Metals Sorption by Chelating Polymers: a Unique Role of Ionic Strength

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The use of polymeric chelating ion exchangers for removal/isolation of trace amounts of dissolved heavy metal ions, such as Pb(II), Cu(II), Ni(II), and Cd(II), is rapidly growing in the following areas:

- Analytical chemistry where preconcentration of metal ions present in analytes is often achieved through selective sorption onto chelating exchangers.
- Pollution control processes where dissolved heavy metals need to be selectively removed from contaminated water/wastewater in preference to nontoxic competing ions, such as Ca^{2+}, Mg^{2+}, and Na^+ (Loureiro et al., 1988; Zhu et al., 1990; Hudson, 1986).

Chelating functional groups of these metal-selective polymers are always derived from weak-acid or weak-base organic ligands (Lewis bases), which also have very high affinity toward hydrogen ions. Therefore, under acidic conditions ($pH \leq 2.0$), the metal removal capacities of these chelating polymers are essentially lost because of the formidable competition from hydrogen ions. Raising pH in such cases is often an expensive proposition for treating heavy-metal-laden industrial wastewaters, while in the area of analytical chemistry coprecipitation of dissolved metals with Fe(III) hydroxides poses problems for quantitative analyses. Because of their high affinities toward hydrogen ions, these chelating polymers are always regenerated with dilute mineral acids, namely, HCl and H_2SO_4.

We have recently identified a new class of specialty chelating polymers which exhibit a significant increase in metal-ion selectivity at acidic pH with an increase in aqueous-phase ionic strength or electrolyte concentration. Thus, simply by adding electrolytes, such as NaCl, $NaNO_3$, and Na_2SO_4, the heavy-metal uptake of these chelating polymers can be enhanced even under highly acidic conditions. Such a unique property has not been observed with other widely used chelating polymers having iminodiacetate, aminophosphonate or carboxylate functional groups. The primary intent of this work is to present some convincing experimental results that confirm unusual effects of ionic strength on dissolved heavy metals uptake by this new chelating polymer.

Experiments: Materials and Procedure

Chelating exchangers

This study includes experimental results of a commercially available synthetic chelating exchanger, XFS 4195 (Dow Chemical Co., Michigan); two other well-known chelating exchangers, namely, IRC-718 and ES-467 (Rohm and Haas Co., Pennsylvania) are included in this study primarily for comparison and to highlight the unusual properties of XFS 4195. Chemical compositions of the functional groups and other salient properties are provided in Table 1. Except for the differences in functional groups, all three chelating polymers are identical, that is, macroporous with polystyrene matrix and divinylbenzene cross-linking. These resins were obtained in spherical bead forms with sizes varying from 0.3 mm to 0.8 mm. They were conditioned following the standard procedure of cyclic exhaustion with 1N hydrochloric acid and 1N NaOH. Total exchange capacity of XFS 4195 (nitrate form) was found to be 1.72 mmol/g of air-dried resin.

Equilibrium isotherms and column runs

Isotherm test results were obtained by minicolumn runs where aqueous solutions of fixed composition and pH (predetermined) were passed through short glass columns containing approximately 0.5–1.0-g resin in question. The resin in the minicolumn was considered to have attained equilibrium when the effluent metal ion concentration was at least 95% of the influent concentration. Following equilibration and a short rinse with deionized water, the minicolumn was regenerated with 4% hydrochloric acid or 4% ammonia. Metal ion concentrations in the spent regenerant were analyzed using an atomic absorption spectrophotometer (Perkin Elmer Model 4380), and the resin's metal uptake at equilibrium was determined by mass balance.

Column runs (run 1 and run 2 in Figure 1) and *in-situ* regeneration experiments (HCl vs. NH_3 regeneration in Figure 2) were carried out using a constant-flow pump and plexiglass columns with teflon tubing. The hydrodynamic conditions, namely, superficial liquid-phase velocity (SLV) and empty bed

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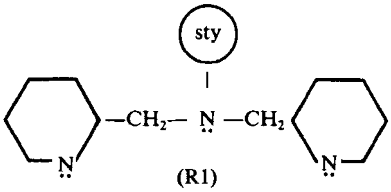
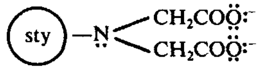
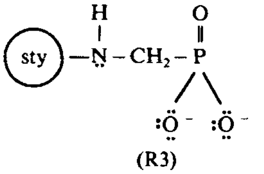
Table 1. Composition of Chelating Polymers

Functionality	Composition*	Matrix, Porosity	Acid/Base Characteristic
Bispicolylamine	 (R1)	Polystyrene, Macroporous	Weak Base
Imino-Diacetate	 (R2)	Polystyrene, Macroporous	Primarily Weak Acid
Amino-Phosphonate	 (R3)	Polystyrene, Macroporous	Primarily Weak Acid

* sty denotes monomeric styrene

contact time (EBCT), were kept constant separately for these two sets of column runs and provided in Figures 1 and 2. Other pertinent details about similar experimental procedure have been provided by Zhu et al. (1990).

