effluent (C_t) were taken at regular intervals and analysed. t is the service time/operating time of the column. The breakthrough and saturation point of the column are defined when the values of C_t/C_0 are 0.05 and 0.9 respectively.

Analytical procedures

The concentrations of Cu (II) and PA in the aqueous solutions were measured by the atomic adsorption spectrophotometer (AAS, Thermo, USA) at $\lambda_{\text{Cu}} = 324.75$ nm and UV-vis spectrometry (Agilent 8453, USA) at an absorption wavelength of 334.5 nm respectively. After complete dryness, the resin before and after loading with Cu (II) and PA was characterized by FTIR (Nexus S870, USA).

The equilibrium adsorption amount (q_e mmol/g) was calculated using Equation (1). The data of adsorption isotherms were fitted to Langmuir and Freundlich models as shown in Equations (2) and (3)

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

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (2)$$

$$q_e = K_f C_e^{1/n} \quad (3)$$

where, C_0 and C_e are the initial and equilibrium concentrations (mmol/L), and m is the mass of resin (g), V is the volume of the 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 used to interpret kinetic data. The non-linear forms as Equations (4) and (5) were considered a better way to obtain the kinetic parameters (Li *et al.* 2011)

$$q_t = q_e - \frac{q_e}{e^{k_1 t}} \quad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where, q_t and q_e are adsorption amount during t time and at equilibrium (mmol/g), accordingly. k_1 and k_2 (g/mmol/min) are the constants associated with the adsorption rates.

RESULTS AND DISCUSSION

Resin comparisons in mutual influence of Cu (II) and PA uptake

The adsorption of Cu (II) and PA onto R-NH₂ and four commercial resins were compared at pH 5.0. From Figure 1, as expected in the sole system, D001 and D201 showed sole high adsorption capacity toward Cu (II) or PA, while S984 and R-NH₂ was also proven to be able to remove both pollutants. Neither Cu (II) nor PA could be efficiently adsorbed by XAD-4, mainly because the two adsorbates are relatively hydrophilic while the resin is hydrophobic (Zhang *et al.* 2008). As for binary systems, the uptake of Cu (II) onto R-NH₂ and S984 was enhanced by 346 and 54% when PA was coexistent, while that onto D001 dropped by 22.6%. There was also a slight increase of Cu (II) adsorption for D201. On the other hand, PA adsorption was also improved in the co-presence of Cu (II) for the two polyamine resins but a little reduced with D201. The equilibrium capacities of Cu (II) and PA onto R-NH₂ reached 0.743 and 1.651 mmol/g. Results suggest the total adsorption capacities of pollutants in binary systems follow the order: R-NH₂ > S984–D201 > D001 > XAD-4. These observations support R-NH₂ as an efficient means of co-removing Cu (II) and PA from wastewaters.

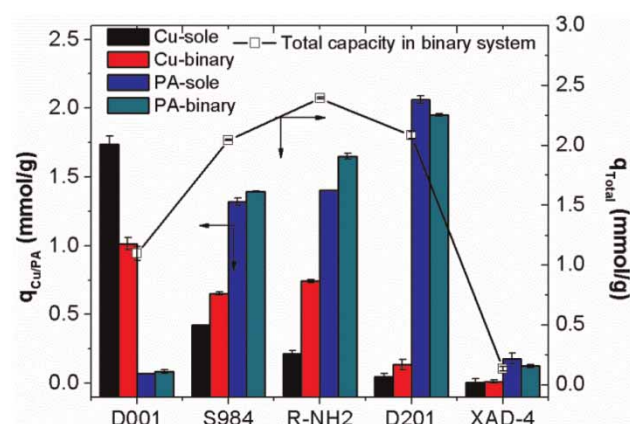


Figure 1 | The adsorption capacities of Cu (II) and PA and total pollutants in sole and binary system onto different resins (resin dosages were all 0.25 g/L; the initial concentrations of Cu (II) and PA in the sole and binary systems were set as 0.5 and 1.0 mmol/L, respectively; pH 5.0; 303 K).

