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Effect of pH on Competitive Adsorption of Cu(II), Ni(II), and Zn(II) from Water onto Chitosan Beads

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Abstract. The amounts of adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from single, binary, and tertiary nitrate solutions onto glutaraldehyde cross-linked chitosan beads were measured. The beads had an average particle size and pore volume of 2 mm and 0.06 cm^3/g, respectively, and had a BET surface area of 60 m^2/g. All experiments were performed at 298 K as a function of initial pH (2.0–5.0), total metal concentration (0.77–17.0 mol/m^3), and molar concentration ratio (0.25–4) in the aqueous phase. It was shown that the amount of metal adsorption generally increased with increasing solution pH. Competitive adsorption was significant in binary and tertiary systems when Cu^{2+} was present. The selectivity factor reached maximum in an equilibrium pH range of 5.1–5.3 and 4.5–4.9 for the Cu-Ni and Cu-Zn binary systems, respectively. This adsorbent provided a possibility for selective separation of Cu^{2+} from such multi-component solutions.

Keywords: competitive adsorption, selectivity, chitosan beads, Cu(II), Ni(II), Zn(II)

Introduction

Waste streams from metal plating facilities, mining operations, and electronic device manufacturers may contain low-to-medium levels of metals (up to 1,000 ppm). Because most of heavy metals are toxic and are not biodegradable, accumulation and distribution of these metals to our environments occur which is of concern to the public. They must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. For treatment of such metal-bearing effluents, chemical precipitation, electrodeposition, ion exchange, membrane, and adsorption have been applied. Of these methods, chemical precipitation (OH^-, S^{2-}, etc.) is known to be the most economic but is ineffective for dilute solutions. Ion exchange and reverse osmosis are generally effective, but they have high maintenance and operation costs and subject to fouling. Adsorption is the promising alternatives for this purpose, especially using low-cost adsorbents like clay materials, agricultural wastes, and seafood processing wastes (Bailey et al., 1999).

Chitosan is a partially acetylated glucosamine biopolymer existed in the cell wall of some *fungi* such as the Mucorales strains. It is produced cheaply because it mainly results from deaceylation of chitin, the second abundant biopolymer in nature next to cellulose (Coughlin et al., 1990; Felse and Panda, 1999; Muzzarelli, 1983). Chitosan is a known adsorbent for metals such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}, VO^{2+}, and UO_2^{2+} because its amino groups ($-NH_2$) can serve as coordination sites (Delben and Muzzarelli, 1989; Eiden et al., 1980; Mitani et al., 1992; Monteiro and Airoldi, 1999; Onsoyen and Skaugrud, 1990; Yang and Zall, 1984). Also, it has many useful features including hydrophilicity, biocompatibility, biodegradability, and anti-bacterial property. Compared to chitin, the adsorption ability of heavy metals with chitosan is superior due to its higher content of amino groups.

The adsorption of heavy metals with raw and chemically modified chitosans has been widely studied (Eiden et al., 1980; Guibal et al., 1994; Huang et al.,

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1996; Inoue et al., 1993; Jansson-Charrier et al., 1996; Juang et al., 1999; Kawamura et al., 1993; Kurita et al., 1986; McKay et al., 1989; Mitani et al., 1992; Rorrer et al., 1993; Udaybhaskar et al., 1990; Yang and Zall, 1984). For example, Yang and Zall (1984) and Huang et al. (1996) found that the selectivity decreases in the order $Cu^{2+} > Cr^{3+} = Cd^{2+} > Pb^{2+} \gg Zn^{2+}$ and $Cu^{2+} = Hg^{2+} \gg Pb^{2+} = Cd^{2+} > Ni^{2+}$, respectively, using raw chitosan. Using polyaminated chitosan resins, the selectivity decreased in the order $Hg^{2+} > UO_2^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$ (Kawamura et al., 1993). Such comparisons were made merely based on single-metal systems and the same initial solution pH. Little attention was paid to clearly examining the amounts of metal adsorption in binary and tertiary systems. In this work, the adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from single, binary, and tertiary solutions onto chitosan beads was studied. All experiments were carried out at different initial pH, total metal concentrations (up to 1,000 ppm), and molar concentration ratios. Selectivity factors in the binary systems were also obtained and discussed.