Results and Discussion

Ionic strength effects

Figure 3 shows the results of the batch equilibrium tests in which aqueous-phase Ni(II) concentration (2.0 mg/L) and the pH (3.0) were kept constant but aqueous-phase ionic strength (or electrolyte concentration) was varied by adding sodium nitrate. Note that the nickel(II) distribution coefficient, q_{Ni}/C_{Ni}, increased more than an order of magnitude as more and more sodium nitrate (plotted as nitrate) was added in the aqueous phase (q_{Ni} = mg Ni/gm resin, C_{Ni} = mg Ni/mL of water). Figure 4 shows the fractional copper uptake capacities of the three chelating polymers in Table 1 as a function of pH under identical conditions where ionic strength at equilibrium was fairly high and close to 0.2 mol/L (Melling and West, 1984). At pH near 1.0, the copper removal capacities of chelating exchangers, IRC-718 and ES-467, with iminodiacetate and aminophosphonate functionalities, have practically dropped to zero, while XFS 4195 retained over 90% of its total capacity.

Fixed-bed column runs were performed using the newly identified resin with a view to selectively removing trace concentration of copper(II) ions (5.0 mg/L) in the presence of competing calcium ions. Two column runs were carried out under identical hydrodynamic conditions, that is, at the same superficial liquid-phase velocity (SLV) and empty-bed contact time (EBCT), as indicated in Figure 1. Influent compositions were also the same for both the column runs except that in Run 1, competing calcium ion concentration (200 mg/L) was ten times smaller than the calcium concentration (2,000 mg/L) in Run 2. Figure 1 shows the effluent histories of copper ion for these two runs, and surprisingly, the effluent history for Run 2, in spite of increased calcium concentration, always remained in the righthand side of Run 1: that is, the copper concentration at the exit of the ion-exchange bed was significantly lower for Run 2 than Run 1 during the entire length

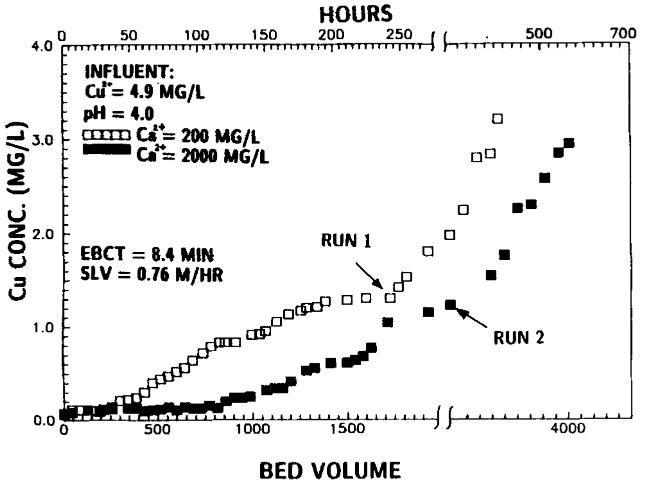


Figure 1. Cu(II) effluent histories for the new resin during two column runs at varying background calcium concentrations.

SLV = superficial liquid velocity; EBCT—empty bed contact time

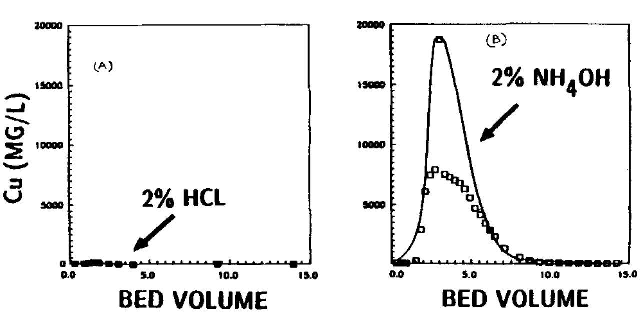


Figure 2. Ineffective hydrochloric acid regeneration (a) vs. efficient ammonia regeneration (b) for copper-loaded XFS 4195 in a column under identical hydrodynamic conditions.

