

SYNTHESIS AND CHARACTERISTICS OF A CHELATING RESIN AS AN EXTRACTANT AND CHROMOGENIC REAGENT OF HEAVY METAL IONS IN SOLID PHASE EXTRACTION*

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Abstract A new chelating resin (CPS-DMA-SABA) was synthesized with the chloromethylated cross-linked polystyrene porous beads (CPS) as raw materials, which were bonded with salicylidene-*o*-aminobenzoic acid (SABA) on the surface *via* a quaternary ammonium unit as a linker. The results showed that CPS-DMA-SABA would easily change into a zwitterionic chelating resin (CPS-DMA-SABZ) when washed with distilled water. CPS-DMA-SABA was characterized by elemental analysis, infrared spectra and thermo-gravimetric analysis. The ion sorption capacities of CPS-DMA-SABA were found to be 1916 $\mu\text{g/g}$ for Zn^{2+} with pH at 4.5, 1620 $\mu\text{g/g}$ for Cu^{2+} with pH at 6.2, 1291 $\mu\text{g/g}$ for Ni^{2+} with pH at 6.6 and 780 $\mu\text{g/g}$ for Cr^{3+} with pH at 5.5, respectively. The experiments showed CPS-DMA-SABA also changed its color when meeting with the metal ion in the aqueous solution. As a consequence, CPS-DMA-SABA can not only be used as a solid phase extractant but also an indicator for confirming the heavy metal ion in solutions.

Keywords: Solid phase extractant; Zwitterionic chelating resin; Heavy metal ion; *o*-Aminobenzoic acid; Synthesis.

INTRODUCTION

Water pollution by heavy metal ions, such as Zn^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Cr^{3+} , Hg^{2+} , Pb^{2+} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ etc., has become a serious issue due to their toxicity and tendency to bioaccumulation. Besides, these metal ions are also the raw materials widely used in electrical articles, paints, chloro-alkali and pharmaceutical. Therefore, the removal and recovery of heavy metal ions from wastewater take on great importance. Various separation methods for heavy metal ions have been employed for the industrial needs, including chemical precipitation, membrane filtration, adsorption and ion-exchange. Chelating polymers have been used as one of the most effective materials to remove and recover heavy metal ions from wastewater, which has developed into the solid phase extraction (SPE)^[1–6]. The chelating polymers in SPE are selected as adsorbents and extractants rather than the analytic materials, which are used in the fluorescent qualitative detection and the spectrophotometric quantitative determination for heavy metal ions, for example, salicylidene-*o*-aminobenzoic acid (SABA) is a Schiff base used as a chromogenic reagent and applied to the fluorescent spectrophotometric determination of heavy metal ions^[7–11]. Whereas, these analytic materials can not be used for indicating absorption saturation level of heavy metal ions in SPE^[12]. In view of the above, the new chelating resins were designed and synthesized for detection and removal for heavy metal ions by bonding SABA on the surface of the cross-linked

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polystyrene porous beads chemically *via* a quaternary ammonium unit in the paper. The results showed the synthesized resin can be simultaneously used as a chromogenic material to detect heavy metal ions in aqueous solutions, and it can also be used as an extractant to separate and pre-concentrate heavy metal ions from waste water in SPE. Meanwhile we also found that CPS-DMA-SABA could easily change into a novel zwitterionic chelating resin (CPS-DMA-SABZ) when washed with distilled water. It's observed that the zwitterionic chelating resin CPS-DMA-SABZ not only takes full advantages of the conventional chelating resins that are easily regenerated in alkaline eluent, but also exhibits some distinguished properties, such as high electrostatic density. The pendent ionic groups, which have the opposite sign on the polymer chains, allow their applications to ions-exchange for the detection, determination, removal and recovery of heavy metal ions from the aqueous solutions.