Adsorption equilibrium isotherms onto R-NH₂

The adsorption isotherms of Cu (II) and PA onto R-NH₂ for both sole and binary systems were intensively studied and the results are shown in Figure 2. Over a wide range of Cu (II) concentrations, the uptake of Cu (II) was generally enhanced with increasing concentrations of PA. The presence of Cu (II) also had a positive effect on PA uptake when initial concentrations of PA were lower than 1.0 mmol/L, yet had a slightly negative effect with concentrations higher than 1.0 mmol/L. As shown in Table 2, in all cases, the Freundlich model fits better, with higher correlation coefficients ($R^2 > 0.98$). Ultimately, the affinity parameter (K_f) for Cu (II) showed a positive correlation with the concentration of co-existent PA while that for PA demonstrated little change. It clearly suggests that Cu species in PA coexistent systems had a higher affinity for sites in R-NH₂.

Adsorption kinetic processes

The effect of contact time on the adsorption of Cu (II) and PA by R-NH₂ is shown in Figure 3. The kinetic data are described with pseudo-first-order and pseudo-second-order

models. Kinetic parameters are listed in Table 3. Data are better described by the pseudo-second-order model ($R^2 > 0.995$) than by the pseudo-first-order model, suggesting the overall process was controlled by chemisorptions (Shen et al. 2011). The uptake of PA was much faster than that of Cu (II) (k_2 , PA $\sim 10 k_2$, Cu), indicating a different adsorption mechanism. Cu (II) uptake in the binary system clearly surpassed that in sole systems after 30 min, yet the adsorption rates were similar, indicating a comparable mechanism for Cu species adsorption in the two systems. As for PA, the adsorption amounts in the binary system were smaller in the first stage (<12 hours), then gradually larger than those of the sole system in the second stage (>12 hours). This phenomenon was just consistent with the results of the slower adsorption rate k_2 for PA species in the binary system. The equilibrium capacity of both Cu (II) and PA were in the order binary system > sole system.

Column dynamic adsorption

Typical breakthrough curves for Cu (II) and PA adsorption onto R-NH₂ are shown in Figure 4. For Cu (II), the breakthrough and saturation in the binary system occurred at

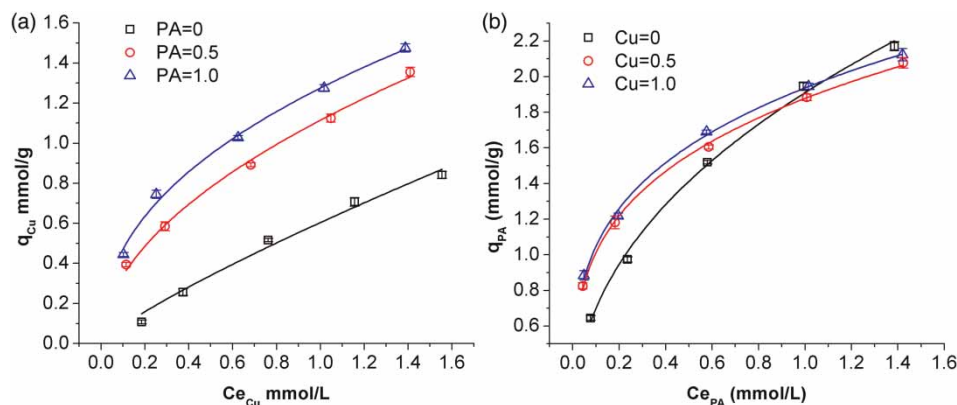


Figure 2 | The equilibrium adsorption of Cu (II) (a) and PA (b) on R-NH₂ in sole and binary systems with different initial concentrations fitting by Freundlich model (resin dosage was 0.25 g/L; the initial concentrations of Cu (II) and PA were 0.2, 0.5, 1.0, 1.5 and 2.0 mmol/L; pH 5.0; 303 K).