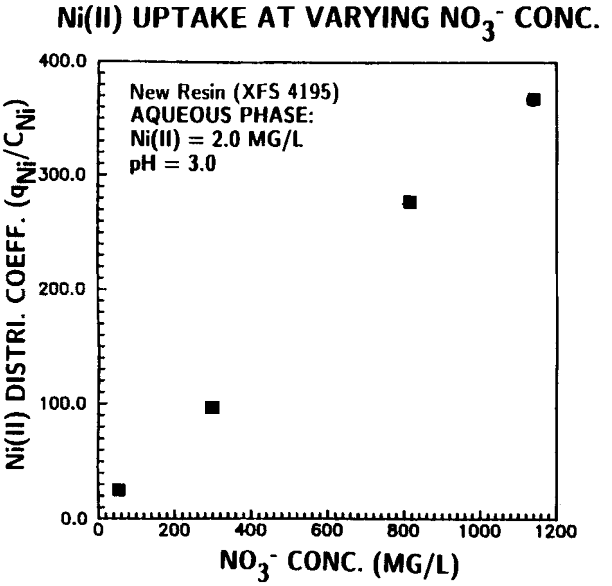


Figure 3. Effect of ionic strength [or sodium nitrate concentration] on Ni(II) distribution coefficient at a constant pH for XFS 4195.

of the run. These results suggest that the ion-exchange column offered greater equilibrium copper removal capacity in the presence of a higher concentration of competing Ca^{2+} concentration. Note that nitrate (NO_3^-) was the only anion present in the system: that is, feed solutions were prepared by dissolving calcium and cupric nitrates. Nitrate is an extremely poor ligand; any significant complexation between Cu^{2+} and NO_3^- can, therefore, be ruled out. Secondly, since the hydrodynamic conditions for the two column runs were identical, diffusion-controlled kinetics are not the reasons for such an anomalous behavior. Similar observations (not presented here) were also made for Ni(II) removal where an increased concentration of Ca^{2+} enhanced Ni(II) removal capacity.

Results in Figures 1, 3 and 4 clearly indicate that: first, an increased ionic strength (or electrolyte concentration) at acidic pH significantly increases dissolved heavy metals uptake by resin XFS 4195; second, compared to Cu(II), Ni(II), or other transition metal cations, calcium and sodium have negligible affinity toward XFS 4195. The second aspect was verified independently (Roy, 1989), and copper affinity was found to be over four orders of magnitude greater than calcium and about six orders of magnitude greater than sodium.

Column regeneration

The chelating polymer XFS 4195 was saturated with dissolved copper(II) and subsequently regenerated separately with (i) 2% HCl and (ii) 2% NH_3; Figure 2A and Figure 2B show desorption behaviors of Cu(II) during the two regenerations under identical hydrodynamic conditions. Note that the acid regeneration was quite ineffective indicating the resin's high metal-ion affinity even under the extreme acid condition (theoretical pH less than zero). In contrast, ammonia regeneration was very efficient. One critical difference between the two regenerants is that 2% hydrochloric acid (almost completely ionized) has much higher ionic strength than 2% ammonia (almost completely undissociated). Other heavy metals, Ni(II), Pb(II), and Cd(II), were also desorbed very efficiently with ammonia.

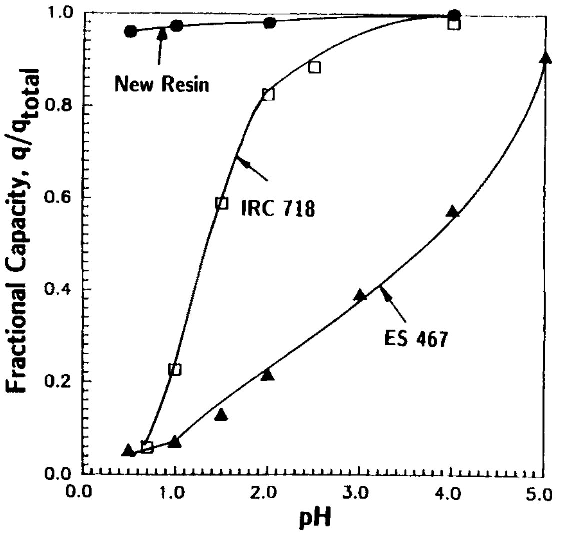


Figure 4. Fractional copper uptake for three chelating exchangers as a function of pH in equilibrium with copper chloride solution.