Experimental

Materials

Chitosan produced from lobster shells was offered as flakes from Ying-Huah Co., Taiwan, without further purification. The degree of deacetylation of the flakes was found to be 87 mol% following the procedures of Tan et al. (1998). The molecular weight of chitosan was measured to be 4.1×10^5 by the Mark-Houwink equation from viscosity data of solutions containing different amounts of chitosan in 3.5 vol% acetic acid. The point of zero charge of chitosan was found to be 8.2 using acid-base titration measurements.

Nitrate salts of heavy metals and inorganic chemicals were supplied by Merck Co. as analytical-reagent grade. The aqueous solution was prepared by dissolving $Cu(NO_3)_2$, $Ni(NO_3)_2$, and/or $Zn(NO_3)_2$ at different molar ratios in deionized water (Millipore Milli-Q). The total metal concentration varied from 0.77 to 17 mol/m^3. The initial solution pH was adjusted in the range 2.0–5.0 by adding a small amount of HNO_3 or NaOH. It should be noted that the initial solution pH was selected such that no metal hydroxide precipitations were experimentally found in bulk aqueous solution during the adsorption process. It is known that Cu^{2+} is easier to precipitate than Ni^{2+} and Zn^{2+} in the aqueous solution under comparable conditions (pH, metal concentration, etc.). In the case of single Cu^{2+}, the final pH should be less than 5.0 because it begins to precipitate at around pH 5.4 at high Cu^{2+} concentration (15.7 mol/m^3).

Preparation of Chitosan Beads

Chitosan flakes (6 g) were dissolved in 200 cm^3 of 1 vol% acetic acid. The solution was agitated for 1 d and then settled for about 7 d at 40°C until the viscosity was within 300–450 c.p. The resulting solution was sprayed through a thin nozzle into 1 dm^3 of 1 wt% glutaraldehyde solution (Sigma Co.). Spherical chitosan beads formed were allowed to stand in solution for 2 h at 30°C. After filtration, the beads were washed with deionized water and then with 20 vol% isopropanol three times to remove any impurities. Finally, they were dried at −20°C for 36 h in a freeze dryer (Eyela RD-5N, Japan). This is an efficient way that can preserve porosity of the resins because water and isopropanol in the resins were frozen prior to its removal by vacuum evaporation (Rorrer et al., 1993).

Chemical modification of linear chitosan chains with glutaraldehyde can render the resins insoluble in acidic media and improve mechanical strength/resistance to chemical degradation. It also improves diffusion property and accessibility to internal sites (Guibal et al., 1998). The resin diameter was about 2 mm, and the BET surface area was 60 m^2/g from N_2 isotherms using a sorptiometer (Micromeritics ASAP 2000). The porosity and pore volume of the beads were measured to be 0.6–0.7 and 0.06 cm^3/g, respectively, using a mercury porosimeter (Micromeritics Autopore II 9200). In addition, the apparent density was approximately 0.36 g/cm^3.

Adsorption Experiments

In adsorption experiments, an amount of dry resins (0.05 g) and 50 cm^3 of aqueous solution were placed in a 0.1-dm^3 glass-stoppered flask and shaken at 130 rpm for 48 h using a thermostated shaker (Firstek B603, Taiwan). The temperature was fixed at 298 K. Preliminary tests had shown that the adsorption studied was complete after 24 h. After equilibrium, the pH was measured with a pH meter (Horiba F-23) and the concentrations of metals were analyzed using an atomic absorption spectrophotometer (GBC 932). The amount of metal adsorbed q_M (mol/kg) was obtained by:

$$q_M = (C_0 - C_M)V/W \tag{1}$$

where C_0 and C_M are the initial and equilibrium concentrations in aqueous phase (mol/m^3), respectively, V is the volume of solution (m^3) and W is the amount of dry beads used (kg). Each experiment was duplicated at least under identical conditions. Reproducibility of the measurements was within 3%.

