

PREPARATION OF A CHELATING RESIN AND ITS APPLICATION TO IRON REMOVAL

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Abstract

A chelating resin has been synthesized by incorporation of linear polymer into porous resin matrix, followed by grafting the polymer chain with a ligand. The polyacrylate-type resin support was activated by amination prior the impregnation of the linear polymer to the surface. Hydroxylamine was reacted with the linear polymer to form metal binding sites along the chain. The resin beads in which hydroxamic acid groups are involved in linear array can form stable metal chelates with Fe (III) by self assembly, capturing the metal ion by changing its shape spontaneously in an aqueous solution. The adsorption characteristics as ion extraction, adsorption isotherm and regeneration cycles are examined. ICP-AES technique was used to measure the concentration of the remanent metal ion in solution. The chelating resin has a capacity of adsorption of 1.12 mmol Fe (III) per gram of resin at pH = 4.2. Fe (III) was completely adsorbed from a solution 0.02 M in a pH range between 4 and 5. After saturation, the chelating resin was successfully regenerated with hydrochloric acid.

1. Introduction

Molecular recognition of metal ions is a remarkably important concept which can provides basic idea of material design especially in terms of high selectivity [1]. Highly selective adsorbents for metal ions can be applicable to the treatment of polluted water containing toxic metals [2] as well as the enrichment of trace metal ions prior to the instrumental analysis [3]. To develop materials for these applications, we have introduced the idea of self-assembly by use of linear polymeric molecules having numerous metal binding sites. Ferrichrome and ferrioxamine-B are biologically important ionophores [4,5], which can transport Fe(III) to the mother plant by selective tris-chelate complex formation [6]. These molecules commonly involve hydroxamic acid as graft in a linear oligo-peptide chain and these ligands can firmly capture Fe(III) by changing the shape spontaneously in an aqueous solution. We have attempted to mimic these biological systems by synthetic linear polymer in which hydroxamic acids are grafted. The linear polymeric ligand has been synthesized by the reaction of maleic anhydride copolymer with hydroxylamine. The hydroxamic acids in the linear polymer are expected to take most suitable steric configuration around the metal ion by changing its shape. To adopt this spontaneous self-assembly like ferrioxamine to the adsorbent, we have fixed the linear copolymer having grafted ligand into porous spherical resin support. The newly prepared adsorbents have been examined and applied to the selective adsorption of Fe (III).

2. Experimental

Stock solution of Fe (III) was prepared by dissolution of reagent grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water. Porous spherical resin HP2MG (Mitsubishi Chemicals Co.) was used as the polymer matrix. This resin is a macroporous-type cross-linked polyacrylate copolymer with a specific surface area and pore volume of $470 \text{ m}^2\text{g}^{-1}$ and $1.2 \text{ cm}^3\text{g}^{-1}$, respectively. The resin beads were washed with dioxane in a soxhlet system and dried under vacuum before use.

The preparation of the chelating resin involved several steps [7]. First, the resin was refluxed with diethylenetriamine for 12 hours at 100°C using dioxane as solvent to activate the surface. The mixture was gently stirred to avoid the attrition of the resin beads. In a second step, the aminated resin was suspended in acetonitrile in a rotary evaporator under vacuum for one hour at room temperature to release the air contained in the pores. Then a linear polymer [Poly (methyl vinyl ether-alt-maleic anhydride)] was added and kept rotating for 3 hours under atmospheric pressure. The solvent was removed until a viscous suspension was formed and the resin beads were filtered and washed with a mixture of dioxane/acetonitrile. To functionalize the resin with hydroxamic acid groups, a methanol solution of hydroxylamine was added and shook for 2 days. Finally, the chelating resin was thoroughly washed in a column with 1M HCl, 1M NaOH and water. Then it was dried under vacuum at 50°C for 3 days.

The concentration of metal ion was determined by an inductively coupled plasma emission spectrometer (ICP-AES), SEIKO Model SPS-1200A. A digital pH meter, TOA HM-265 was used for the pH measurements.

3. Results and discussion

3.1 Ion adsorption

Samples of the functionalized resin were shook together either with a 0.0025M or 0.025M iron solution at several values of pH in a thermostated room at 25°C during 5 days for percentage of extraction and capacity studies, respectively. Fig. 1 shows the percentage of extraction of Fe(III) and the adsorption capacity of the prepared resin as a function of pH. Complete adsorption of iron was attained at pH higher than 4 and a favorable adsorption was observed at acidic pH range 2-4. The maximum adsorption capacity of the resin was 1.12 mmol g^{-1} at pH around 4. Despite the solutions were properly buffered prior the reaction, the pH shifted to lower values in both experiments due to the formation of HCl when chelating iron ions.

