

## Recovery of Cu(II) and Cd(II) by a chelating resin containing aspartate groups

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### Abstract

A chelating resin, crosslinked poly(glycidyl methacrylate-aspartic acid) (PASP), was synthesized by anchoring sodium aspartate to crosslinked poly(glycidyl methacrylate) for the recovery of Cu<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solutions. The resin was characterized by Fourier transform infrared spectroscopy, scanning electron microscope and mass balance. In non-competitive conditions, the adsorptions tended toward equilibrium at 60 min and the equilibrium adsorption capacities were 1.40 and 1.28 mmol/g PASP for Cu<sup>2+</sup> and Cd<sup>2+</sup>, respectively. The adsorption isothermals of the metal ions by PASP followed the Freundlich isotherm. Adsorption of Cu<sup>2+</sup> was affected slightly in the presence of NaNO<sub>3</sub> (0–0.3 M) but the uptake of Cd<sup>2+</sup> decreased significantly in the same condition. Except pH ≥ 4.0, the adsorption capacity of each metal ion decreased with lowering of solution pH. The reusability of PASP in adsorptions was investigated for five successive adsorption–desorption operations. When the pH of Cu<sup>2+</sup>/Cd<sup>2+</sup> mixture was 2 or 2.5, the competitive adsorption tests confirmed this resin had good adsorption selectivity for Cu<sup>2+</sup> with the coexistence of Cd<sup>2+</sup>.

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**Keywords:** Chelating resin; Adsorption; Heavy metals; Selectivity; Freundlich isotherm

### 1. Introduction

As industry expands, heavy metal ion contamination is exacerbated. When heavy metal ions are assimilated into living organisms, they accumulate in living bodies, causing serious diseases even at very low concentrations [1–3]. Therefore, many separation methods have been developed for removing heavy metal ions from aqueous solutions, including reduction and precipitation, coagulation, reverse osmosis, electrodialysis, and adsorption [3–11]. Among these technologies, adsorption of heavy metal ions using chelating resins is highly popular because they are reusable, easy to handle and have higher adsorption efficiencies and selectivity.

To prepare a chelating resin, numerous studies have synthesized adsorbents through the polymerization of conventional chelating monomers such as acrylic acid [12], methacrylic acid

[13], allylthiourea [14], vinylpyridine [15], and vinylimidazole [16]. Several researchers have firstly prepared a synthetic polymer, then reacted it with low-molecular weight ligands to form chelating resins [1,4,6,17–25]. In addition, modification of a natural polymer matrix by functionlization reactions has also been used to create a chelating resin [5,11,26–29].

Concerning the chemical structure, aspartic acid (Asp) possesses two carboxylic acids and one amine group that can share three pairs of electrons with a single metal ion. It can be easily introduced to the side chain of a polymer owing to the reactive amine hydrogen that responds to the epoxy groups. In polymer science, glycidyl methacrylate (GMA) is a commercial industrial material, cheaper than any other vinyl monomers that possess an epoxy ring in the side chain. After addition polymerization, the reactive epoxy rings of poly(glycidyl methacrylate) (PGMA) can react with low-molecular weight ligands to form a chelating resin [4,20–25]. However, most researchers were interested in anchoring amines to PGMA. Synthesis of a chelating resin through a reaction of PGMA with an amino acid has rarely been reported. Therefore, this article presents an attempt

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to prepare crosslinked poly(glycidyl methacrylate) beads via the suspension polymerization of GMA and poly(ethylene glycol) diacrylate. These beads were then functionalized with aspartic acid to form chelating resins for the removal of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from an aqueous solution. The effects of solution conditions including pH value, ionic strength and metal ion concentrations on the adsorption behaviors and desorption/repeated use of the resins were investigated. Furthermore, studies on the adsorption of toxic metal ions from a single-metal ion solution are basic and important research topics. However, there are usually two or more metal ions in industrial wastewater. Selective adsorption of a specific metal ion from a multimetal mixture can reduce the amount of heavy metal ions in wastewater as well as improve the applications of the recovered metal ion. Accordingly, the competitive adsorptions between  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from their mixtures were also studied in this article.

## 2. Experimental

### 2.1. Materials

Glycidyl methacrylate (GMA), dimethyl sulfoxide (DMSO), poly(ethylene glycol) diacrylate (PEGDA), cyclohexane, copper nitrate, cadmium nitrate, nitric acid, sodium nitrate and sodium hydroxide (Aldrich) were used as received. Azoisobutyronitrile (AIBN) was recrystallized by standard procedures. Aspartic acid (Aldrich) was neutralized by NaOH solution before reacting with crosslinked poly(glycidyl methacrylate) (CPGMA). The average molecular weight of poly(vinyl alcohol) (PVA) was 2000 and was obtained from Tokyo Kasei Kogyo Company (TDI), Japan. All the reagents were certified of ACS reagent grade.

