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ORIGINAL PAPER

Carboxyethylated polyaminostyrene for selective copper removal

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Abstract In order to prepare copper selective chelating resin, *β*-alanine functionality was introduced into polystyrene matrix by the aza-Michael addition of poly(4-aminostyrene) to acrylic acid. The resin was characterized by elemental analysis and pH potentiometric titration in terms of the degree of carboxyethylation ($DS = 1.3$) and protonation constant of the amine group ($\log K_H = 7.48$). The optimum pH for Cu^{2+} adsorption was found to be 7–8 (0.1 M ammonium acetate buffer) and the contact time required to achieve the equilibrium was about 1 h. The adsorption kinetics follows a pseudo-second order reaction rate, where the initial stage is governed by intraparticle diffusion. The adsorption isotherm data are in good agreement with the Langmuir model. The resin shows high adsorption capacity (1.26 mmol/g) and exhibits high selectivity toward Cu^{2+} ions with no affinity to Zn^{2+}, Co^{2+}, Cd^{2+} ions and only weak affinity to Ni^{2+} ions.

Keywords Chelating resin · Polyaminostyrene · *β*-alanine · Adsorption kinetics · Adsorption isotherm

Introduction

The selective removal of metal ions from aqueous solutions has been a significant topic in previous research, which has demonstrated that chelating resins are very useful for analytical and industrial applications [1–5]. A large number of chelating groups have now been incorporated into polymer matrices, such as amino acids, aminophosphonic acids, Schiff bases, 8-hydroxyquinoline, 1,10-phenanthroline, amidoxime, and so on. These functional groups are usually responsible for the

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efficiency and adsorption selectivity of chelating resins; therefore, the specific affinity of the resin can be improved by incorporation of a chelating group that has been previously shown to have an exceptionally high stability constant for a target metal ion.

Previous studies have demonstrated that β-alanine derivatives such as iminodipropionic acid (Idp) [6] or Idp-like ligands [7–9] are more selective toward Cu^{2+} ions than are the well-known iminodiacetate (Ida) analogues or corresponding amines. Among Idp containing ligands, *N,N*-di(2-carboxyethyl)anilines having electron-donor substituents in para- and/or meta-positions exhibited the highest selectivity [9]. Therefore, incorporating a metal-binding site with a β-alanine functional group into a polymer could potentially generate a copper-selective chelating resin. In our previous research, we have exploited this idea and were successful in preparing a number of chelating resins with β-alanine functionality onto different oxide supports (silica gels and fillers, macroporous glasses, alumina, titania, zirconia) [10, 11] or onto polyaminosaccharides such as chitosan [12] or chitin-glucan [13]. Some of the prepared chelating resins exhibited high selectivity in extracting Cu^{2+} ions from a mixture of transition metal ions; however, non-selective binding by the oxide or polysaccharide matrices also took place. In this respect, a polystyrene matrix could prove to be beneficial because it is inert to metal binding and is sufficiently rigid.

Therefore, a chelating resin, based on polystyrene matrix and having a β-alanine functional group that is directly conjugated with a phenyl ring, can be predicted to form stronger metal complexes and to have better selectivity for Cu^{2+} than do resins with amine or Ida functionalities. In this article, we characterize a novel chelating resin containing *N*-phenyl-β-alanine functional groups—poly(*N*-(2-carboxyethyl)-4-aminostyrene), or CE-PAS—prepared by the aza-Michael reaction of the polyaminostyrene (PAS) with acrylic acid. The kinetics, equilibrium, and selectivity of transition metal adsorption are studied. Novel copper selective chelating resin could have wide-ranging analytical applications in selective separation and pre-concentration techniques. Its use would permit the analysis of lower concentrations of copper-containing samples than would otherwise be possible, and would reduce and simplify the sample matrix. Copper loaded CE-PAS also has a potential for use as a stationary phase in immobilized metal affinity chromatography for bio-separation and purification of peptides, proteins, nucleic acids, hormones, and enzymes.

Experimental

Materials and reagents

Poly(4-aminostyrene) (PAS, 200-400 mesh) was purchased from Bachem Holding AG, Bubendorf, Switzerland (Catalog No. D-2210). Acrylic acid (Aldrich 14,723-0) and 3-bromopropionic acid (Aldrich 10,128-1) were used without additional purification for resin preparation. A carbonate-free KOH solution was prepared by precipitating carbonate with $Ba(OH)_2$ and passing the solution through Dowex 50 W-X8 ion-exchange resin (in the potassium form) to remove excess Ba^{2+} ions [14].