EXPERIMENTAL

Instruments

^1H -NMR was recorded with a Bruker AV-400MHz spectrometer ($\text{C}_2\text{D}_6\text{SO}$). Chemical shifts (δ , values) are given in parts per million with tetramethylsilane as an internal standard. Fourier transform infrared spectra were recorded on a Nicolet MAGNA-IR 550 (II) spectrophotometer using KBr pellets. The concentration of various metal ions was determined by TAS-990 flame atomic absorption spectrometry (FAAS) with an air-acetylene flame (Beijing Purkinje General Instrument Limited Company, Beijing). A Shimadzu TG/DTA simultaneous measuring instrument DTG-60/60H (Kyoto, Japan) was used for thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA). Elemental analysis was carried out on a Carlo Erba-EA1108 elemental analyzer.

Reagents and Solutions

Chloromethylated cross-linked polystyrene porous beads (CPS) were purchased from Hecheng Science and Technology Factory, Tianjin, China and used as received. 5-Chloromethylsalicylaldehyde (5-CS) was synthesized according to our previous work^[13]. The dimethylaminomethylated CPS (CPS-DMA) were prepared with CPS and dimethylamine in dioxane solution, and had a nitrogen content of 5.58%. *o*-Aminobenzoic acid and the other reagents were reagent grade and were used without further purification.

The stock solutions of nitrate salts of Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} at the concentration of 1000 mg/L in 1% HNO_3 were prepared in distilled water and standardized by complexometric titration before use. The working solutions of the heavy metal ions were prepared appropriately by diluting the stock solutions. The buffer solutions for pH adjustment were acquired containing suitable amounts of NaHSO_4 for pH = 2, $\text{CH}_3\text{COONH}_4$ - CH_3COOH for pH = 4–6 and NH_3 - NH_4Cl for pH = 8–10.

Synthesis of CPS-DMA-S, CPS-DMA-SABA and CPS-DMA-SABZ

The general synthetic routes for chelating resins and model compounds are shown in Scheme 1.