### 2.2. Preparation of crosslinked poly(glycidyl methacrylate) (CPGMA)

CPGMA was prepared via the suspension polymerization as follows: PVA (3 g) dissolving in deionised water (130 ml) was used to be a continuous medium. The oil system containing GMA (20 g), PEGDA (1 g), cyclohexane (6 g) and AIBN (0.2 g) was added to a flask containing the continuous medium and kept at 62 °C for 6 h with continuous stirring. Finally, the temperature of the reaction system was raised to 82 °C for 5 min to evaporate cyclohexane. The white microbeads obtained by the polymerization were filtered off and washed repeatedly with hot water (62 °C) and ethanol to remove unreacted chemicals and then dried in vacuum at 60 °C.

### 2.3. Preparation of a chelating resin containing aspartate groups

CPGMA (10 g) and 30 ml DMSO were mixed in a flask and kept at 60 °C for 1 h with stirring. Then aspartic acid (15 g) neutralized by NaOH solution was added to the mixture of CPGMA/DMSO and stirred for 48 h at 85 °C. After this, the resins containing sodium aspartate were collected by filtration and washed again 10 times with deionized water and then dried

in vacuum at 60 °C for 48 h. Scheme 1 gives the synthesis process of the resin. To identify the chelating resin easily, we named this resin PASP.

### 2.4. Characterization of PASP

The functional groups of CPGMA and PASP were analyzed by Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer, Spectrum One). All the samples were prepared by mixing with KBr and pressed to form pellets. The mole content of aspartate group in PASP was calculated by mass balance. The surface morphology of PASP was observed under a scanning electron microscope (SEM, Hitachi S-4100, Japan). The resin was coated with a thin layer of platinum.

### 2.5. Adsorption studies

All the adsorption studies were conducted by mixing PASP (75–85 mg) and 20 ml of metal ions in a flask with a magnetic stirrer at about 120 rpm and at 25 ± 0.2 °C. The ionic strength of the metal ion solutions were controlled by adding  $\text{NaNO}_3$ . The pH value of each metal ion solution was adjusted with 0.5N  $\text{HNO}_3$  or NaOH solution. After the adsorption test, the PASP-metal ion complexes were separated from the solution by filtration. The concentrations of  $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$  in the filtrates were determined by atomic absorption spectrophotometer (AAs, Perkin-Elmer, AAnalyst100). The adsorption capacities  $Q$  (mmol/g PASP) in various adsorption times were obtained by using the following expression:

$$Q = \frac{(C_0 - C_f)V}{m} \quad (1)$$

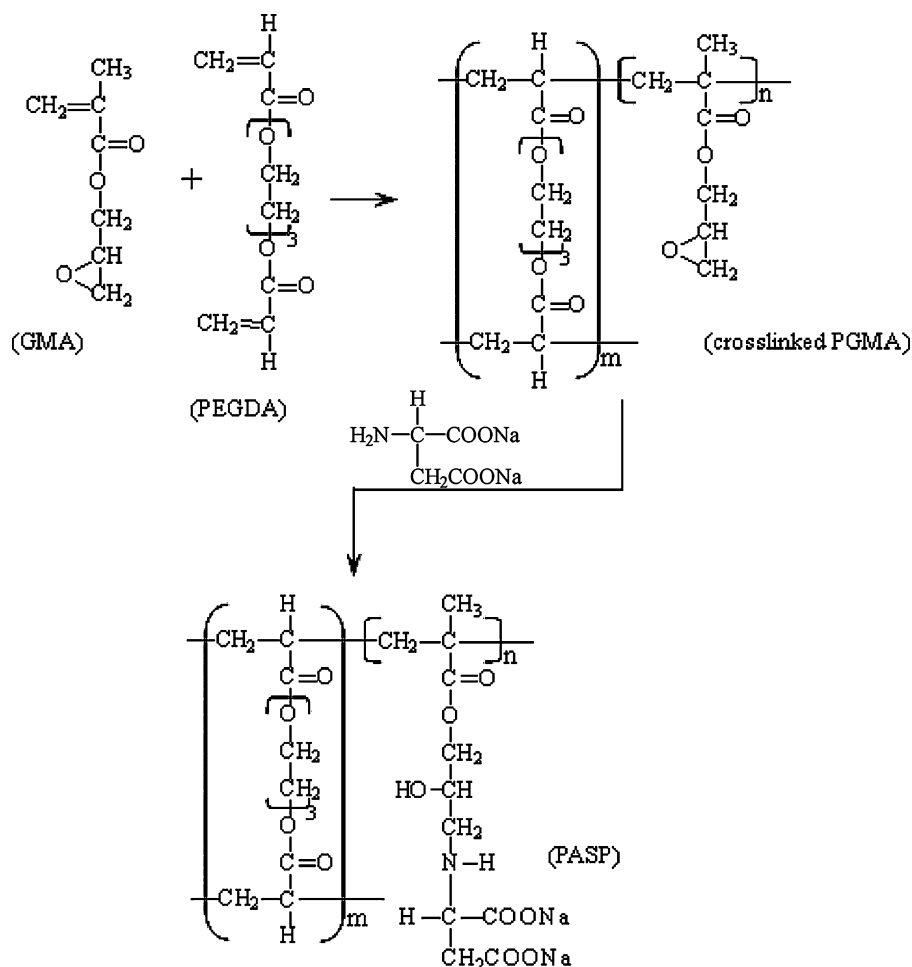
where  $C_0$  and  $C_f$  are the initial and final concentrations (mmol/l) of metal ion in the aqueous solution, respectively,  $V$  is the volume of metal ion solution (0.02 l in this article), and  $m$  is the weight of PASP resin (g). The competitive adsorptions for  $\text{Cu}^{2+}$  with the coexistence of  $\text{Cd}^{2+}$  under the same initial concentrations (10 mM) were also studied according to the above procedures.