The KOH solution was then standardized against a commercial 0.1000 M HCl solution. Stock metal ion solutions (0.1 M) were prepared from analytical grade nitrates and were standardized by complexometric titration with a 0.1000 M standard EDTA solution [15].

Preparation of CE-PAS resin

A typical procedure was as follows: 1.00 g of air-dried poly(4-aminostyrene) (2.23 mmol of *N*) was treated with acrylic acid (AA) or 3-bromopropionic acid (3-BP) at varying temperatures, solvents, and reaction times. All samples were filtered and washed thoroughly with ethanol and finally with a large volume of deionized water until a neutral pH of the wastes was achieved. The obtained yellow resins were then dried overnight at 80 °C. The experimental conditions and some characteristics of the obtained samples are summarized in Table 1. The elemental analyses of the products were performed by Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa. IR spectra were recorded with a Perkin Elmer Spectrum-One FTIR spectrometer (4000–400 cm^{-1}) using a smart orbit accessory for single-reflection attenuated total reflectance.

Resin titration

High precision potentiometric titrations were performed with a PC-controlled system assembled with a Crison MicropH 2002 pH meter, a Crison MicroBU 2030 microburette, an Orion 90-02-00 (double junction AgCl/Ag) reference electrode, and a Russel SWL/S7 glass electrode. The titrations were performed by the addition of known amounts of standard carbonate-free 0.1 M KOH solution under an atmosphere of CO_2 and O_2-free nitrogen at 25.0 ± 0.1 °C and ionic strength 0.1 M KNO_3 in a Metrohm EA880T double-wall glass cell with a Metrohm E649 stirrer. The glass electrode was calibrated in terms of hydrogen ion concentration by

Table 1 Synthesis conditions and composition of CE-PAS resins

Sample	Synthesis conditions	Elemental analysis data			*N* (mmol/g)	*DS*[b]
		%C	%N	%H		
PAS		85.48	3.12	7.79	2.23	–
CE-PAS(1)	3.5 g 3-BP/10 mL H_2O/3 g NaOH; 60 °C; 24 h	80.55	2.76	7.34	1.97	0.68
CE-PAS(2)	5 mL AA/10 mL H_2O; 25 °C; 24 h	65.20	1.82	6.80	1.30	3.26[a]
CE-PAS(3)	5 mL AA/10 mL H_2O/3 g NaOH; 25 °C; 24 h	84.98	3.00	7.62	2.14	0.37
CE-PAS(4)	10 mL AA/10 mL toluene; 60 °C; 5.5 h	76.04	2.51	7.76	1.79	1.14
CE-PAS(5)	3 mL AA/6 mL toluene; 25 °C; 20 h	76.03	2.47	7.11	1.76	1.32

[a] Polyacrylic acid formed along with CE-PAS

[b] $DS = \frac{\left(\frac{\%C}{\%N}\right)_{\text{CE-PAS}} - \left(\frac{\%C}{\%N}\right)_{\text{PAS}}}{\frac{3M(\text{C})}{M(\text{N})}}$

using buffers in the pH range 4–9 with ionic strengths adjusted to 0.1 with KNO_3 [16]. The stabilization criteria used for recording the potential was $\Delta E/\Delta t \leq 0.1$ mV/min, which corresponds to a stabilization time for each point of around 30–60 min. The controlling program was written by Prof. C.A.R. Gomes (Universidade do Porto, Portugal).

Adsorption kinetics experiments

Kinetics was performed in batch reactor; 0.1 g of the dried CE-PAS was added into 250 mL of a Cu^{2+} solution with an initial concentration of 3×10^{-5} M and an initial solution pH of 7.5 (0.1 M ammonium acetate buffer). The mixture was stirred in a magnetic stirrer at 300 rpm at 25 °C, and samples were taken from the solution at desired time intervals for the analysis of Cu^{2+} ion concentrations in the solution.