Results and Discussion

Equilibrium Adsorption in Single-Metal Systems

Figures 1–3 show the effect of equilibrium pH (pH$_{eq}$) on the amounts of adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} (q_M) onto chitosan resin in single systems. The value of q_M normally increases with increasing pH$_{eq}$. This is due to competitive adsorption of proton and metal ions onto chitosan. As indicated above, the uptake of transition metals is mainly effected *via* coordination with the $-NH_2$ groups on chitosan. It is likely that two $-OH$ groups and one $-NH_2$ group are grabbed

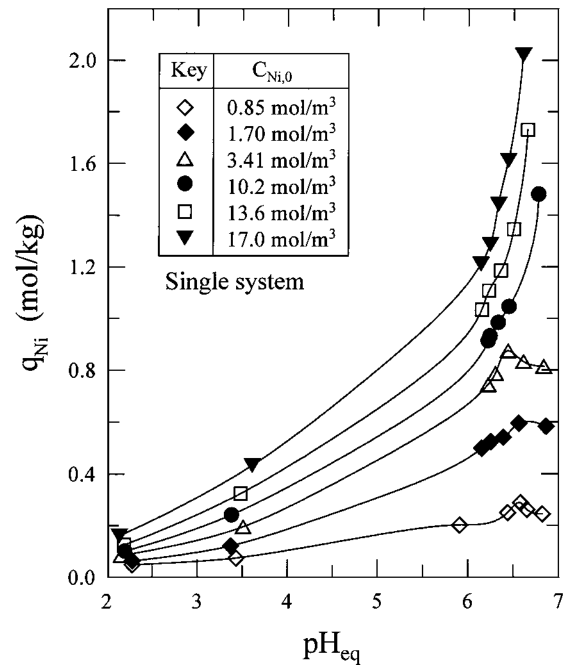

Figure 2. Equilibrium adsorption of Ni^{2+} at different initial metal concentration in single systems.

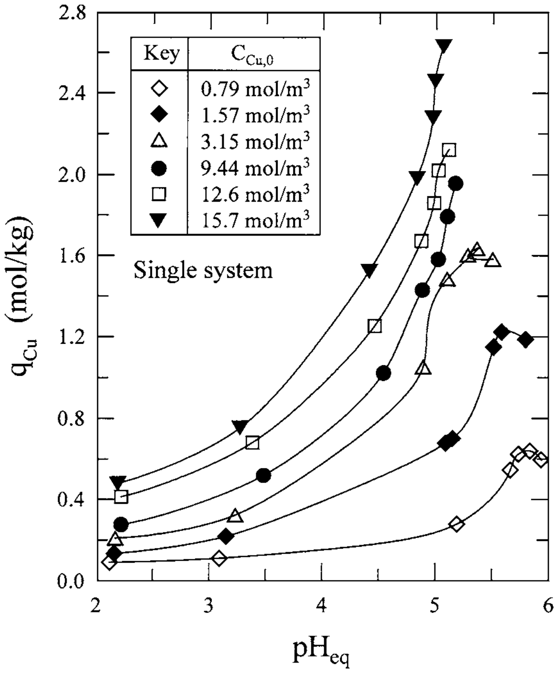

Figure 1. Equilibrium adsorption of Cu^{2+} at different initial metal concentration in single systems.

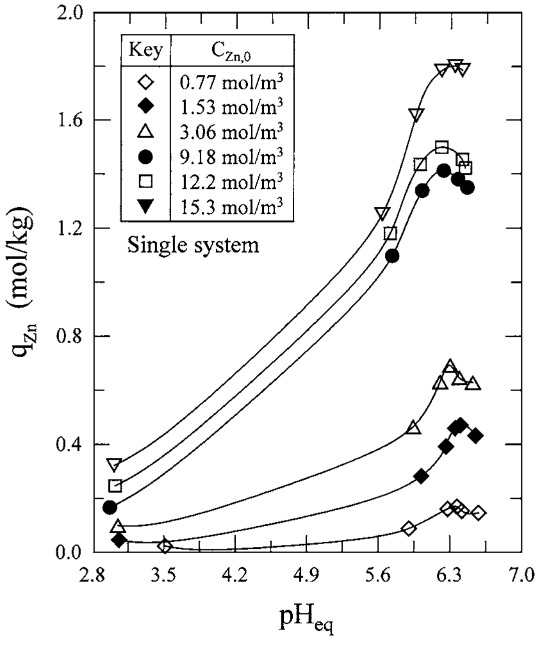

Figure 3. Equilibrium adsorption of Zn^{2+} at different initial metal concentration in single systems.