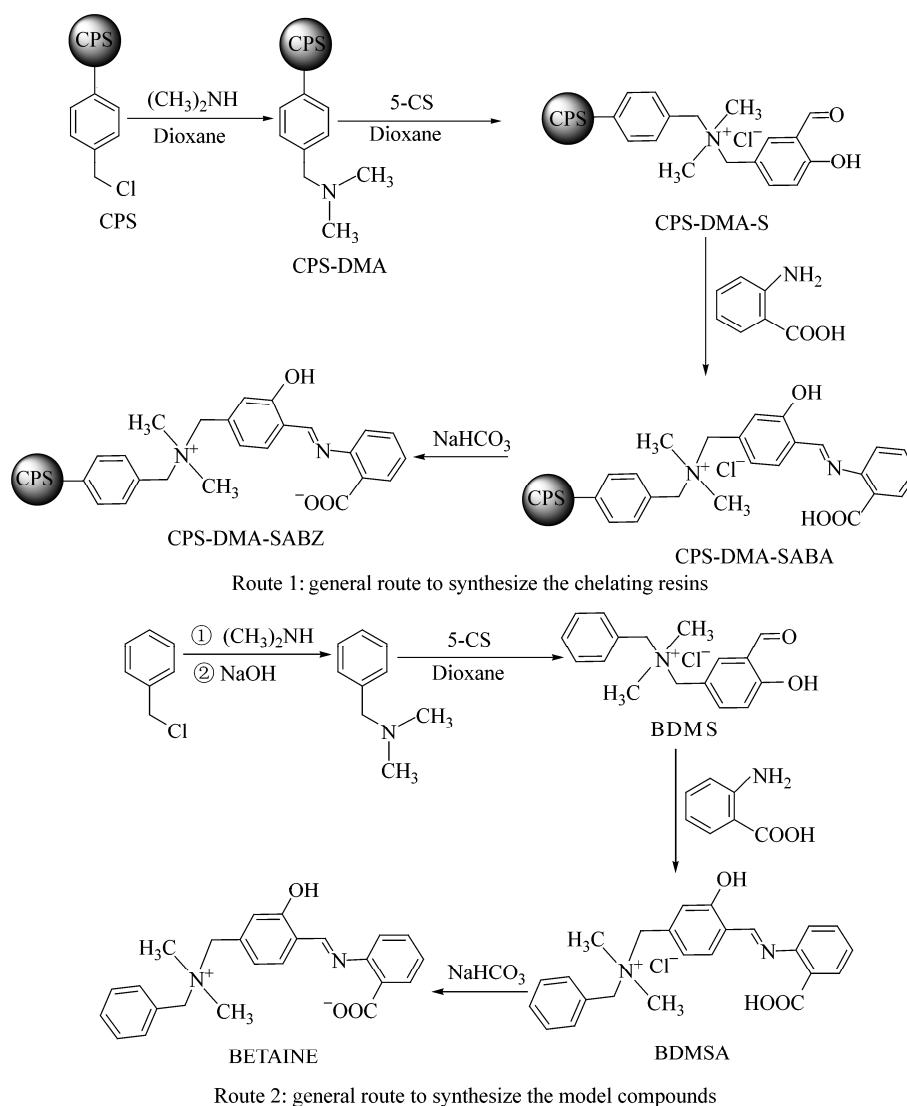
Synthesis of CPS-DMA-S

CPS (5.0 g) was added into the dioxane solution (35 mL) containing dimethylamine (15 g) and swollen for 2 h in a 3-necked flask, then refluxed for 48 h under the condition of mechanical stirring. The aminated CPS (CPS-DMA) was obtained and its nitrogen content was 5.58%. Then CPS-DMA was added into the dioxane solution (50 mL) containing 5-CS (21 g) and the mixture stirred at the room temperature for 48 h. The pale white spherical product (CPS-DMA-S) was filtered off, washed with heated ethanol and distilled water. After being dried under vacuum at 50 °C for 48 h, 8.26 g of the resin containing the quaternary ammonium and salicylaldehyde units was obtained. Elemental analysis of CPS-DMA-S gave N 2.63%, Cl 6.91%.

Preparation of CPS-DMA-SABA and CPS-DMA-SABZ

CPS-DMA-S (8.26 g) and *o*-aminobenzoic acid (10 g) were added into the alcohol solution (30 mL), and then refluxed for 50 h. The orange red spherical product was filtered off, washed with 20 mL of the acidic ethanol for three times and dried at 50 °C for 48 h under vacuum condition, 12.2 g of the orange red chelating resin

(CPS-DMA-SABA) was obtained. Elemental analysis of CPS-DMA-SABA gave N 4.02% and Cl 5.54%. Then CPS-DMA-SABA was washed with 3% NaHCO_3 aqueous solution and changed into the orange lake zwitterionic resin (CPS-DMA-SABZ). Elemental analysis of CPS-DMA-SABZ only gave N 4.37%.



Scheme 1 Routes to synthesize the chelating resins and model compounds

Synthesis of model compounds

In order to simply investigate the color changes and adsorption properties for heavy metal ions of the chelating resins, the small molecular model compounds had been first synthesized to imitate the synthetic reactions of the chelating resins. Scheme 1 clearly shows that the molecular structural differences between the model compounds (BDMS, BDMSA and BETAINE) and the chelating resins (CPS-DMA-S, CPS-DMA-SABA and CPS-DMA-SABZ) were only polyethylene chain. So long as we understand the structures, colors of the model compounds and their complexes, we will ascertain the color changes and absorption mechanism of the chelating resins.

Thermal and Chemical Stability of CPS-DMA-SABA and CPS-DMA-SABZ

The thermal stabilities of CPS-DMA-SABA and CPS-DMA-SABZ were determined by TGA analysis using DTG-60/60H thermogravimetry analyzer by using a heating rate of 10 K/min from 40 °C to 700 °C under

nitrogen flow. To check chelating resins applicabilities, their resistance to chemical changes was tested by soaking them in 25 mL of 10 mol/L of HCl, 5 mol/L of HNO₃ and 5 mol/L of NaOH solution at room temperature for 12 h respectively.