Equilibrium adsorption experiments

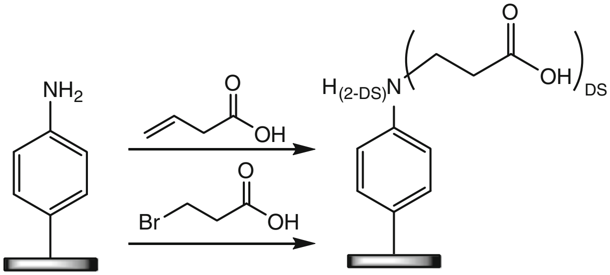
The equilibrium adsorption isotherm was obtained using the batch experiments by contact of 0.01 g of resin with 50 mL of pH 7.5 0.1 M ammonium acetate buffer solution containing increasing concentrations of $Cu(NO_3)_2$. The mixture then was shaken for a period of 24 h, which was longer than the adsorption equilibrium time. The amounts of Cu^{2+} ions adsorbed were calculated from the concentration difference before and after the adsorption. The mass balance equation was used for the calculation of adsorption capacity (q_e, mmol/g).

Similar experimental procedures were used for the determination of adsorption performance at equilibrium when investigating the effect of pH or the influence of the presence of competitor ions. Metal ion concentrations in all the samples in this study were determined by atomic absorption spectrometry on a Philips AAS PU 9200X. The pH of the solutions was measured after equilibration at the end of each experiment, using a Crison MicropH 2002 pH meter.

Results and discussion

Synthesis and characterization of CE-PAS

The general structure of CE-PAS obtained by the derivatization of the primary amino groups in PAS by the reaction with acrylic or 3-bromopropionic acid is presented in Scheme 1. Several samples of CE-PAS were prepared in order to optimize the synthesis conditions by means of achieving the highest degree of substitution (*DS*). The reaction conditions and the elemental analysis data obtained for PAS and its carboxyethylated derivatives are summarized in Table 1. From the elemental analysis data, the *DS* was calculated as: $DS = \frac{\Delta_{C/N}}{3M_{C/N}}$; where $\Delta_{C/N}$ is the C/N percentage ratio difference of the elements in the CE-PAS and in the original PAS, and $M_{C/N}$ is the ratio of C to N molar masses. Since CE-PAS(5) had the highest *DS,* it was used for further study.



Scheme 1 Synthesis of CE-PAS

Carboxyethylation of the PAS was accurately reflected in the FT–IR spectrum by the appearance of absorption bands corresponding to the protonated (1715 cm^{-1}) and deprotonated (1600 and 1370 cm^{-1}) carboxylic groups. The presence in the spectrum of the adsorption bands of the protonated amine (R_3N^+–H) at 2700–2900 and 1330 cm^{-1} indicate that CE-PAS exhibits a zwitter-ionic structure characteristic of amino acids. No bands attributed to the amide group were observed to show crosslinking via carboxylic groups.

CE-PAS is a weak amphoteric polymer and the following protolytic equilibria have to be considered:

$$-\mathrm{NR_2} + \mathrm{H_3O^+} \rightleftarrows -\mathrm{NHR_2^+} + \mathrm{H_2O} \quad K_{\mathrm{H},1}$$

$$-\mathrm{COO^-} + \mathrm{H_3O^+} \rightleftarrows -\mathrm{COOH} + \mathrm{H_2O} \quad K_{\mathrm{H},2}$$

The potentiometric titration curve of 0.1 g CE-PAS in 0.1 M KNO_3 by 0.1 M KOH is shown in Fig. 1. The data can be modeled with the extended Henderson-Hasselbalch equation: [17]

$$\mathrm{pH} = \log K_{\mathrm{H}} + n \log \frac{\alpha}{1-\alpha} \quad (1)$$

where K_{H} is an apparent protonation constant, α is the degree of neutralization of the resin acid groups, assuming the same pH in the resin and in the solution, and n is an empirical parameter. The ion-exchange and chelating resins, because of their polymeric nature and chemical differences in the functional group environments, generally show n values higher than 1.

The titration data of CE-PAS follow Eq. 1 in the $0.2 < \alpha < 0.8$ region, and the least-squares regression of the linearized plot pH versus $\log \frac{\alpha}{1-\alpha}$ yielded $\log K_{\mathrm{H},1} = 7.48 \pm 0.02$ and $n = 2.50 \pm 0.06$ ($R^2 = 0.999$). The protonation constant of CE-PAS is close to the corresponding value obtained for nonpolymeric amino acid—*N,N*-di(2-carboxyethyl)-*p*-toluidine, $\log K_{\mathrm{H},1} = 6.88$ [18]. From the titration curve, it is also possible to obtain the proton adsorption capacities with respect to carboxylic and amino groups, which have been found to be $q(\mathrm{-COOH}) = 2.38$ and $q(\mathrm{-NR_2}) = 1.75$ mmol/g. The amino group content and the degree of substitution which can be expressed as $DS = \frac{q(-\mathrm{COOH})}{q(-\mathrm{NR_2})} = 1.36$ are in good agreement with those calculated from the elemental analysis data (Table 1).