by one metal and the fourth site is occupied by a H_2O molecule or the —OH group on the third carbon atom (Delben and Muzzarelli, 1989; Eiden et al., 1980; Monteiro and Airoldi, 1999; Schlick, 1986). Hence, we have

$$M^{2+} + n\mathrm{RNH_2} \Leftrightarrow M(\mathrm{RNH_2})_n^{2+} \qquad (2)$$

On the other hand, the amino groups of chitosan would react with H^+ according to

$$\mathrm{H^+} + \mathrm{RNH_2} \Leftrightarrow \mathrm{RNH_3^+}, \quad K_p \qquad (3)$$

The protonation constant ($\log K_p$) is about 6.2 (Jansson-Charrier et al., 1996), thus, more than 20% of the amino groups of chitosan are protonated even at pH 7.

Experiments revealed that the pH becomes always larger after adsorption. Moreover, the higher the C_0 value, the smaller of such pH increment. Increasing pH means a small extent of reaction Eq. (3) and a large extent of reaction Eq. (2). In fact, previous studies have indicated that proper pH adjustment leads to an increase in metal adsorption capacity onto chitosan (Guibal et al., 1994; Inoue et al., 1993; Jansson-Charrier et al., 1996); e.g., Inoue et al. (1993) found a steep rise of $q_{\mathrm{Cu}}/C_{\mathrm{Cu}}$ at a $\mathrm{pH_{eq}}$ of $4 \sim 5$ using chitosan.

As clearly shown in Figs. 1–3, q_M will decrease with a further increase in $\mathrm{pH_{eq}}$. The uncoordinated —OH groups on chitosan chains become —O— at high pH, likely leading to an increase in the degree of "solubilization" of the coordinated metal-chitosan complexes (Ji, 1999). In fact, such behavior is more apparent at lower q_M of the chitosan resins (Figs. 1 and 2) because the larger amount of the uncoordinated —OH groups. According to solution chemistry (Morel and Hering, 1993), on the other hand, the pH trend of species distribution indicates that another positively charged metallic species $\mathrm{Cu_2(OH)_2^{2+}}$ becomes dominant than $\mathrm{Cu^{2+}}$ at $\mathrm{pH} > 6.5$, especially at a sufficiently high C_0 (15.7 mol/m^3). This may partly explain the decrease of q_M at high pH.

An attempt was made to correlate q_M and liquid-phase equilibrium concentration (C_M) in single metal systems when $\mathrm{pH_{eq}}$ is fixed. Under comparable conditions (e.g., $\mathrm{pH_{eq}} = 5.0$), q_M decreases in the order $\mathrm{Cu^{2+}} > \mathrm{Zn^{2+}} > \mathrm{Ni^{2+}}$ (Fig. 4). In all cases, the isotherms possess a stepped shape over the whole concentration range ($C_M < 13$ mol/m^3). This behavior was also reported with dye adsorption on chemically modified chitosan (Yoshida et al., 1993). The two-parameter Langmuir and Freundlich equations are inapplicable, as reflected by the dashed lines in Fig. 4 that are obtained by fitting the Langmuir equation at a restricted concentration range ($C_M < 8$ mol/m^3). The isotherm data were generally force-fitted to the Langmuir or Freundlich equation over a limited concentration range in previous studies (Guibal et al., 1998; Huang et al., 1996; Juang et al., 1999; McKay et al., 1989; Mi et al., 1999b; Mitani et al., 1992; Udaybhaskar et al., 1990; Yang and Zall, 1984). Moreover, the BET multilayer equation is not suitable to describe such isotherms because of the chemical nature of metal adsorption onto chitosan.

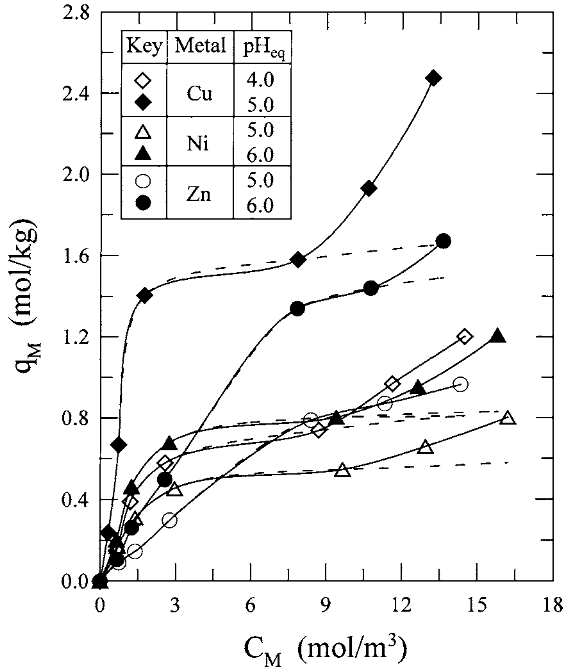

Figure 4. Adsorption isotherms of metals at different equilibrium pH in single systems.