### 2.6. Desorption and repeated use

Desorption of metal ions was performed by mixing PASP-metal ion complexes and 0.2 M  $\text{HNO}_3$  solution with a magnetic stirrer at about 120 rpm and 25 ± 0.2 °C for 5, 15, 30, 60, and 120 min, respectively. After filtration, the final metal ion concentrations in the aqueous solution were also analyzed by AAs. The desorption ratio ( $D$  %) was calculated as follows:

$$D(\%) = \frac{\text{mmol of metal ions desorbed to the } \text{HNO}_3 \text{ solution}}{\text{mmol of metal ions adsorbed onto PASP resin}} \quad (2)$$

The PASP resins collected from the desorption process were washed thoroughly with deionised water. Then, they were immersed in 0.1 M NaOH solution and stirred for 10 min at room temperature. Finally, these resins were rinsed thoroughly with



deionised water and dried by vacuum pump at 60 °C for repeated use.

### 3. Results and discussion

#### 3.1. Preparation and characterization of PASP

The chelating resin, PASP, was synthesized via an epoxy group reaction of CPGMA with sodium aspartate (Scheme 1). Fig. 1(A) shows the FT-IR spectrum of CPGMA. The peak at 1730 cm<sup>-1</sup> was caused by the stretching vibration of the ester carbonyl groups. Three absorption bands at 1270, 910 and 850 cm<sup>-1</sup> corresponded to the epoxy groups. In the spectrum of PASP (Fig. 1(B)), the strong peaks at 1590, 1650 and 3400 cm<sup>-1</sup> were caused by the stretching vibrations of C=O in carboxylate salts (–COO<sup>-</sup>), secondary amine (–NH–) and hydroxyl (–OH) groups [30], respectively. Prior to obtaining PASP, the resins had been rinsed in deionized water for removing unreacted sodium aspartate. Thus, Fig. 1 indicates that CPGMA functionalized with sodium aspartate to form PASP was carried out successfully. However, the band at 1270 cm<sup>-1</sup> still existed, implying that numerous epoxy groups within CPGMA did not react with sodium aspartate. Considering the polymerization procedures in Section 2.2, there was at least 9 g (0.063 mol) of

GMA within 10 g of CPGMA. That is, over 11 g of sodium aspartate would convert 10 g of CPGMA into PASP resin, or 1 g of PASP contained 2.97 mmol of sodium aspartate. Table 1 demonstrates 1 g of PASP only contains 1.46 mmol of sodium aspartate, which is in good agreement with the results of the FT-IR measurements. Additionally, Fig. 2 shows the diameter of PASP to

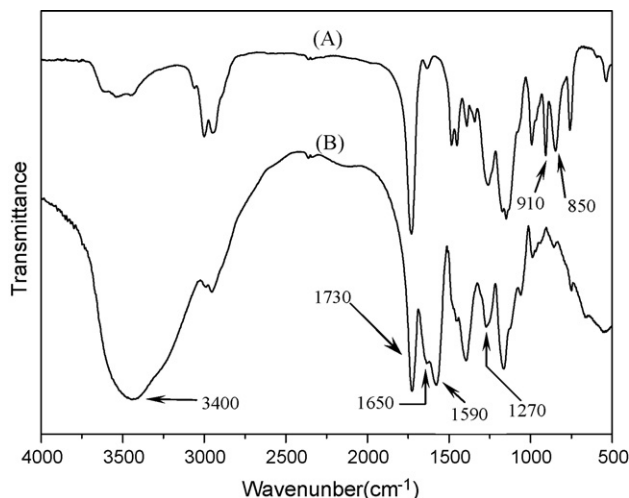


Fig. 1. FT-IR spectra of CPGMA (A) and PASP (B).