Data from Melling and West (1984).

Separation of copper(II) and nickel(II)

Both Cu(II) and Ni(II) are transition-metal cations with strong Lewis-acid characteristics and exhibit similar properties and applications in many respects such as low solubilities of their hydroxides and sulfides, toxicity to living organisms and animals, excellent plating characteristics for ferrous and nonferrous alloys, and so on. Understandably, bulk separation of Cu(II) and Ni(II) by synthetic sorbents is a difficult separation problem.

The chelating resin XFS 4195 was saturated first in a column with a solution containing both Cu(II) and Ni(II) at 200 mg/L at pH = 5.0. The column was subsequently eluted, first with 2% HCl and then with 2% NH_3. Note in Figure 5 that Ni(II) and Cu(II) have essentially been separated; during HCl elution, bulk of Ni(II) was eluted while ammonia elution resulted in complete desorption of Cu(II). Changeover of eluent with other chelating exchangers (IRC-718, ES-467 and others)

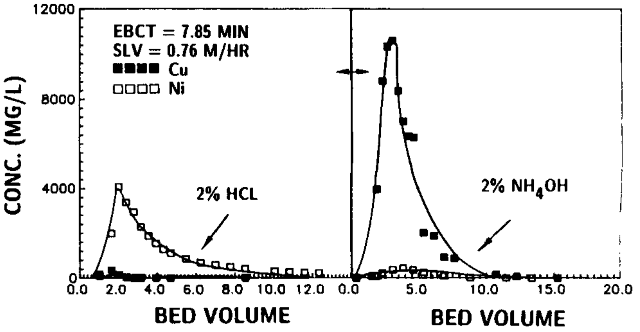


Figure 5. Separation of Cu(II) and Ni(II) from a loaded XFS 4195 column using gradient elution with HCl and NH_3.

does not yield such an excellent separation between copper and nickel ions. It is likely that this new chelating polymer may be an effective solid phase for bulk separation of metal ions by the gradient elution technique using continuous annular chromatography (Begovich et al., 1983).

In summary, the results in Figures 1-5 show that the newly identified chelating polymer offer the following advantages:

- It increases dissolved metal uptake with an increase in aqueous-phase ionic strength under acidic conditions (Figure 3).
- It retains its metal-removal capacity even at pH as low as 1.0 (Figure 4).
- It can be easily regenerated with ammonia (Figure 2).
- It may act as an effective sorbent for bulk separation of metal ions (Figure 5).

In the areas of analytical chemistry and pollution control, the foregoing properties are quite unique and can complement the shortcomings of other widely used chelating polymers and adsorbents.

Underlying mechanism: a hypothesis

Contrary to other chelating polymers, XFS 4195 has only nitrogen donor atoms (altogether three) in each functional group (see Table 1); this resin will, therefore, act as an anion exchanger when protonated or coordinated to metal ions. The negative logarithms of the three acid dissociation constants (pK_{a1}, pK_{a2}, and pK_{a3}) for the monomeric functional group were calculated using the procedure of Perrin, Dempsey and Serjeant (1981). The method uses published Hammet and Taft constants and the linear free energy relationship (LFER) to take into account the effects of various substituents on the change in pK_a values for various organic acids and bases. Based on the computed monomeric pK_a values, the approximate ranges of polymer-phase pK_a values for XFS 4195 are predicted as follows:

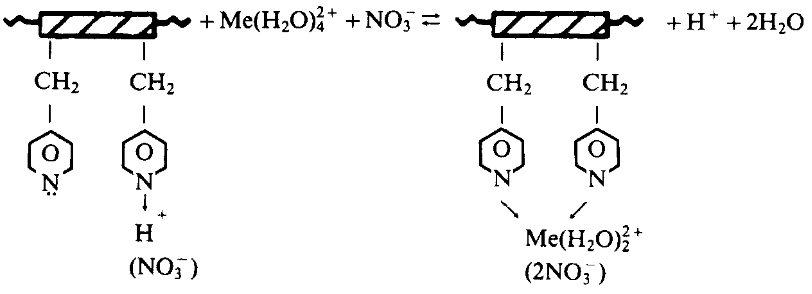
$pK_{a1} \leq -1.0$ (corresponds to one pyridine group)

