Structural Design of Nanoporous Silica Polyamine Composites for Metal Separations in Water

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Abstract

Over the past ten years research at the University of Montana in collaboration with Purity Systems Inc, both located in Missoula, Montana, has resulted in a novel class of chelator materials composed of amorphous, nanoporous silica gels and modified polyamines. These materials offer some distinct advantages over conventional polystyrene based resins especially for applications in the mining industry. This paper will report on the relationship between polymer structure and metal selectivity, the relationship between chelator structure and metal selectivity and further comparisons with polystyrene analogs.

Introduction

A research collaboration between the Department of Chemistry at the University of Montana and Purity Systems Inc both located in Missoula, Montana has resulted in a novel class of chelator materials composed of nanoporous amorphous silica gels and hydrophilic polymers [1-10].

These composite materials utilize silica gels with average pore diameters of 25 nanometers, surface areas of ~300-400 m^2/g and pore volumes >1.0 mL/g. It has been found that the distribution of pore sizes is critical to obtaining composite materials with the desired characteristics. Silica gels with a relatively small number of pores that are less than 10 nm in diameter are optimal. We have found that the best trade off between back pressure and good mass transfer kinetics is obtained with silica gels having particle sizes in the 150-250 micron range for use in fixed bed or rotating column reactors.

The hydrophilic polymers employed are either branched or linear polyamines with molecular weights ranging from 1200 - 25,000. The techniques used for silanizing the silica gel, grafting the polyamine to the silanized surface and covalently binding ligands which make the composite selective for a given metal or group of metals have been previously reported [5-9]. In our IWC presentation in 2006 we reported cation and anion separations utilizing a new method of preparation of the materials which used a mixture of chloropropyl trichlorosilane and methyl trichlorosilane [11]. This "mixed silane approach" afforded materials with superior performance characteristics. We also reported on the use of immobilized metals as a means of capturing toxic anions such as arsenate and selenate and on our preliminary comparisons between these composite materials and conventional polystyrene resins [11]. In this paper we report two new aspects of the properties of these composites: 1) the variation in metal selectivity of two composites made from two different polymers (branched poly(ethyleneimine) and linear poly(allylamine)) but having the same functional group (amino acetate); 2) a comparison of two composites having amido-diaminoacetate and amidotriaminoacetate functionality. These studies reveal that metal selectivity is, surprisingly, as sensitive to polymer structure as it is to chelator ligand structure. In addition, we report further results on the comparison of these composites with polystyrene resins.

Results and Discussion

Composite strucure and metal selecivity

The dependence of metal ion selectivity on polymer structure

We previously noted that polyamine composites containing the same functional group but made from two different polymers (WP-2, amino acetate

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© 2009 al-Farabi Kazakh National University Printed in Kazakhstan functional group made from poly(ethyleneimine) (PEI) MW=23k, Figure 1 and BP-2, amino acetate functional group made from poly(allylamine) (PAA) MW=15k) had slightly different capacity and selectivity for manganese in the presence of other metals [12, 13] The two composites were synthesized by reaction of the polyamine composites, WP-1 (poly(ethyleneimine)) or BP-1 (poly(allyamine)) with chloro acetic acid. The branched poly(ethyleneimine) contains about 30 primary amines (RNH_2 groups), 35% secondary amines (R_2NH groups and 30% tertiary amines (R_3N groups) while the linear poly(allylamine)) contains only primary amines. This results in a very different pattern of acetate substitution where in the case of WP-2 only 71% of the amines are modified on average and meaning that there are very few iminodiacetic acid (IDA) sites while in the case of BP-2 145% of the amines are modified meaning that there are almost 50% of the IDA sites (Figures 1 and 2).

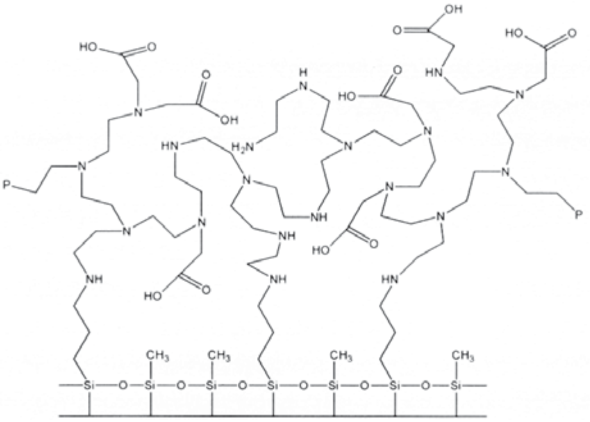


Fig. 1. WP2, Branched poly(ethyleneimine) modified with chloroacetic acid 2.03 mmol acetate per gram (71% of amines modified)