Metal Ion Sorption Capacity of CPS-DMA-SABA

The metal ion adsorption capacity of the resins was tested as follows: the dried resin (1.0–1.5 g) was added into a heavy metal ion solution (50 mL, 500 mg/L) in the beaker flask and it was shaken for 120 min at 25 °C to reach equilibrium. Meanwhile the effect of pH on the adsorption capacities of heavy metal ions was also studied by adjusting the heavy metal ion solution prior to equilibration over a pH range from 2 to 12. The residual concentration of heavy metal ion was detected by FAAS. The adsorption capacities were calculated using the following equation:

$$q = \frac{c_0 - c}{c_0} \times 100 (\%) \quad Q_m = \frac{c_0 - c}{W} \times V \times 1000$$

where q is the adsorptivity (%); Q_m is the metal ion adsorption capacity, µg/g; c_0 and c are the initial and final concentrations of the metal ion solutions, mg/mL; V is the volume of the solution, mL; W is the weight of dry resin, g.

RESULTS AND DISCUSSION

Structural Characterization

N,N-dimethylbenzylamine was first prepared with benzyl chloride and dimethylamine in dioxane solution like the synthetic reactions of the chelating resins. The boiling point of the prepared *N,N*-dimethylbenzylamine was 182–184 °C, which was in accord with the standard value (183–184 °C)^[14]. *N,N*-dimethylbenzylamine is a tertiary amine that is known to react with 5-CS and form the quaternary ammonium substituted salicylaldehyde derivative (BDMS)^[15, 16]. BDMS was white crystal and its melting point was 194–195 °C. The analytic data are seen in Tables 1 and 2.

Table 1. Analytic results of BDMS, BDMSA and BETAINE

Compound	Appearance	Melting point (°C)	Elemental analysis (calculated)			
			C	H	N	Cl
BDMS	white crystal	194–195	66.63 (66.77)	6.33 (6.59)	4.57 (4.58)	11.62 (11.69)
BDMSA	orange red	215–216	67.88 (67.84)	5.87 (5.93)	6.61 (6.59)	7.63 (8.34)
BETAINE	reddish orange	66–68	74.13 (74.21)	6.16 (6.23)	7.27 (7.24)	

Table 2. Spectra data of BDMS, BDMSA and BETAINE

Compound	IR (cm ⁻¹)	¹ H-NMR (δ)
BDMS	3351, 3031, 2912, 2832, 1685, 1617, 1467, 1211, 936	3.30 (s, 6H), 4.51 (s, 4H), 5.13 (s, 1H), 6.82 (d, J = 3.73 Hz, 1H), 7.02–7.47 (m, 8H), 10.22 (s, 1H)
BDMSA	3447–3347, 3029, 2913, 2817, 1640, 1616, 1466, 1213	3.30 (s, 6H), 4.50 (s, 4H), 5.11 (s, 1H), 6.88–8.17 (m, 12H), 8.33 (s, 1H), 11.02 (s, 1H)
BETAINE	3347, 3029, 2913, 2831, 1643, 1638, 1432, 1211, 936	3.27 (s, 6H), 4.49 (s, 4H), 5.00 (s, 1H), 6.64–8.13 (m, 12H), 8.29 (s, 1H)

BDMSA was a Schiff base, which can be synthesized by the condensation of BDMS with *o*-aminobenzoic acid in acidic ethanol solution easily. As shown in Tables 1 and 2, BDMSA was orange red crystal and its melting point was 215–216 °C. The strong band at 1685 cm⁻¹ that is due to the C=O stretch vibration disappeared while a new resonance at 1640 cm⁻¹ assigned to the C=N stretch was found in the IR. We found that chlorine content of BDMSA was lower than the calculated value, which showed that BDMSA lost HCl very easily. BDMSA was completely changed into the orange lake BETAINE when washed with 3% NaHCO₃ solution.

Several techniques are employed to characterize the structure of the resins (CPS-DMA-S, CPS-DMA-SABA and CPS-DMA-SABZ) during the synthetic sequences. CPS reacted with HNMe_2 in the dioxane solution to give the aminated resin (CPS-DMA), which suggested that 1 g resin contains 3.991 mmol tertiary amines. Then CPS-DMA reacted with 5-CS in the dioxane solution to produce pale white CPS-DMA-S containing the quaternary ammonium and salicylaldehyde units. Elemental analysis of CPS-DMA-S gave N 4.02% and Cl 5.54% while the nitrogen content of CPS-DMA-S was lower than it. Titrimetric analysis of CPS-DMA-S by using the AgNO_3 standard solution showed that 1 g of resin had 3.813 mmol salicylaldehyde units. The main peaks of CPS-DMA-S in FT-IR spectrum are 3324, 3025, 2917, 2832, 1688, 1612, 1468 and 1218 cm^{-1} corresponding to the stretching vibration of OH (phenolic), $\equiv\text{CH}$, CH_3 , CH_2 , $\text{C}=\text{O}$, $\text{C}=\text{C}$ and $\text{C}-\text{O}$ respectively.