Table 2 | Isotherm parameters of Langmuir and Freundlich models for Cu (II) and PA adsorption

Target	Coexistent species (mmol/L)	Freundlich model			Langmuir model		
		K_f (mmol ¹⁻ⁿ L ⁿ /g)	1/n	R^2	q_{max} (mmol/g)	b (L/mmol)	R^2
Cu(II)	[PA] = 0	0.604	0.829	0.985	1.774	0.687	0.992
	[PA] = 0.5	1.114	0.515	0.994	1.528	1.594	0.948
	[PA] = 1.0	1.275	0.433	0.994	1.770	2.747	0.964
PA	[Cu] = 0	1.910	0.435	0.996	2.679	2.656	0.956
	[Cu] = 0.5	1.878	0.268	0.999	2.044	10.366	0.858
	[Cu] = 1.0	1.937	0.266	0.998	2.123	9.802	0.867

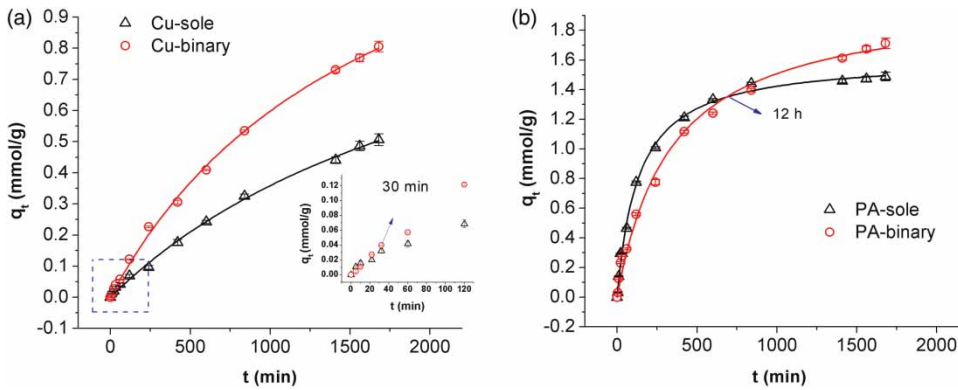


Figure 3 | Kinetic study of Cu (II) (a) and PA (b) adsorption on R-NH₂ in sole and binary systems fitting by second-order kinetic equation (resin dosage was 0.25 g/L; the initial concentrations of Cu (II) and PA in the sole and binary systems were set as 0.5 and 1.0 mmol/L, respectively; pH 5.0; 303 K).

Table 3 | Kinetic parameters for the adsorption of Cu (II) and PA on R-NH₂ in sole and binary system. The initial concentrations of Cu (II) and PA were 0.5 and 1.0 mmol/L

Targets	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e,fit}$	k_1	R^2	$q_{e,fit}$	k_2	R^2
Sole Cu	0.759	6.449×10^{-4}	0.996	1.237	3.296×10^{-4}	0.997
Binary Cu	1.035	8.748×10^{-4}	0.998	1.589	3.799×10^{-4}	0.999
Sole PA	1.433	0.006	0.988	1.614	0.005	0.997
Binary PA	1.670	0.003	0.982	2.022	0.001	0.995

240 and 3,720 mL, respectively, much later than those in the sole system at 70 and 2,895 mL. The saturation capacity of Cu (II) in the binary system reached 1.305 mmol/g, around 2.21 times of that in the sole system (0.59 mmol/g). For PA, breakthrough appeared at around 700 mL (583 BV) showing the high capacity of R-NH₂ toward PA. The saturation capacity of PA in the binary system reached

3.305 mmol/g, around 1.18 times that of the sole system (2.781 mmol/g).