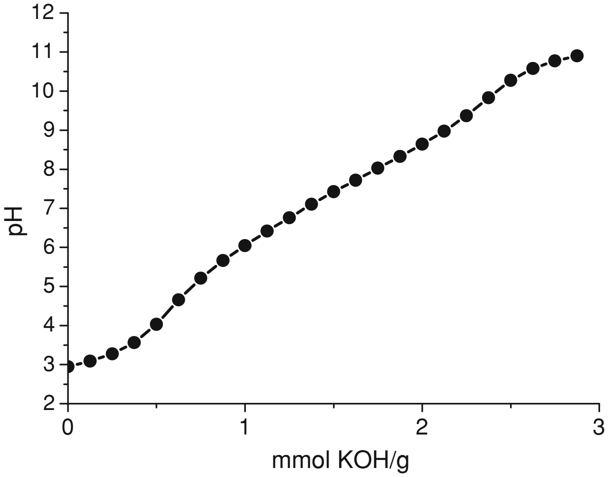


Fig. 1 Potentiometric titration curve of CE-PAS (0.1 g) by 0.1 M KOH (0.1 M KNO_3, 25 °C)

Effect of pH on Cu^{2+} adsorption by CE-PAS

The solution pH is an extremely important factor affecting the amount of metal ions adsorbed by the chelating resins. It not only governs the speciation of the metal ions in an aqueous solution, but also determines the status (protonated/deprotonated) of the groups present in the resin.

Figure 2 shows the effect of pH on the adsorption process in the experiment when the pH of each solution was adjusted with dilute acid or alkali. The pH values ranged from 2 to 6. At a higher pH, with the absence of complex forming agents, the transition metal ions would precipitate, and then it would be difficult to determine the actual adsorption performance of the resin. Maximum adsorption was noted at pH 6. However, adsorption did not reach its highest possible value, which is why the ammonium acetate buffer was chosen, as it prevents precipitation of copper hydroxides by the formation of acetate complexes (at mild acidic or neutral pH) and amine complexes (at alkaline pH). The pH values in this experiment ranged from 4 to 9.5. As shown in Fig. 2, in the presence of ammonium acetate buffer, Cu^{2+} ions were scarcely adsorbed by CE-PAS when the pH was lower than 5. As the pH value was increased, the Cu^{2+} retention increased gradually, as expected, reaching an adsorption capacity of approximately 1.4 mmol/g at the optimum pH 8, after which it slightly decreased to about 1 mmol/g at pH 9.5.

The mechanism of pH dependence of Cu^{2+} adsorption can be explained on the basis of the nature of the metal-binding sites in the CE-PAS and the solution chemistry of metal ions in water. At lower pH of 4–5, the amino groups of CE-PAS are fully protonated and only the carboxylate groups, which are capable of forming only very weak complexes with Cu^{2+} ions, are available for metal binding. As the pH increases, more amino groups become available for subsequent chelation of metal ions by the β-alanine groups of the resin. The subsequent decrease in Cu^{2+}

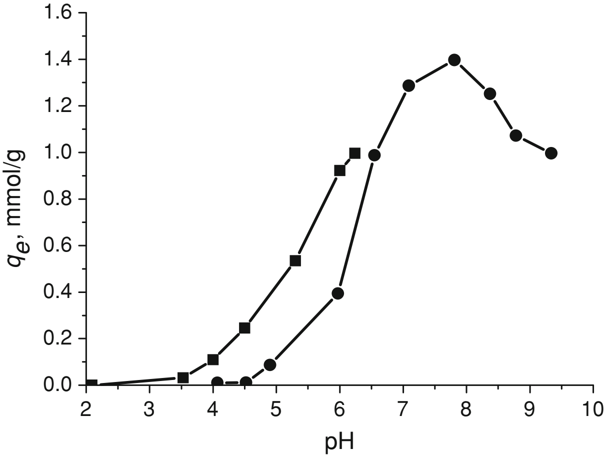


Fig. 2 Effect of pH on the adsorption of Cu^{2+} on CE-PAS from aqueous solutions, with pH adjusted using HCl and KOH (*filled square*) or 0.1 M ammonium acetate buffers (*filled circle*)

retention is most probably due to the concurrent complexation with ammonia present in the buffer.