An increase in q_M at high C_M (Fig. 4) may be a result of micro-precipitation of metals due to the possibility of small change of the pH at the vicinity of the adsorbent particles. However, Rorrer et al. (1993) explained the stepped rise of q_M at high C_M in adsorption of $\mathrm{Cd^{2+}}$ onto glutaraldehyde-modified chitosan beads by the pore-blockage mechanism. The distribution of metals adsorbed is determined by intraparticle diffusion rate of metals into the porous matrix, which is in turn by concentration gradient of metals and the bead porosity. At low C_0, the initial metal flux through the matrix is low so the metals bind with amino sites near the outer surface of the beads. Finally, the adsorbed metal complexes clog the pores near the outer surface so metals can no longer diffuse to the sites deep within the interior surface. In this case metals is mostly loaded in a shell near the outer surface. In contrast, at high C_0 the initial flux is high and so metals shoot deep into the interior matrix until the pore are finally clogged. Hence, metals more uniformly load into the bead and q_M is higher. The SEM-EDS graphs have indicated that the sites of Cu^{2+} adsorption inwardly penetrate within the tripolyphosphate-modified chitosan resins to a large extent with increasing Cu^{2+} concentration (Mi et al., 1999).

Competitive Adsorption in Binary-Metal Systems

Figures 5–7 show the amounts of adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} in binary systems at different metal concentration ratios. It is found that q_{Cu} is always larger than q_{Ni} in Cu-Ni binary system, regardless of the concentration ratio (0.25–4). This is also the case for Cu/Zn binary system (Fig. 6). Chitosan exhibits an absolutely high binding ability for Cu^{2+}, as reported earlier (Coughlin et al., 1990; Huang et al., 1996; Mitani et al., 1992; Yang and Zall, 1984). In Ni-Zn binary system, q_{Ni} and q_{Zn} strongly depend on the concentration

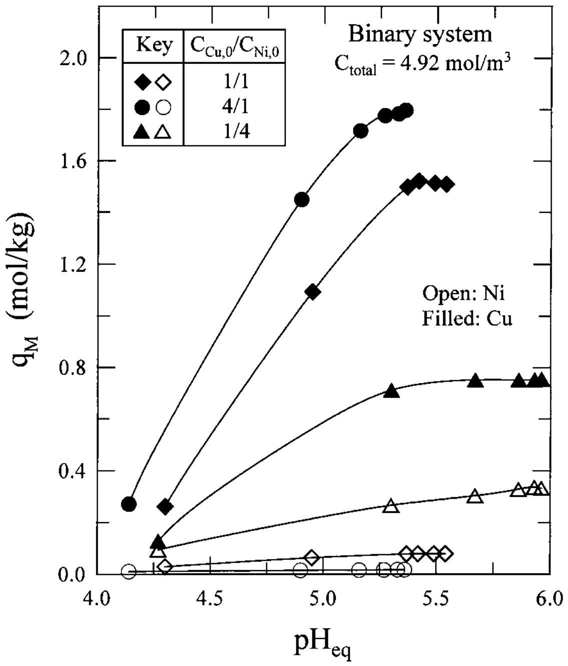

Figure 5. Equilibrium adsorption of Cu^{2+} and Ni^{2+} at different initial concentration ratios in binary systems.