Possible mechanism

To investigate the adsorption mechanisms, resin with Cu (II), PA and their mixes were characterized by FTIR. From Figure 5, evidence of the presence of the amine group (-NH₂) in R-NH₂ can be found at 1,571.7 and 1,108.0 cm⁻¹ (Gurgel & Gil 2009). Amine peaks at 1,571.7 cm⁻¹ almost disappeared in both samples of R + Cu and R + PA, proving that amine group participated in the adsorption of both Cu (II) and PA. Moreover, bands at 1,558.4, and 1,395.8 cm⁻¹ illustrate the presence of the symmetrical stretching vibration of carboxyl groups (Liu *et al.* 2011a), directly confirming the plentiful loading of PA on the resins. As for R + Cu + PA, the FTIR curve was closely similar to that of R + Cu, probably because of the larger capacity toward PA.

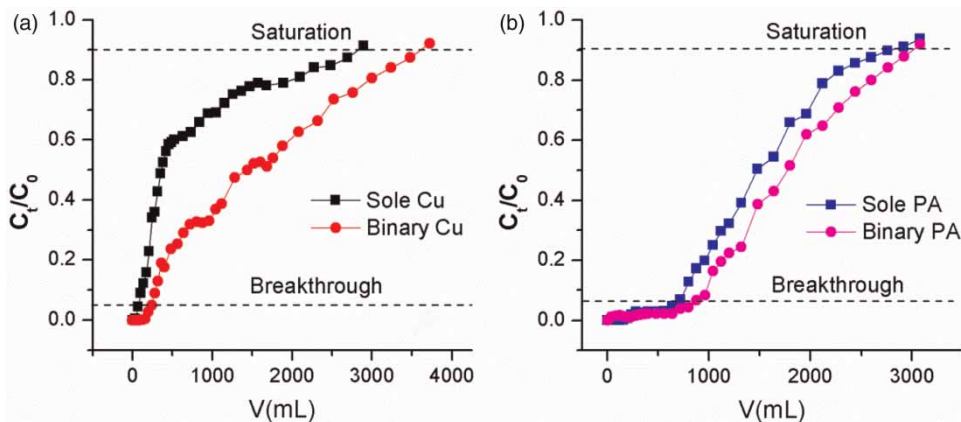


Figure 4 | Breakthrough curves of Cu (II) (a) and PA (b) adsorption onto R-NH₂ in sole and binary systems (0.500 g resin; flow rate = 10 BV/h; the initial concentrations of Cu (II) and PA in the sole and binary systems were set as 0.5 and 1.0 mmol/L, respectively; pH 5.0; 303 K).

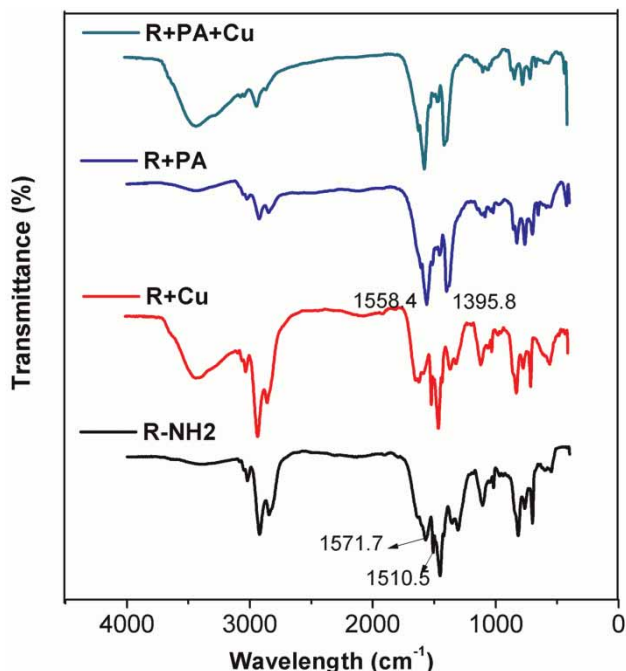


Figure 5 | FTIR spectra of resin before and after loading Cu (II), PA and both them.