The orange red CPS-DMA-SABA was prepared with CPS-DMA-S and *o*-aminobenzoic acid in acidic ethane solution. The FT-IR spectrum of CPS-DMA-SABA showed bands at 3349–3303, 2916, 2832, 1668, 1647, 1537, 1438, 1347 and 1221 cm^{-1} , which were assigned to the stretching frequencies of COOH , OH, CH, CH_3 , CH_2 , $\text{C}=\text{C}$ and $\text{C}-\text{O}$, respectively. The peak at 1688 cm^{-1} belongs to aldehyde $\text{C}=\text{O}$ disappeared in CPS-DMA-S IR spectrum, the new peaks at 1668 and 1438 cm^{-1} were due to carboxylate COOH stretching vibration, and peak at 1647 cm^{-1} was attributed to $\text{C}=\text{N}$ of CPS-DMA-SABA in the IR spectrum. We also found that the color of CPS-DMA-SABA became deep when it was washed with distilled water. The elemental analytic data showed CPS-DMA-SABA had no chlorine content after swelling and washing with 3% NaHCO_3 aqueous solution, therefore, we confirmed that CPS-DMA-SABA had changed into the zwitterionic chelating porous beads (CPS-DMA-SABZ).

CPS-DMA-SABA weight loss of about 4.43%, when temperature went up to $135\text{ }^\circ\text{C}$, could be seen in the TGA curve, which may be attributed to the loss of HCl. The thermo-degradation of CPS-DMA-SABA and CPS-DMA-SABZ sped up at $187\text{ }^\circ\text{C}$ and $203\text{ }^\circ\text{C}$ respectively, which may be due to the loss of quaternary ammonium salt and aromatic carboxylate. CPS-DMA-SABA and CPS-DMA-SABZ were found to be stable at room temperature. The experiments also indicated that CPS-DMA-SABA and CPS-DMA-SABZ were protonated in strong acid solutions. CPS-DMA-SABA could lose HCl and transformed into CPS-DMA-SABZ in the alkaline solution. CPS-DMA-SABZ may lose protons further and transformed into the negative CPS-DMA-SABZ in the strong alkaline solution.

Chromogenic Reactions of Model Compounds and Chelating Resins with Heavy Metal Ions

Now the model compounds had the same ligands and functional units as the chelating resins, the chromogenic reaction phenomena of CPS-DMA-SABA and CPS-DMA-SABZ with the metal ions might be similar to those of the model compounds respectively. In order to ascertain the chromogenic phenomena of CPS-DMA-SABA and CPS-DMA-SABZ with the metal ions, the complex reactions of the model compounds with the metal ions were first investigated and compared in the solutions, and the results are shown in Table 3.

Table 3. Chromogenic reactions of chelating resins and model compounds

	Zn^{2+}	Cu^{2+}	Ni^{3+}	Cr^{3+}
BDMSA	Orange red	Dim greenish-yellow	Yellow	Faint green
BETAINE	Orange red	Dim greenish-yellow	Yellow	Faint green
CPS-DMA-SABA	Yellowish red	Greenish-yellow	Orange yellow	Dark green
CPS-DMA-SAAZ	Yellowish red	Greenish-yellow	Orange yellow	Dark green

As seen in Table 3, the complex colors of the model compounds reacted with Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} were orange red, dim green yellow, yellow and faint green respectively. CPS-DMA-SABA and CPS-DMA-SABZ had also changed their color after absorbing these metal ions respectively, and the phenomena of the resins were synchronous with the model compounds respectively. It's convinced that the heavy metal ions absorption mechanisms of CPS-DMA-SABA and CPS-DMA-SABZ were similar to the formation of the small complexes, and CPS-DMA-SABA and CPS-DMA-SABZ could be used as the indicator to pre-demonstrate and detect the single heavy metal ion in the solution according to its color change.