Table 1  
Moles of sodium aspartate within PASP calculated from mass balance

Descriptions	Values
Weight of CPGMA (g)	9.9927
Weight of PASP (g)	13.4740
Weight of sodium aspartate within 10 g PASP (g)	3.4813
Moles of sodium aspartate within PASP (mmol/g PASP)	1.46

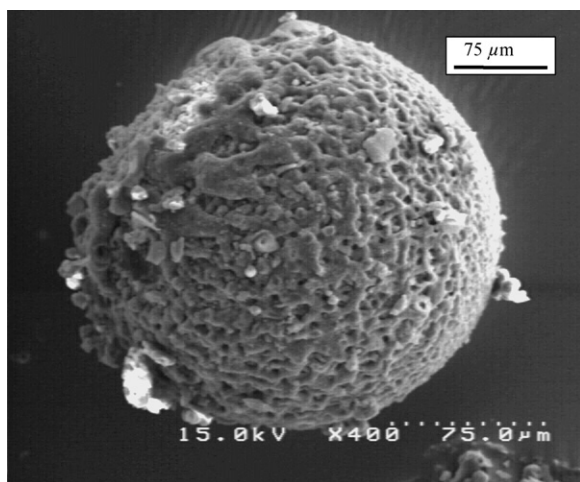


Fig. 2. SEM image of PASP.

be around 200  $\mu\text{m}$  with many pores on the surface. PASP is not a perfect sphere owing to the evaporation of cyclohexane penetrating and deforming the microbeads.

### 3.2. Time-dependent adsorption behavior

Fig. 3 shows the adsorption capacities of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by PASP as a function of time. In single-metal ion systems, the adsorption capacities increased sharply during the first 7 min and tended toward equilibrium at approximately 60 min. Accord-

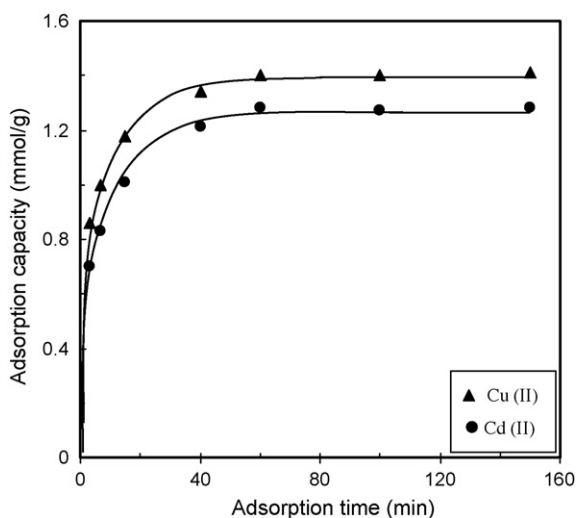


Fig. 3. Effect of adsorption time on the adsorption capacities for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  under noncompetitive condition at 25  $^{\circ}\text{C}$ , pH 5 (initial concentration of metal ion = 10 mM).

ingly, all other adsorption studies in this article were examined for 70 min to confirm the complete equilibria between PASP and metal ions. The blank tests for the adsorptions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by CPGMA were also performed for 70 min and found to be less than 0.009 mmol/g CPGMA. The equilibrium adsorption capacities were 1.40 mmol/g PASP for  $\text{Cu}^{2+}$  and 1.28 mmol/g PASP for  $\text{Cd}^{2+}$ . Numerous researchers [7,31,32] believed that the resins containing carboxylate, sulfonate or phosphate anions preferred cations of high charge and small hydrated volume. The hydrated radius of  $\text{Cu}^{2+}$  (2.07  $\text{\AA}$ ) is less than that of  $\text{Cd}^{2+}$  (2.28  $\text{\AA}$ ) and the ionic radius is in the order of  $\text{Cu}^{2+}$  (0.71  $\text{\AA}$ ) <  $\text{Cd}^{2+}$  (0.97  $\text{\AA}$ ) [33]. That is, the charge density of  $\text{Cu}^{2+}$  is greater than that of  $\text{Cd}^{2+}$ . As PASP adsorbing metal ions, the polymer chains shrink because the fraction of the free chelating site (hydrophilic region) decreases [34,35]. Thus, metal ions are difficult to diffuse toward the free chelating sites and the adsorption process will reach equilibrium. However,  $\text{Cu}^{2+}$  possesses both smaller hydrated and ionic radii that can still diffuse toward the adsorption sites. This means that the equilibrium adsorption capacity of  $\text{Cu}^{2+}$  is greater than that of  $\text{Cd}^{2+}$ .