$pK_{a2} = 2.0\text{–}4.0$ (corresponds to the second pyridine group)

$pK_{a3} = 6.0\text{–}8.0$ (corresponds to the tertiary ammonium group)

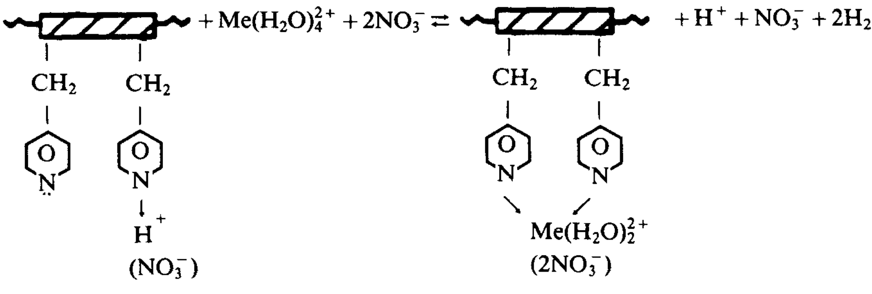
Recently, Garcia and King (1989) computed pK_a values for various weak-base tertiary-amine, polyamine, and vinyl-pyridine resins using the same technique, which showed an acceptable agreement with experimentally determined apparent pK_a values. The computed pK_a values for XFS 4195, however, could not be verified experimentally, because resin titration with acid did not yield any identifiable inflection points. Similar difficulties were also faced by Clifford and Weber (1976) and by Garcia and King (1989) in regard to resin titrations. For XFS-4195, resin titration is particularly difficult, because the first two pK_a values are quite distant from the neutral region.

Considering the computed pK_a values and a general case for XFS 4195 where a proton, H^+, is being exchanged for a metal(II) ion with four coordinated water molecules, $Me(H_2O)_4^{2+}$, at an acidic pH, the exchange reaction can be presented as follows:



(1)

Note that (i) the shaded rectangle represents the common polymer matrix and the tertiary-amine group has not been shown, since it is not responsible for the sorption of metal ions at acidic pH due to its relatively high pK_a value ($pK_{a3} > 6.0$); (ii) one of the pyridine groups remains unprotonated even under acidic condition, because first acid dissociation constant, pK_{a1}, is lower than zero; and (iii) to maintain electroneutrality, an anion (say NO_3^-) is to be included in the lefthand side of Eq. 1, which is essentially identical to the following reaction where both the polymer phase and aqueous phase have been shown to be electrically neutral independently:



(2)

When Cl^- or SO_4^{2-} are present instead of NO_3^-, Eqs. 1 and 2 will remain the same except that NO_3^- is to be replaced by Cl^- or $1/2\ SO_4^{2-}$. Assuming ideality, the equilibrium constant of Eq. 1 is given by:

$$K_{eq} = \frac{[\overline{RMe}][H^+]}{[\overline{RH}][Me^{2+}][NO_3^-]} \tag{3}$$

where $[\overline{RMe}]$ and $[\overline{RH}]$ represent the polymer-phase molar concentrations of Me^{2+} and H^+, respectively, while the others represent corresponding aqueous-phase molar concentrations. The Me^{2+}/H^+ separation factor is a dimensionless measure of relative selectivity between Me^{2+} and H^+, and equal to the ratio of Me^{2+} concentration in the polymer phase and the aqueous phase to that of H^+ and given as follows:

$$\text{Separation factor, } \alpha_{Me/H} = \frac{[\overline{RMe}][H^+]}{[\overline{RH}][Me^{2+}]} \tag{4}$$

Comparing Eqs. 3 and 4,

$$\alpha_{Me/H} = K_{eq}[NO_3^-] \tag{5}$$

Since K_{eq} is a constant, an increased anion concentration (electrolyte concentration added as $NaNO_3$, Na_2SO_4, etc.) will increase the separation factor; that is, an enhanced selectivity or metal-ion uptake by the chelating exchanger. This, however, is an oversimplified model that does not account for resin-phase nonidealities and any swelling/shrinking effect. Various anomalous observations and the unique role of ionic strength, as presented here, are amenable to qualitative understanding with the aid of the foregoing mechanism in Eqs. 1-5, but any elaboration in that regard is being avoided here. It is likely that this study will stimulate both syntheses of other pyridine-base chelating exchangers and a more rigorous quantitative approach to estimate heavy metals sorption onto them under adverse conditions.

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