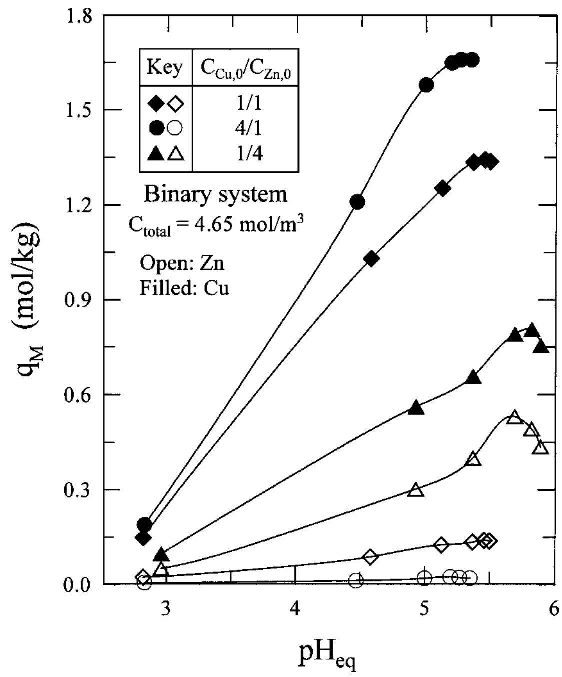

Figure 6. Equilibrium adsorption of Cu^{2+} and Zn^{2+} at different initial concentration ratios in binary systems.

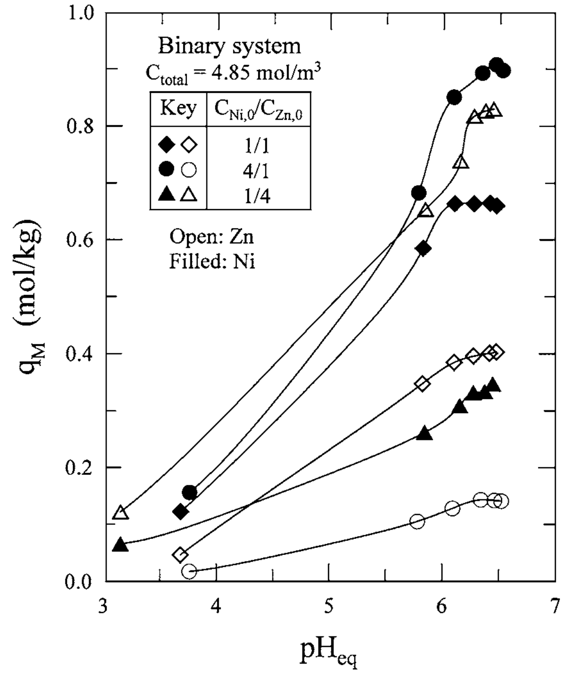

Figure 7. Equilibrium adsorption of Ni^{2+} and Zn^{2+} at different initial concentration ratios in binary systems.

ratios. It is seen that $q_{Ni} > q_{Zn}$ under an equimolar condition, which is different from that in single systems. Satisfactory explanation cannot be given at this stage.

In order to quantify competitive effect, the selectivity factor of metals (β) is calculated. In the case of Cu-Ni system, for example, it is defined by

$$\beta_{Cu/Ni} = \frac{(q_{Cu}/q_{Ni})}{(C_{Cu,0}/C_{Ni,0})} \tag{4}$$

The pH-dependent of selectivity factors are shown in Figs. 8–10.

Clearly, β for Cu/Ni and Cu/Zn systems increases with increasing their concentration ratios. This indicates synergistic effect of competitive adsorption for Cu^{2+}. The selectivity factor reaches maximum in a pH_{eq} range 5.1–5.3 and 4.5–4.9 for Cu-Ni and Cu-Zn binary systems, respectively. Under the ranges investigated, a maximum β of about 27 and 22 is obtained for Cu^{2+} over Ni^{2+} and over Zn^{2+}, respectively, at an initial concentration ratio of 4. In practice, the selectivity factors obtained in two binary systems are larger than those in single systems in which obtained simply means the ratio of amounts of adsorption of two metals at a fixed equilibrium pH (Figs. 1–3). The increase of