### 3.3. Effect of initial concentration on adsorption

The influence of the initial concentrations of metal ions on adsorption capacities is presented in Fig. 4. The adsorption capacities increased first with increasing the initial concentration of metal ion then reached a plateau value. When the initial concentrations of metal ion were less than 3 mM, the quantity of adsorption sites in PASP were vastly more than the amount of metal ion in 20 ml solution. After the adsorption process, the metal ions were almost adsorbed by PASP and the residue concentrations of metal ion in the solution were less than 0.5 ppm. Thus, the adsorption capacities of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  were nearly identical. These high adsorption efficiencies were attributed to the hydrophilic nature of hydroxyl ( $-\text{OH}$ ), amine ( $-\text{NH}-$ ), and carboxylate ( $-\text{COO}^-$ ) groups in PASP, which had an adequate affinity to the metal ions. Additionally, the long side chain of PASP acted as a spacer arm that could catch metal ions easily. As the concentrations of metal ion increased, PASP adsorbed

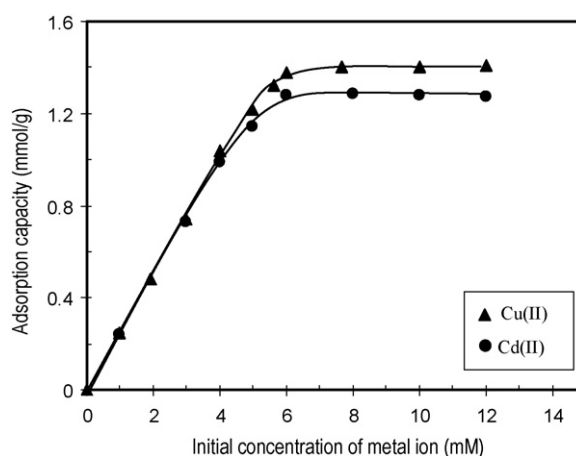


Fig. 4. The influence of the initial concentrations of metal ions on the equilibrium adsorption capacities by PASP at 25  $^{\circ}\text{C}$ , pH 5 (adsorption time = 70 min).

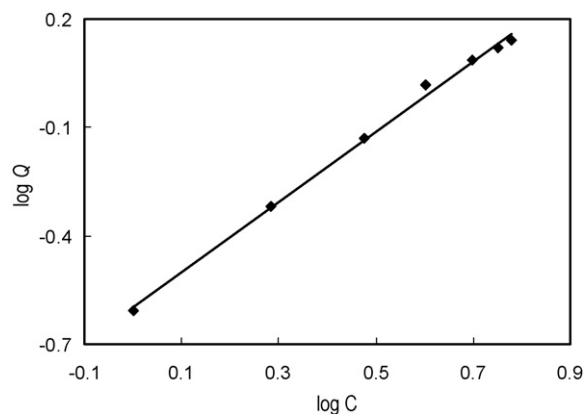


Fig. 5. Freundlich adsorption for  $\text{Cu}^{2+}$  by PASP at 25 °C.

many metal ions and the polymer chains shrunk.  $\text{Cd}^{2+}$  would be hard to diffuse toward the free chelating sites within PASP but  $\text{Cu}^{2+}$  could diffuse to the free sites. This is why the curves of adsorption capacity diverge at high concentrations of metal ions.

The Freundlich isotherm is formulated as

$$Q = kC^n \quad (3)$$

where  $Q$  is the amount of metal ions adsorbed,  $C$  is the concentration of metal ion at equilibrium and  $k$ ,  $n$  are the Freundlich constants. Eq. (3) gives  $\log Q = n \log C + \log k$ . The plot of  $\log Q$  versus  $\log C$  should result in a straight line with slope equal to  $n$  and intercept equal to  $\log k$ . Accordingly, Fig. 5, for example, illustrates a linear Freundlich plot for the adsorption of  $\text{Cu}^{2+}$  on PASP. The Freundlich constants for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  have been calculated and tabulated in Table 2. The plots are linear and show good fit for the metal ions, indicating the uptake of metal ions occur on heterogeneous surfaces by multilayer adsorptions.

### 3.4. Effect of ionic strength on adsorption

The presence of salt in wastewaters is one of the important factors that may impede the adsorption of heavy metal ions. Fig. 6 shows the adsorptions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by PASP in the presence of 0–0.3 mol/l of  $\text{NaNO}_3$ . Obviously, as the concentrations of  $\text{NaNO}_3$  in  $\text{Cd}^{2+}$  solution increased (from 0 to 0.3 M), the adsorptions of  $\text{Cd}^{2+}$  decreased significantly (from 1.28 to 0.97 mmol/g PASP). However, even when the concentration of  $\text{NaNO}_3$  (0.3 M) was much greater than that of  $\text{Cu}^{2+}$  (0.01 M), the adsorption capacity of  $\text{Cu}^{2+}$  decreased only slightly (<5%). In other words, the presence of  $\text{NaNO}_3$  in  $\text{Cu}^{2+}$  solution was not an important controlling parameter in the adsorption pro-

Table 2  
Freundlich isotherm constants of PASP for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$

Metal ion	Freundlich constants		$R^2$
	$k$	$n$	
$\text{Cu}^{2+}$	0.253	0.970	0.9968
$\text{Cd}^{2+}$	0.250	0.947	0.9947