Effect of Contact Time on Metal Ions Sorption Capacity

In order to investigate the effect of the heavy metal ions uptake time on the sorption capacities of CPS-DMA-SABA and CPS-DMA-SABZ, 1.0 g of resin was added into 100 mg of individual metal ion (Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+}) solutions at pH = 5, respectively, then stirred together for 1, 2, 4, 8, 16 and 32 min at room temperature. The metal ions absorbed by the resin were eluted with 2 mol/L HNO_3 and analyzed by the recommended procedure. The absorption saturation of resin with time is graphically presented in Fig. 1.

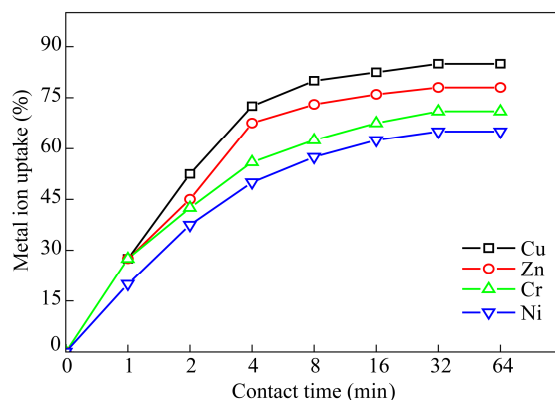


Fig. 1 Kinetics of uptake of metal ion on CPS-DMA-SABA at pH = 5.0

The loading half-time ($t_{1/2}$) that is the time required to reach 50% of the total loading capacity of the resin, was estimated from Fig. 1. The loading half-time of CPS-DMA-SABA was found to be less than 5 min for the metal ions (Zn^{2+} 2.4, Cu^{2+} 2.0, Ni^{2+} 4.5 and Cr^{3+} 3.3 min). The short loading half-time and the fast uptake rate of heavy metal ions on the resins reflects that CPS-DMA-SABA has good accessible and high hydrophilic chelating sites to bind heavy metal ions in aqueous solutions.

Adsorption Kinetics of Metal Ions Adsorption Process

Kinetics analysis for adsorption process is very important for the design of adsorbents because the kinetics provide essential information on adsorption mechanism and uptake rate. For testing the adsorption kinetics of metal ions, Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} ions were selected as targets. Figure 1 displays time dependence of metal ions adsorption capacity onto the CPS-DMA-SABA. The adsorption capacities of all four metal ions reach an equilibrium state within 1 h.

In order to investigate the mechanisms of metal ions adsorption process, the kinetic parameters for the adsorption behavior were analyzed using the pseudo-first-order and pseudo-second-order model equations. The results are shown in Fig. 2. The pseudo-first-order kinetic model assumes that the process mechanism is originated from physical adsorption and the equation is used as following^[17]:

$$\lg(q_e - q_t) = -\frac{K_1}{2.303}t + \lg q_e$$

where q_e and q_t are the amount of heavy metal ions adsorbed on the adsorbent in mg (metal)/g (adsorbent) at equilibrium and at time t , respectively, and K_1 is the constant of pseudo-first-order adsorption in min^{-1} . And the pseudo-second-order kinetic model is based on chemical adsorption (chemisorption) and the equation is given by^[18]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where K_2 is the rate constant of pseudo-second-order adsorption in $\text{g mg}^{-1} \text{min}^{-1}$.