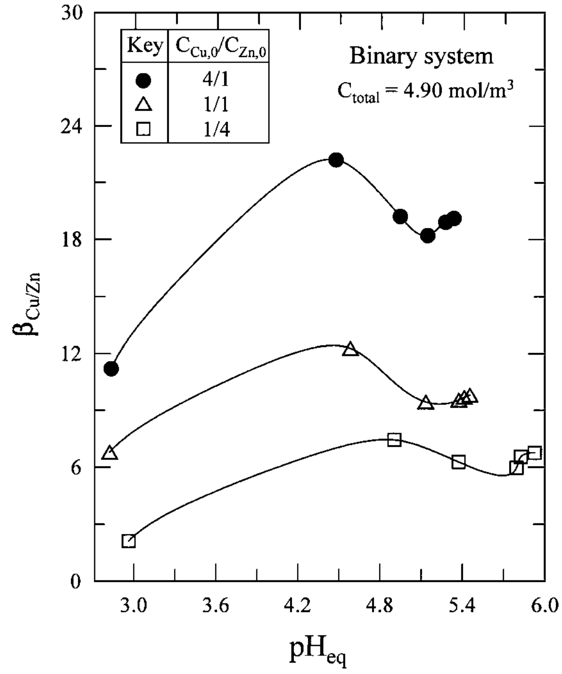

Figure 9. Selectivity factor of Cu^{2+} over Zn^{2+} at different initial concentration ratios in binary systems.

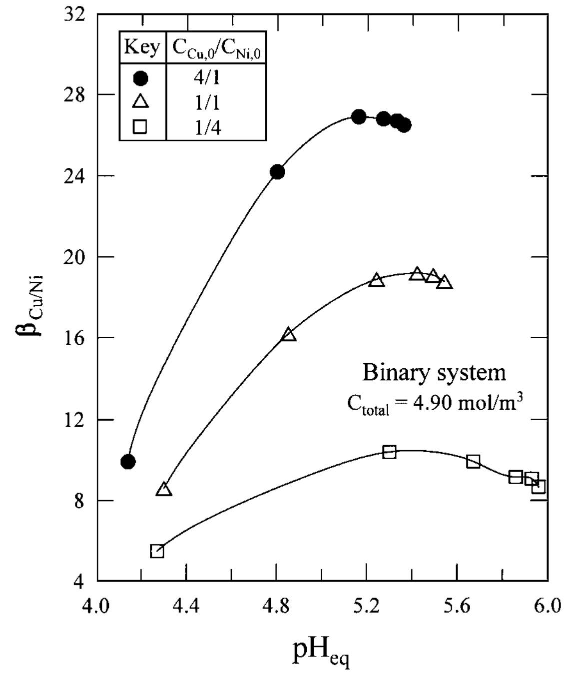

Figure 8. Selectivity factor of Cu^{2+} over Ni^{2+} at different initial concentration ratios in binary systems.

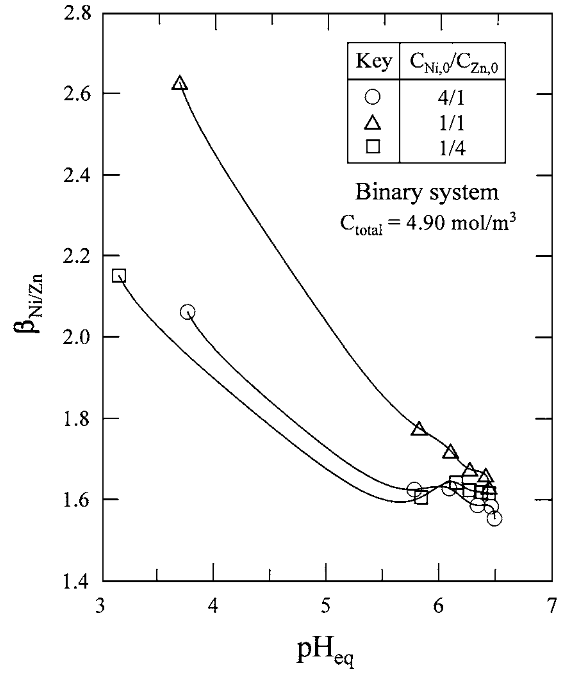

Figure 10. Selectivity factor of Ni^{2+} over Zn^{2+} at different initial concentration ratios in binary systems.

β in Cu-Zn binary system at a high enough pH_{eq} is due to the drop of q_{Zn} (Fig. 6). There are no certain trends of β with respect to initial concentration ratio in Ni-Zn binary systems. This implies that Ni^{2+} and Zn^{2+} have comparable binding ability with chitosan. It is noted that β reaches to 1.5–1.7 at $pH_{eq} > 6$.