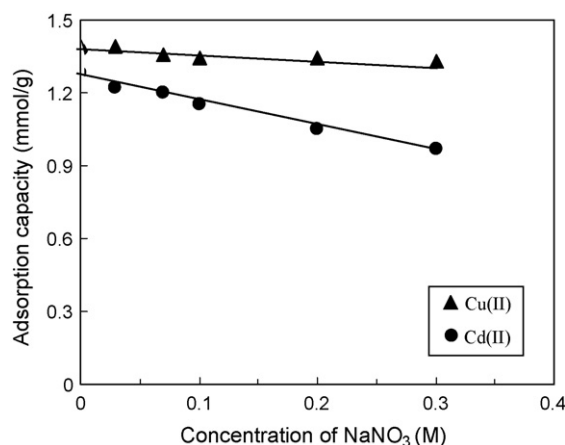


Fig. 6. The adsorptions of metal ions by PASP in the presence of  $\text{NaNO}_3$  at 25 °C, pH 5 (initial concentration of metal ion = 10 mM; adsorption time = 70 min).

cess. As stated above, the charge density of  $\text{Cu}^{2+}$  is greater than that of  $\text{Cd}^{2+}$ . The attraction of the aspartate group for  $\text{Cu}^{2+}$  is stronger than that for  $\text{Cd}^{2+}$ . Therefore, the adsorption of  $\text{Cu}^{2+}$  is affected slightly in the presence of  $\text{NaNO}_3$  but the uptake of  $\text{Cd}^{2+}$  decreases significantly in the same conditions.

### 3.5. Effect of pH on adsorption

Fig. 7 shows the effect of the solution pH on the adsorptions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by PASP, respectively. The pH in a range of 1–5 was chosen to avoid the precipitations of  $\text{Cu}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_2$ . The adsorption capacities increased with an increase in solution pH, but the increment was insignificant in the pH range of 4.0–5.0. Additionally, no adsorption was observed at pH 1. At low pH values, high concentrations of  $\text{H}^+$  can react with carboxylate ions ( $\text{COO}^-$ ) and amine groups ( $-\text{NH}-$ ) within PASP to form protonation, which induces an electrostatic repulsion of metal ions. Therefore, competition exists between  $\text{H}^+$  and metal ions for adsorption sites and decreases the adsorption capacity. At pH 1, because the concentration of  $\text{H}^+$  was much greater than that of the metal ions, the adsorption capacities of metal ions being 0 should be reasonable.

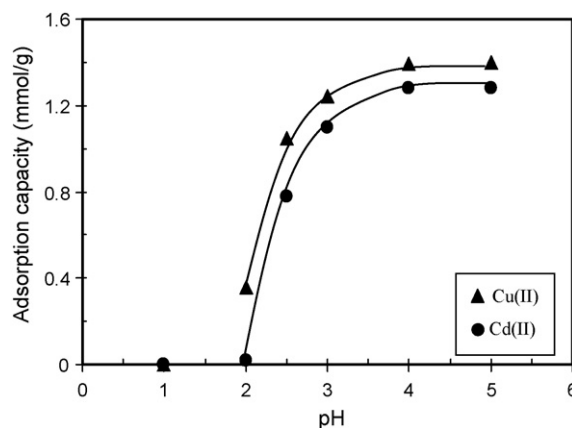


Fig. 7. Effect of the pH on the adsorptions of metal ions by PASP at 25 °C (initial concentration of metal ion = 10 mM; adsorption time = 70 min).

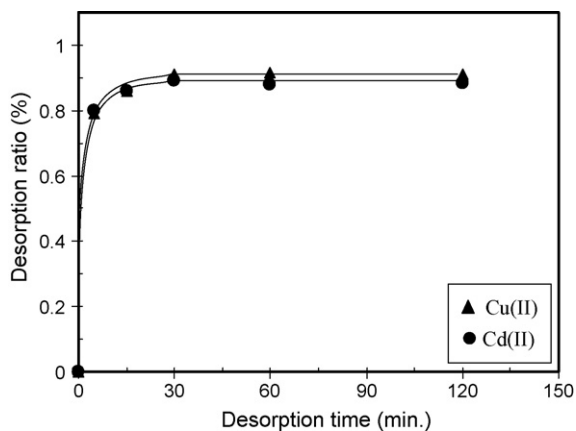


Fig. 8. Desorption of metal ions from PASP–metal ion complexes by 0.2 M HNO<sub>3</sub> solution at 25 °C.