Adsorption kinetics of Cu^{2+} by CE-PAS

A fast adsorption rate is always desirable in any separation process. The kinetics of the adsorption of Cu^{2+} ions by CE-PAS, as presented in Fig. 3a, reveals that the adsorption process was initially very rapid; but thereafter, the rate decreased progressively, to reach equilibrium at around 60 min. The adsorption equilibrium time for CE-PAS is comparable or even shorter than that for commonly used Ida resins [19, 20]. This shorter-time indicates easier approachability of the binding sites for metal ions at the CE-PAS surface.

The kinetic adsorption results can be analyzed with various adsorption kinetic models to reveal the control factors in the adsorption process. The pseudo-first order and pseudo-second order kinetic models have often been used to fit the experimental adsorption kinetic results, which basically consider three steps for adsorption process: external film diffusion (eliminated by vigorous stirring), intraparticle diffusion, and an interaction step. The pseudo-first order and pseudo-second order models can be given by Eqs. 2 and 3, respectively: [21, 22]

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{2}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

where q_e (mmol/g) is the amount of metal ion adsorbed at equilibrium, q_t (mmol/g) is the amount of metal adsorbed at time t (min); and k_1 (min^{-1}) and k_2 (g/(mmol min)) are the rate constants of the Lagergren's pseudo-first order and the Ho's pseudo-second order adsorption models, respectively.

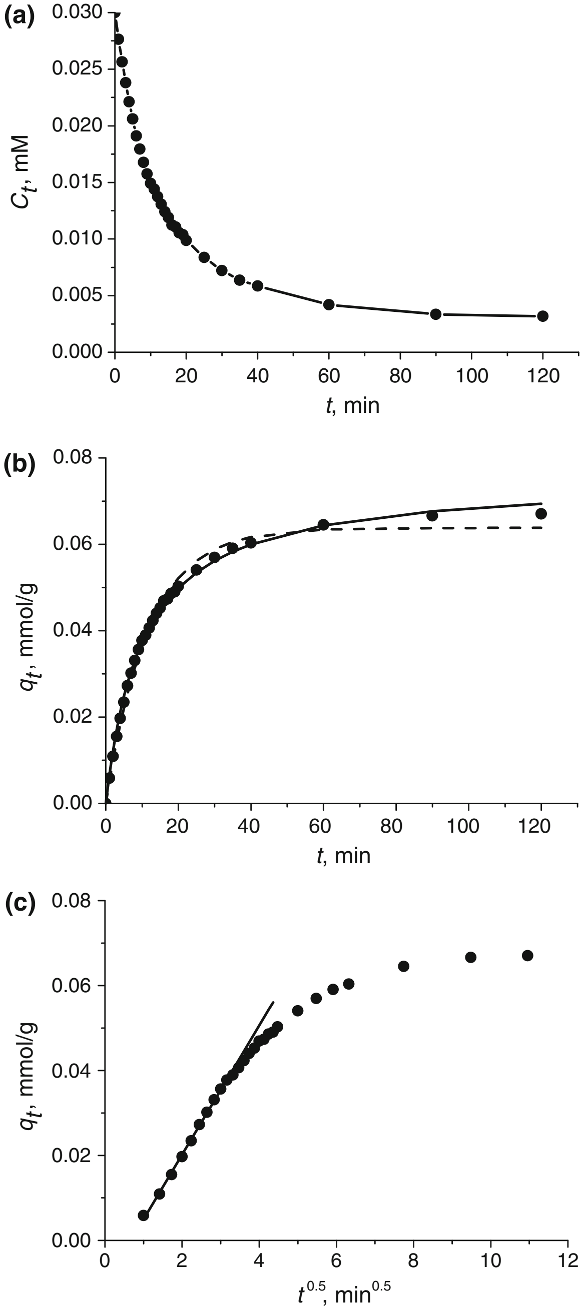


Fig. 3 Adsorption kinetics of Cu^{2+} on CE-PAS: experimental results showing the change of Cu^{2+} ion concentration in the bulk solution with adsorption time (**a**); fitting of the experimental data by the pseudo-first order (*dashed line*) and the pseudo-second order (*solid line*) kinetic models (**b**); the diffusion-controlled kinetic model (**c**)