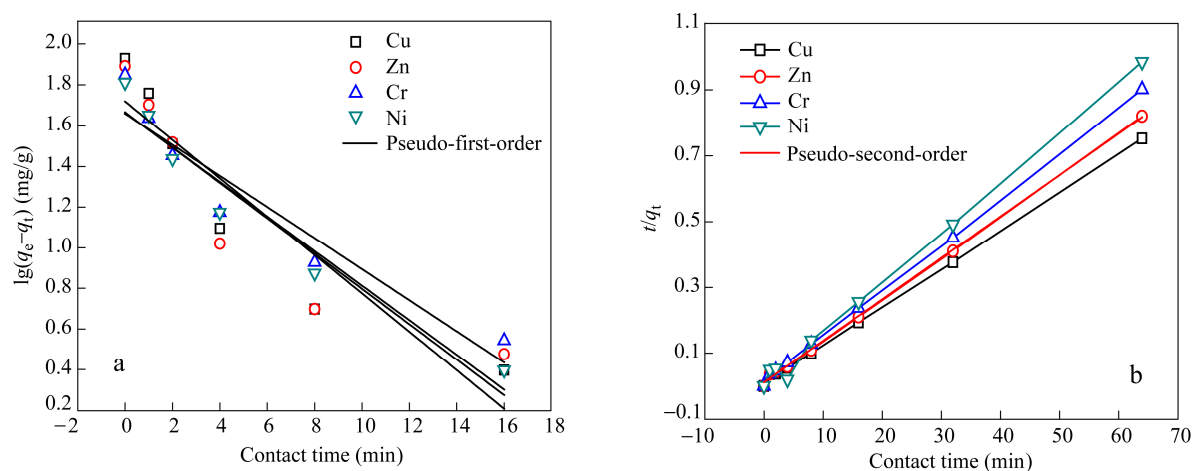


Fig. 2 Kinetic adsorption of Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} onto the CPS-DMA-SABA

As seen from Fig. 2, the linear spots accord with the pseudo-second-order kinetic model is better than that with the other one. In sum, metal ions adsorption process can be well described by the pseudo-second-order kinetic model.

The estimated parameter values and regression correlations calculated by nonlinear regression analysis using OriginPro 8.0 for the above models are listed in Table 4. The pseudo-second-order kinetic model got the higher correlations coefficients ($R^2 > 0.99$). It can also be indicated that the metal ions adsorption process on the CPS-DMA-SABA is promoted by a chemical process involving valence forces through sharing or exchange of electrons^[19].

Table 4. Kinetic adsorption parameters

Metal ions	Pseudo-first-order		Pseudo-second-order		
	K_1	R^2	$K_2 \times 10^6$	q_e	R^2
Cu^{2+}	0.2175	0.876	1.4205	86.5052	0.999
Zn^{2+}	0.2003	0.835	1.8019	79.3651	0.999
Cr^{3+}	0.1763	0.914	2.7772	72.3066	0.999
Ni^{2+}	0.1961	0.947	4.0942	66.4894	0.996

Effect of pH Value on Metal Ions Sorption Capacity

It's generally known that pH value can not only affect the surface charge properties of the chelating resins in terms of dissociation and protonation of the chelating groups^[3-5], but also has significant effect on the metal ion solubility and the loading capacity in solution. Taking Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} for example, the effect of pH value on the adsorption capacities of chelating resins for Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} were investigated, and the results are shown in Fig. 3.

As seen in Fig. 3, the pH value has significant effect on the ion adsorption capacity of CPS-DMA-SABA. The adsorption capacities were the highest at pH 4–9. It can be found that the adsorption capacity increases sharply with a pH rise from 2 to 4 but increases slightly with a pH rise from 4 to 9. When the pH value went up to 4.0, the adsorption capacity growth of CPS-DMA-SABA slowed down, and the adsorption capacities of CPS-DMA-SABA were not influenced by pH in the range of 4.0–9.0. The maximum adsorption capacities of CPS-DMA-SABA were 1916 $\mu\text{g/g}$ for Zn^{2+} with pH at 4.5, 1620 $\mu\text{g/g}$ for Cu^{2+} with pH at 6.2, 1291 $\mu\text{g/g}$ for Ni^{2+} with pH at 6.6 and 780 $\mu\text{g/g}$ for Cr^{3+} with pH at 5.5.