### 3.6. Desorption and repeated use

Desorption of metal ions from PASP–metal ion complexes was carried out using 0.2 M HNO<sub>3</sub> solution at 25 °C. As stated previously, no adsorption was observed at pH 1, demonstrating 0.1 M H<sup>+</sup> could forbid the adsorptions of Cu<sup>2+</sup> and Cd<sup>2+</sup>. To improve the desorption efficiency, the desorption studies were carried out in 0.2 M HNO<sub>3</sub> solution. Fig. 8 shows the desorption ratio of PASP–metal ion complexes as a function of time. The desorption process reached equilibrium at about 30 min and the desorption ratios were approximately 90%. Table 3 displays the adsorptions of Cu<sup>2+</sup> and Cd<sup>2+</sup> after 5 cycles of consecutive adsorption–desorption procedures. The adsorption capacities showed a slight decrease then remained stable. After 5 cycles of adsorption–desorption operations, the adsorption capacities of Cu<sup>2+</sup> and Cd<sup>2+</sup> were around 1.27 and 1.12 mmol/g, respectively. This shows PASP is a good reusable sorbent in removal of Cu<sup>2+</sup> and Cd<sup>2+</sup> from their single-metal ion solutions. When PASP–metal ion complexes were placed in HNO<sub>3</sub> solution to release metal ions, H<sup>+</sup> could replace the metal ions adsorbed by aspartate groups within PASP to form carboxylic acids (–COOH) and amine salts (–NH<sub>2</sub><sup>+</sup>), respectively. If these PASP resins were used to adsorb metal ions in the previous adsorption conditions, only 15–25% of initial adsorption capacities were observed. However, after these resins were neutralized with NaOH solution to form carboxylate salts (–COONa) and secondary amines (–NH–), the re-adsorption capacities could attain about 90% of initial uptake values.

Table 3  
The adsorption capacities of PASP after repeated adsorption–desorption operations at 25 °C, pH 5

Metal ion	Adsorption capacity (mmol/g PASP)					
	Recycle 0	Recycle 1	Recycle 2	Recycle 3	Recycle 4	Recycle 5
Cu <sup>2+</sup>	1.40	1.28	1.26	1.25	1.28	1.27
Cd <sup>2+</sup>	1.28	1.13	1.12	1.14	1.11	1.12

Concentration of metal ion = 10 mM; adsorption time = 70 min.

### 3.7. Competitive adsorption

The competitive adsorptions of Cu<sup>2+</sup> with Cd<sup>2+</sup> under the same initial concentrations (10 mM) are given in Fig. 9. In the range of pH 2.5–5, Fig. 7 displays the difference in noncompetitive adsorption capacities between Cu<sup>2+</sup> and Cd<sup>2+</sup> to be less than 0.2 mmol/g PASP. However, Fig. 9 reveals that adsorption capacities of Cu<sup>2+</sup> and Cd<sup>2+</sup> are inhibited by each other. The decrement in adsorption capacity of Cd<sup>2+</sup> is greater than that of Cu<sup>2+</sup>. Therefore, the adsorption of Cd<sup>2+</sup> is impeded more significantly in the presence of Cu<sup>2+</sup>. In competitive adsorptions, the ratio of adsorption capacity of Cu<sup>2+</sup> to that of Cd<sup>2+</sup> can be expressed as selectivity coefficient  $S_{Cu/Cd}$ . Thus, as pH of the solution decreases, the selectivity coefficient  $S_{Cu/Cd}$  increases. At pH 2.5, the adsorption capacity of Cu<sup>2+</sup> is 0.85 mmol/g PASP and the selectivity coefficient  $S_{Cu/Cd} = 3.3$ . This implies the mole ratio of Cu<sup>2+</sup> adsorbed by PASP from the same concentration of Cu<sup>2+</sup>/Cd<sup>2+</sup> mixture is 77%. The result cannot meet our expectations. At pH 2, although the adsorption capacity of Cu<sup>2+</sup> is only 0.36 mmol/g PASP, the selectivity coefficient  $S_{Cu/Cd}$  tends to  $\infty$ . In other words, we can separate pure Cu<sup>2+</sup> from Cu<sup>2+</sup>/Cd<sup>2+</sup> mixture by controlling the solution at pH 2. In noncompetitive adsorptions, Fig. 7 displays the adsorption capacity of Cd<sup>2+</sup> to be only 0.02 mmol/g PASP at pH 2. This indicates the adsorption of Cd<sup>2+</sup> by PASP is inhibited sharply by H<sup>+</sup> at pH 2. Thus, PASP cannot adsorb Cd<sup>2+</sup> at pH 2 because the adsorption is inhibited by both H<sup>+</sup> and Cu<sup>2+</sup>. In addition, Fig. 6 reveals the adsorption of Cu<sup>2+</sup> is affected slightly in the presence of NaNO<sub>3</sub> but the uptake of Cd<sup>2+</sup> decreases significantly in the same condition. Therefore, Fig. 10 shows the competitive adsorptions of Cu<sup>2+</sup> with Cd<sup>2+</sup> from the solutions containing Cu<sup>2+</sup>, Cd<sup>2+</sup> and 0.3 M NaNO<sub>3</sub>. Comparison of Fig. 10 with Fig. 9 reveals the adsorptions of Cu<sup>2+</sup> are not affected by the presence of Cd<sup>2+</sup> and NaNO<sub>3</sub>, but remarkable decrements of adsorption capacity for Cd<sup>2+</sup> are observed. At pH 2.5, Fig. 10 displays that the adsorption capacity of Cu<sup>2+</sup> is still 0.85 mmol/g PASP and the  $S_{Cu/Cd}$