Table 2 Adsorption kinetics parameters fitted by Lagergren's pseudo-first order and Ho's pseudo-second order models; initial concentration of Cu^{2+} 3×10^{-5} M, 25 °C and 0.1 M pH 7.5 ammonium acetate buffer

Kinetics model	Parameter ± confidence interval at $P = 95\%$
Pseudo-first order	
k_1 (min^{-1})	0.085 ± 0.004
q_e (mmol/g)	0.0638 ± 0.0013
R^2	0.990
Pseudo-second order	
k_2 (g/(mmol min))	1.30 ± 0.07
q_e (mmol/g)	0.0753 ± 0.0010
R^2	0.997

Figure 3b shows the comparison of the experimental data fitting with these kinetic models, while Table 2 summarizes the kinetic parameters for both models, together with their correlation coefficients R^2. Based on the coefficients obtained, the conclusion can be made that a better fit to the experimental data is given by the pseudo-second order Eq. 3 than by the pseudo-first order Eq. 2, with the correlation coefficient close to 1. This behavior implies the dependence of the reaction rate on the textural properties of the CE-PAS resin.

The adsorption process following diffusion controlled dynamics [23] with time can be presented by Eq. 4:

$$q_t = k_d \sqrt{t} \tag{4}$$

where k_d (mmol g^{-1} $min^{-0.5}$) is the intrinsic kinetic rate constant for diffusion-controlled adsorption and is related to the initial concentration of the solute in the solution, the specific surface area of the resin, and the diffusion coefficient.

The possibility of fitting the intraparticle diffusion model was tested by plotting metal ion uptake results versus the square root of time, as shown in Fig. 3c, wherein the linear relationship is indeed observed at the initial stage. These results indicate that the intraparticle diffusion of Cu^{2+} ions from the solution to the adsorption sites of CE-PAS is the rate-controlling step at the initial stage of the adsorption process.

Equilibrium adsorption isotherms

In the adsorption process, the solute from the solution adsorbed onto the solid surface is in a dynamic equilibrium with the solute remaining in the solution. The equilibrium adsorption isotherm expresses the relationship between the amount of solute adsorbed onto the solid at a particular temperature and the solute concentration in the solution at equilibrium. The shape of the isotherm not only provides information about the affinity of the solute, but also reflects the possible adsorption mechanism, which can be described by certain adsorption models.

Figure 4 shows that the adsorption of Cu^{2+} ions by CE-PAS increased with increases of the residual Cu^{2+} concentrations in the solution at equilibrium, resulting in a curve convex to the solute concentration axis, and flattened out when

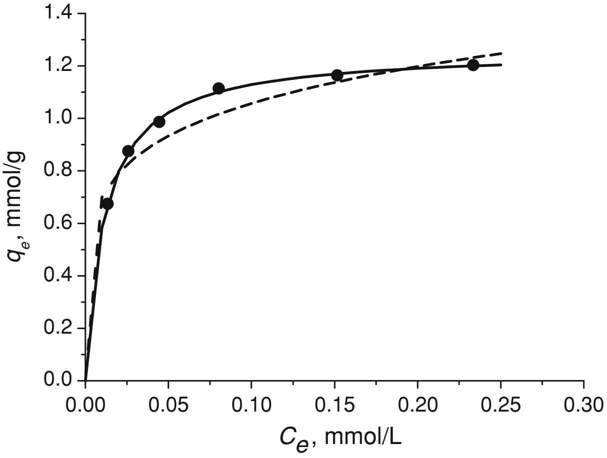


Fig. 4 Cu^{2+} adsorption on CE-PAS as a function of the metal concentration at equilibrium (0.1 M pH 7.5 ammonium acetate buffer, 25 °C). Experimental results fitted with Langmuir (*solid line*) and Freundlich (*dashed line*) adsorption models

all available functional groups were covered with solute. The experimental data included in Fig. 4 resulted from the average of two independent measurements. The present adsorption isotherm data were analyzed by the Langmuir, Eq. 5, and Freundlich, Eq. 6, isotherm models: [24]