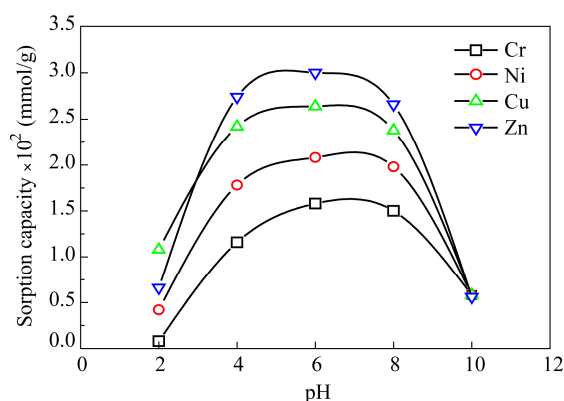
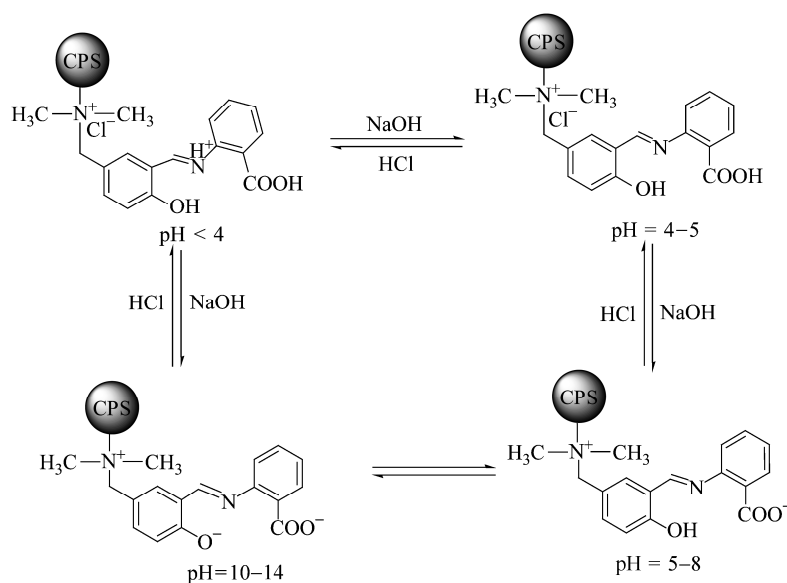


Fig. 3 Dependence of sorption capacity of CPS-DMA-SABA on the pH value

However, the adsorption capacities decline sharply when the PH value is lower than 4 or higher than 9. The probably reasons^[20] (as seen from Scheme 2) are: (1) under the lower PH conditions, the abundant competitive H^+ ions dominantly occupied the binding sites of the metal ions, leading to protonated imine and carboxylate groups of CPS-DMA-SABA, the positive charge repelled and prevented metal ions from transferring into the resin surface, and the complexation abilities of the resins ligands became weak, resulted in lower adsorption capacities of the resins. (2) Under higher PH conditions, the concentration of OH^- is higher, metal ions may react with OH^- to produce precipitation, this may lead the adsorption capacities to getting sharply down. As a consequence, we confirmed that CPS-DMA-SABA was applicable to adsorb and assemble the heavy and transition metal ions from the industrial effluents in a more wide pH range of 4.0–9.0.



Scheme 2 Reactions of CPS-DMA-SABA and CPS-DMA-SABZ with base and acid

CONCLUSIONS

The chelating resin CPS-DMA-SABA has been successfully synthesized and it is very easy to be transformed into the zwitterionic chelating resin CPS-DMA-SAAZ. The yielded resin was characterized by ^1H -NMR spectroscopy, Fourier transform infrared spectra and elementary analysis. The experimental results showed that CPS-DMA-SABA had excellent adsorption properties for Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} . Their optimum adsorption capacities are 1916, 1620, 1291 and 780 $\mu g/g$, respectively. Adsorption kinetic analysis shows the adsorption of

heavy metal ions onto CPS-DMA-SABA is a chemical binding process. Also, the adsorption capacities of all four metal ions reach an equilibrium state within 1 h indicating that the resin has fast uptake rate for the heavy metal ions. In conclusion, the resin not only could be applied for pre-concentration, separation, and determination of Zn^{2+} , Cu^{2+} , Ni^{2+} and Cr^{3+} , but also applied for the spectrophotometric detection of the single metal ion in the solution due to its color change, and it also can be used as the indicator material to show the heavy metal ion absorption saturation level.

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