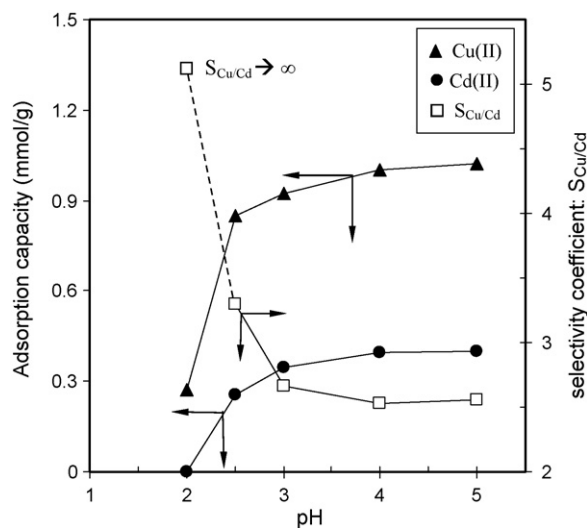


Fig. 9. Effect of pH on the competitive adsorptions and selectivity of Cu<sup>2+</sup> with Cd<sup>2+</sup> from Cu<sup>2+</sup>/Cd<sup>2+</sup> mixture under the same initial concentration (10 mM) at 25 °C (adsorption time = 70 min).

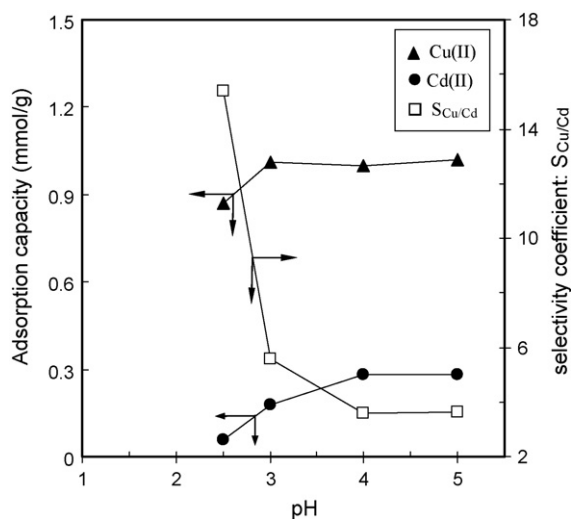


Fig. 10. Effect of pH on the competitive adsorptions and selectivity of  $\text{Cu}^{2+}$  with  $\text{Cd}^{2+}$  from  $\text{Cu}^{2+}/\text{Cd}^{2+}$  mixture under the same initial concentration (10 mM) and in the presence of 0.3 M  $\text{NaNO}_3$  at 25 °C (adsorption time = 70 min).

enlarges to 15.4. That is, the mole ratio of  $\text{Cu}^{2+}$  adsorbed by PASP is 94%. Adding 0.3 M  $\text{NaNO}_3$  to  $\text{Cu}^{2+}/\text{Cd}^{2+}$  mixture can improve the adsorption selectivity of  $\text{Cu}^{2+}$ . In summary, PASP can be applied to the recovery, separation and pre-concentration of  $\text{Cu}^{2+}$  in aqueous systems containing  $\text{Cd}^{2+}$ .

#### 4. Conclusions

In this study, sodium aspartate was anchored to the epoxy group of crosslinked poly(glycidyl methacrylate) to form a chelating resin (PASP) for the recovery of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from aqueous solutions. The adsorptions tended toward equilibrium at 60 min and the adsorption capacities of PASP from their single-metal ion solutions were 1.40 and 1.28 mmol/g PASP for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , respectively. The adsorption of  $\text{Cd}^{2+}$  decreased significantly in the presence of  $\text{NaNO}_3$  but the uptake of  $\text{Cu}^{2+}$  was affected slightly. The adsorptions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by PASP were governed by the Freundlich type isotherm. Within pH 4–5, decreasing the pH of the solution did not produce remarkable changes in adsorption capacities. In the range of pH 4.0–1.0, the resin showed a decrease in adsorption with lowering of solution pH. PASP can be regenerated by mixing with 0.2 M  $\text{HNO}_3$  solution and can be reused with efficiency of about 90% for at least up to five times. In competitive adsorptions, controlling the  $\text{Cu}^{2+}/\text{Cd}^{2+}$  mixture containing 0.3 M  $\text{NaNO}_3$ , the adsorption capacity of  $\text{Cu}^{2+}$  was 0.85 mmol/g PASP and the selectivity coefficient ( $S_{\text{Cu}/\text{Cd}}$ ) was 15.4 at pH 2.5. However, although the adsorption capacity of  $\text{Cu}^{2+}$  was 0.36 mmol/g PASP at pH 2 without  $\text{NaNO}_3$ , the selectivity coefficient ( $S_{\text{Cu}/\text{Cd}}$ ) tended to  $\infty$ . PASP can be applied to the recovery, separation and pre-concentration of  $\text{Cu}^{2+}$  in aqueous systems containing  $\text{Cd}^{2+}$ .

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