$$q_{\mathrm{e}} = \frac{K_{\mathrm{L}} q_{\mathrm{m}} C_{\mathrm{e}}}{1 + K_{\mathrm{L}} C_{\mathrm{e}}} \text{ or } \frac{1}{q_{\mathrm{e}}} = \frac{1}{q_{\mathrm{m}}} + \frac{1}{K_{\mathrm{L}} q_{\mathrm{m}} C_{\mathrm{e}}} \tag{5}$$

$$q_{\mathrm{e}} = K_{\mathrm{F}} C_{\mathrm{e}}^{N} \text{ or } \log q_{\mathrm{e}} = \log K_{\mathrm{F}} + N \log C_{\mathrm{e}} \tag{6}$$

where C_{e} is the concentration of copper in the solution at equilibrium and q_{e} is the equilibrium amount of copper adsorbed onto CE-PAS; the Langmuir constants K_{L} and q_{m} represent adsorption equilibrium constant and saturated adsorption capacity, respectively. K_{F} is the Freundlich constant that predicts the adsorption capacity, and N is the heterogeneity factor.

The plot $1/q_{\mathrm{e}}$ versus $1/C_{\mathrm{e}}$, shown in Fig. 5a, of the experimental equilibrium adsorption data fits well to the Langmuir isotherm model. From the slope of the curve, the value of q_{m} representing the theoretical saturation capacity has been estimated to be 1.26 mmol/g. Alternatively, the experimental data were analyzed with the Freundlich isotherm model, Eq. 6, by plotting log q_{e} versus log C_{e}, as indicated in Fig. 5b. The present adsorption process does not obey the Freundlich model reasonably well. The same conclusion can be drawn by comparing the nonlinearized isotherms with those of the experimental profile of the system presented in Fig. 4. Various parameters derived from the Langmuir and Freundlich isotherm models are presented in Table 3. In the application of the Langmuir model, Hall et al. [25] proposed an equilibrium parameter R_{L}, which is defined as $R_{\mathrm{L}} = 1/(1 + K_{\mathrm{L}}C_0)$, where K_{L} is the Langmuir constant as described above, and C_0 is the initial metal ion concentration. The values of R_{L} parameter calculated at initial Cu^{2+}

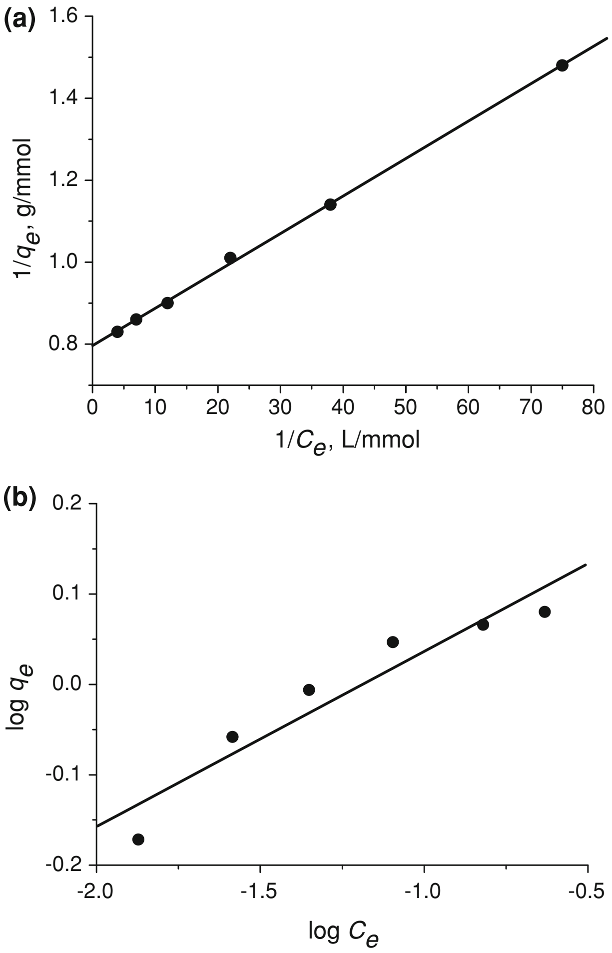


Fig. 5 Linearized Langmuir (**a**) and Freundlich (**b**) isotherms for the adsorption of Cu^{2+} on CE-PAS (0.1 M pH 7.5 ammonium acetate buffer, 25 °C)

concentrations from 0.15 to 0.5 mM were found to range from 0.068 to 0.023, and fulfill the condition of favoring the adsorption process of Cu^{2+} ions on CE-PAS ($0 < R_L < 1$).