3.2 Equilibrium isotherm

The adsorption characteristics of the chelating resin were analyzed by using the Langmuir model of adsorption [8]. The following equation was used to calculate the equilibrium constant (K) and the capacity of the resin (C_s), where C is the metal ion concentration in solution and C_x is that in the resin at equilibrium.

$$C/C_x = (1/KC_s) + (C/C_s) \quad (1)$$

Fig. 2 shows plots of C/C_x against C for the adsorption of Fe(III) by the prepared resin at a fixed pH value of 3.48 at 25°C . A good straight line was obtained. Log K and C_s (in mmol g^{-1}) values were calculated from (1) as 4.18 and 0.46 respectively.

3.3 Column adsorption test

A solution containing 100 ppm of Fe(III) at pH 2.64 was continuously passed through a column packed with the functionalized resin at a rate of 1 ml min^{-1} , which correspond to a space velocity of 2.61 bed volumes per hour. The effluent solution was fractionated into small portions and the iron content in every 10^{th} fraction was measured. The adsorbed metal ion was released from the resin by elution with 6M HCl. Upon rinse with water, the column was used repeatedly. Fig. 3 shows the typical column test curves of three successive runs.

4. Conclusions

A linear polymer was successfully functionalized with hydroxamic acid as ligand and grafted to a porous resin. The adsorption characteristics of the prepared resin were examined with respect to adsorption capacity, % of extraction, equilibrium isotherm studies and column tests. The optimum pH for the adsorption of iron in solution is within the range 2 – 5, reaching the maximum values between 4.5 and 5. The higher adsorption capacity of the chelating resin was within the pH range 3.5 – 4.5, being the maximum value 1.12 mmol g^{-1} . The retention of Fe(III) was attributed to the formation of stable tris-chelate complexes between the ligand and the metal ion by self-assembly arrangement of the linear polymer chain. The present resin can work properly in a wide pH range and can be used repeatedly upon regeneration with concentrated hydrochloric acid.

References

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Figure captions

Fig. 1. Percentage of extraction and adsorption capacity of Fe(III) as a function of pH.

Fig. 2. Langmuir plot for the adsorption of Fe(III) at pH 3.48 and temperature at 25°C.

Fig. 3. Column profile for the adsorption of Fe(III) at pH 2.64. (● First run, ♦ Second run, ■ Third run.)

Fig. 1

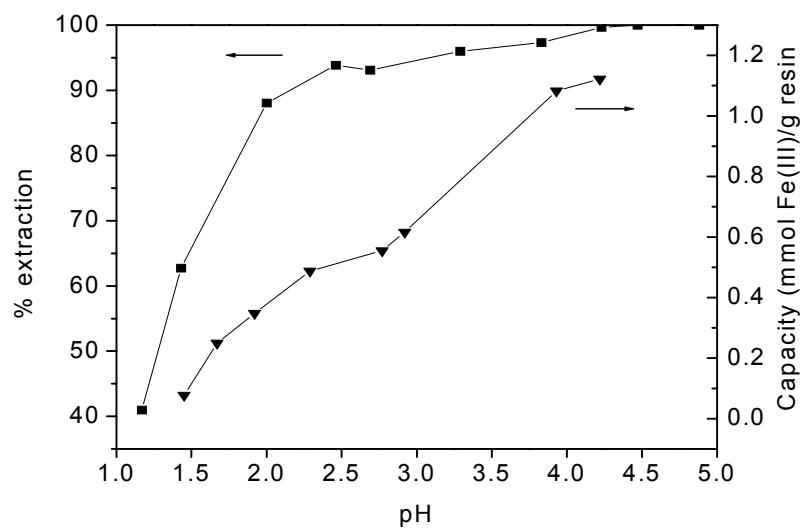


Fig. 2

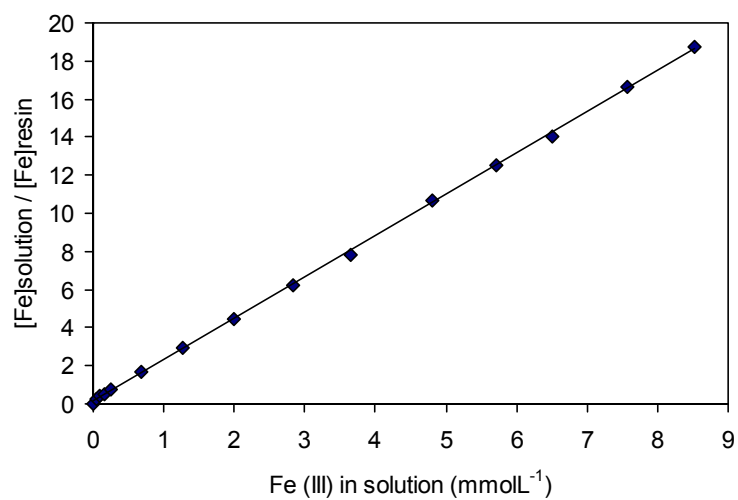


Fig. 3