Competitive Adsorption in Tertiary-Metal Systems

The amounts of adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} in tertiary, equimolar systems are shown in Fig. 11. Basically, q_M exhibits the same order as that obtained in single systems. Anti-synergistic effect of Ni^{2+} adsorption is significant by comparing the results obtained at different initial metal concentrations. The total amount of metal adsorption is about 2.1 mol/kg at an initial concentration of 9.62 mol/m^3 and $pH_{eq} > 5$. The concentration of —NH_2 groups on glutaraldehyde cross-linked chitosan was obtained to be roughly 3.85 mol/kg in this work by measuring the saturation capacity for HCl adsorption (Kawamura et al., 1993). Thus, the average number of —NH_2 groups on chitosan bound with one divalent metal ion should be not far larger than 2 (Monteiro and Airoldi, 1999). With an 87% of deacetylation degree, the equivalent MW is roughly 166 g: 1 kg roughly represents 6 mol —N, and thus 5.2 mol —NH_2. The difference is likely representative of the glutaraldehyde cross-linking. In a word, the present results reveal that chitosan provides a possibility for selective separation of Cu^{2+} from binary and tertiary streams.

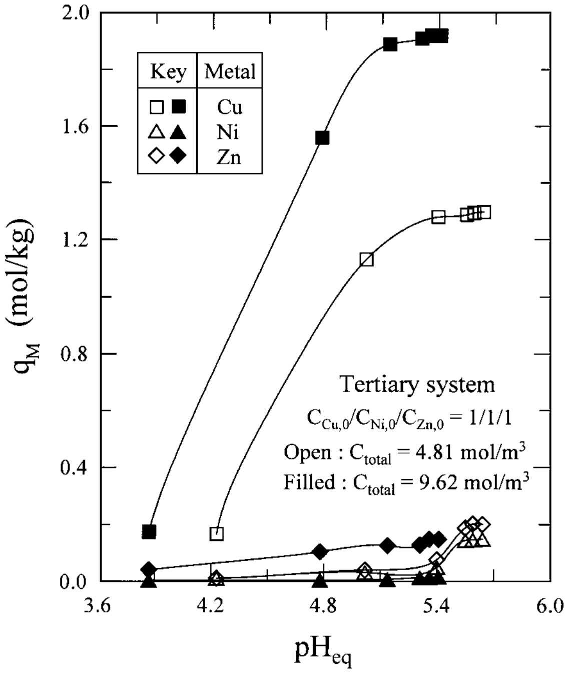

Figure 11. Equilibrium adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} at different metal concentrations in tertiary systems.

Conclusions

Competitive adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from binary and tertiary solutions up to 1,000 ppm onto glutaraldehyde cross-linked chitosan beads was studied at 298 K. In single systems, the amount of metal adsorption (q_M) normally increased with increasing solution pH, due to competitive adsorption of proton and metals. Under comparable equilibrium pH, q_M decreased in the order $Cu^{2+} > Zn^{2+} > Ni^{2+}$. The stepped-shape isotherms did not obey the Langmuir and Freundlich equations, but could be explained by the pore-blockage mechanism. It was shown that the metal adsorption selectivity was highly pH-dependent. Selectivity factors of Cu/Ni and Cu/Zn in binary systems increased with increasing metal concentration ratio, indicating synergistic competition for adsorption of Cu^{2+}. Selectivity factor was maximized in a pH_{eq} range 5.1–5.3 (Cu/Ni) and 4.5–4.9 (Cu/Zn). Under the ranges studied, a maximum selectivity of 27 (Cu/Ni) was obtained at a concentration ratio of 4. In tertiary, equimolar systems, q_M exhibited the same order as that in single systems, and anti-synergistic effect of Ni^{2+} adsorption was significant. This work demonstrated the possibility for selective separation of Cu^{2+} from multi-component streams using chitosan.

Acknowledgments

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Nomenclature

C_M	Liquid-phase metal concentration at equilibrium (mol/m^3)
C_0	Initial or total metal concentration in the aqueous phase (mol/m^3)
K_p	Protonation constant of amino groups in chitosan defined in Eq. (3) (dm^3/mol)

q_M	Amount of metal adsorbed at equilibrium defined in Eq. (1) (mol/kg)
V	Volume of the solution (m^3)
W	Amount of dry chitosan resins used (kg)

Greek Letter

β	Selectivity factor of metal adsorption defined in Eq. (4)

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