Selectivity of adsorption

The adsorption selectivity of CE-PAS in comparison with the parent PAS was studied from the equilibrium solutions of tertiary mixtures containing $Cu(NO_3)_2$ together with Ni^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} nitrates at equal initial concentrations of 0.5 mM, 25 °C, and the optimum pH 7.5 (ammonium acetate buffer) for copper adsorption. Comparison of the adsorption selectivity of the resins is shown in Fig. 6 as the percentage adsorption of the total adsorption capacity. As can be seen, both resins exhibit the highest affinity for Cu^{2+} ions (as predicted by the Irving-Williams

Table 3 Adsorption isotherm constants of Freundlich and Langmuir models for the sorption of Cu^{2+} on CE-PAS (25 °C and 0.1 M pH 7.5 ammonium acetate buffer)

Adsorption model	Parameter ± confidence interval at $P = 95\%$[a]
Langmuir	
K_L (mM)	86 ± 7
q_m (mmol/g)	1.26 ± 0.02
R^2	0.998
Freundlich	
K_F (mmol/g)	1.6 ± 0.3
N	0.18 ± 0.06
R^2	0.910

[a] The parameters were obtained by a non-linear fitting method

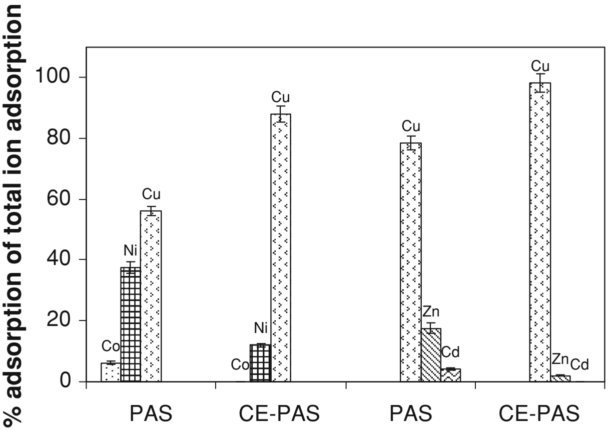


Fig. 6 Metal adsorption selectivity of PAS-based chelating resins from solutions containing Cu^{2+}, Ni^{2+}, and Co^{2+}, or Cu^{2+}, Zn^{2+}, and Cd^{2+} ions at equivalent concentrations of 0.5 mM, 25 °C, and pH 7.5 (0.1 M ammonium acetate buffer)

series: $Cd^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$); however, the carboxyethylated PAS shows a much higher adsorption selectivity for Cu^{2+} in the presence of other metal ions. The metal uptake values show that the total adsorption capacity of carboxyethylated PAS is markedly higher (1.3 mmol/g) compared with that of the parent PAS (0.5 mmol/g). The increase in both selectivity and adsorption capacity is undoubtedly due to the complex formation involving *N*-phenyl-*β*-alanine moiety of CE-PAS.

Conclusions

In this study, a novel chelating resin, CE-PAS, bearing *N*-phenyl-*β*-alanine functional groups was successfully prepared by the aza-Michael addition of poly (4-aminostyrene) to acrylic acid. The designed derivative showed good adsorption performance for Cu^{2+} ions, with an optimum adsorption pH of 7–8, and a contact time required to achieve equilibrium of about 1 h.

The experimental data obtained for the adsorption of copper ions onto CE-PAS were well fitted by the Langmuir isotherm, indicating that the ions are adsorbed on definite sites via chelation with *β*-alanine functional groups, and that the adsorption energy can be assumed to be equal for all the sites. Ho's pseudo-second order reaction rate model was capable of describing the adsorption kinetics, whereas the initial stage of sorption was well-fitted by intraparticle diffusion kinetics. The adsorption of Cu^{2+} in tested conditions (pH 7.5 ammonium acetate buffer) is not affected by the presence of competitor metals (such as Zn^{2+}, Cd^{2+}, Co^{2+}) and only slightly affected by the presence of Ni^{2+} ions.

Thus, the simple *N*-carboxyethylation of a resin with primary amine functionality changed the adsorption selectivity to one markedly favoring Cu^{2+} cations. The novel polymer could have wide-ranging uses in separation and preconcentration techniques covering a variety of analytical and industrial applications due to its high selectivity toward Cu^{2+} in the presence of other transition metal ions, its fast adsorption rate, and its good adsorption capacity.

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