The observations in the kinetic studies clearly showed there are different adsorption mechanism for Cu (II) and PA onto R-NH₂. Adsorption caused by coordination between adsorbates and adsorbents was generally slower than adsorption attributed to electrical attraction or ion exchange. Since the zeta potential of resin showed positive potential at pH 5, there appear to be two kinds of amine sites (-NH₂ and -NH₃⁺) existing on the resin surface (Lu et al. 2010; Kołodyńska 2011). Coordination could be easily formed between Cu (II) and -NH₂, in which N atoms share their lone pair of electrons with Cu (II) to form a bond (Liu et al. 2008). For PA, electrostatic attractions more likely occurred between -NH₃⁺ sites and negative PA species such as HL⁻ and L²⁻ (Lu et al. 2010). The possible interaction mechanisms in the sole systems are suggested by Equations (6)–(8)

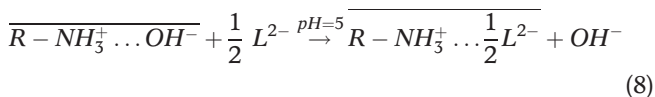
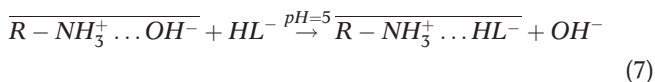
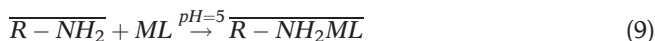


Table 4 | Speciation distributions for Cu (II) and PA in binary system under pH 5.0 (the initial concentration of Cu (II) and PA was 0.5 or 1.0 mmol/L)

Species (%)	[M]: [H ₂ L]		
	2:1	1:1	1:2
M ²⁺ /[M]	69.2	47.6	37.7
ML ⁰ /[M]	30.1	51.4	61.0
L ²⁻ /[H ₂ L]	11.8	14.5	20.7
HL ⁻ /[H ₂ L]	26.7	32.8	47.7
ML ⁰ /[H ₂ L]	60.2	51.4	30.5

The obvious uptake enhancement for both pollutants in the binary system, especially for Cu (II), could be related to the complexation between Cu (II) and PA (Sreejalekshmi et al. 2009). Under pH 5.0, speciation distributions for Cu (II) and PA in the binary system were calculated by the computer program Visual MINTEQ, showing the results in Table 4. Except for free M²⁺, HL⁻ and L²⁻, ML was newly formed in the binary system and became predominant around 30–60% of total Cu and PA species. We speculated that Cu in new ML species could also coordinate with -NH₂ sites to form a steadier geometrical configuration with four, five or six dentate (Liu et al. 2011b). Hence, [Cu-PA] complex possessed a much higher affinity than free Cu (II) to active sites of R-NH₂. On the other hand, the chelating adsorption of ML also made up a new part of PA adsorption, leading to an enhancement of PA removal. It would be a good explanation of the slower kinetic process for binary PA than for sole PA. The new interaction mechanism in the binary system is described by Equation (9)



CONCLUSION

In this study, the self-synthesized polyamine resin R-NH₂ was able to remove both Cu (II) and PA highly efficiently. Compared with those in the sole system, the adsorption capacities of R-NH₂ toward Cu (II) and PA in the binary system were markedly enhanced, especially for Cu (II). PA uptake was much faster than Cu adsorption. Apparently, for the sole systems, Cu (II) was captured through coordination with -NH₂ group while PA was mainly adsorbed as electrostatic attractions between -NH₃⁺ sites and negative PA species such as HL⁻ and L²⁻. In the binary systems, [Cu-PA] complex probably reacted with -NH₂ with a higher affinity, which contributed to adsorption enhancement of

both pollutants. The excellent trends in this work imply the potential for the application of polyamine resin in a simple, green and highly efficient technology for the co-removal of HMI and LMWOA.

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