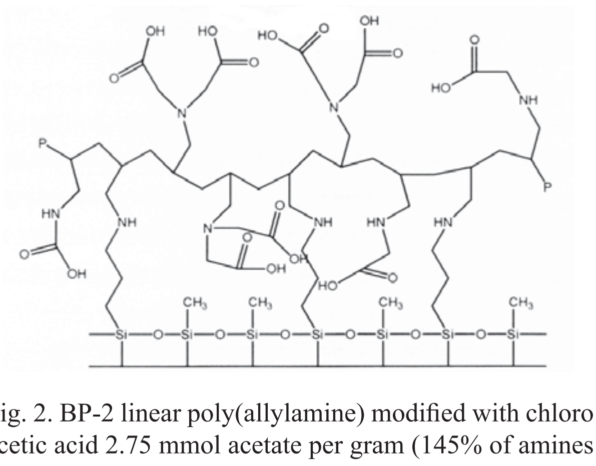


Fig. 2. BP-2 linear poly(allylamine) modified with chloro acetic acid 2.75 mmol acetate per gram (145% of amines modified).

This difference in the type and number of sites on the two composites has a significant influence on the metal selectivity. The amino-acetate functional groups of WP-2 are separated by only two carbons. Therefore relative to BP-2 the WP-2 amino-acetate groups are proximal to amino-acetate groups of adjacent branches in the branched PEI polymer. The close proximity of functional groups and higher density of possible donor atoms will most likely allow cooperative coordination by more than one amino acetate group and perhaps other un-functionalized amines. Thus coordination sites within WP-2 are on average of a higher denticity relative to BP-2. In contrast, the BP-2 composite is constructed from a linear polyamine containing a large fraction of IDA groups separated by five carbon atoms. Cooperation between atoms within a single IDA ligand facilitates metal ion coordination for BP-2. The maximum denticity of this ligand is 3. The higher denticity of the WP-2 adsorption sites must invoke a greater formation constant especially for those ions that prefer to form higher coordinate complexes such as Fe(III) and Ni(II). The lower denticity of the BP-2 coordination sites favors metal ions that prefer low coordination complexes such as the cupric ion. These proposed differences are born out by the pH profiles for the divalent transition metal ions of WP-2 and BP-2 shown in Figures 3 and 4. It can be seen that that WP-2 has significant capacities for all the divalent transition metals tested in the pH range of 1 to 2 and in particular for nickel at pH values down to 0.5. In contrast the pH profiles of the same metals for BP-2 show little affinity for any of the divalent metals except copper and for ferric ion. The hypothesis that the lower denticity of the BP-2 sites is responsible for these differences is further born out by a comparison of these polyamine composites with the polystyrene resin, IRC 748 which has only isolated amino diactetic acid sites (Figure 5). The overall selectivity of this resin for copper and ferric ion over the other divalent ions including nickel is apparent as observed for BP-2. In the case of IRC 748 however, significant adsorption of all the divalent ions is observed at pH =2 presumably because of the absence of amino acetate sites present in BP-2 which have a denticity of only two.

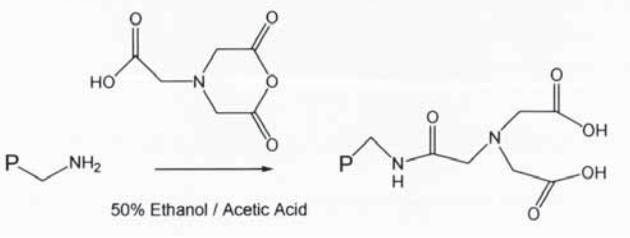
The selectivity of BP-2 for copper over nickel and the other divalent ions can be useful for separations of copper from the other divalent ions, especially nickel which is often found in significant quantities codeposited with copper in sulfide and latterite ores [14]. We have performed breakthrough tests on the two polyamine materials referred to above in order to see if the batch pH profiles translate to effective separations of these two metals for BP-2 in particular. Representative results of these tests are illustrated in Figures 6 and 7.

At pH=2 the greater selectivity of BP-2 for copper is clearly shown in Figures 6 and 7. WP-2 co-loads nickel giving only an 86.9 % copper purity in the strip while BP-2 passes nickel and gives a 99.8% copper strip. The selectivity of BP-2 for copper over nickel persists at pH=1 and 3. At pH =1.0 however, the capacity drops to 2.2 mg/g composite while at pH=3 the capacity increases to 26.6 g/mL while maintaining the same selectivity giving and 99.9% copper strip. WP-2 at pH=1 does exhibit good selectivity for copper over nickel giving a 99.9% pure copper strip but with a capacity of only 9.4 mg/g composite. IRC 748 does do a good job of separating copper from nickel at pH=1 with a relatively low capacity of 6.5 mg/g but unlike BP-2 this selectivity is not preserved at higher pH values of 2 or 3 as the batch capacities suggest (Figure 5).

Overall these studies show that the structure of the polyamine and its impact on the nature of the coordinating groups in the modified composites has a profound influence on metal selectivity.

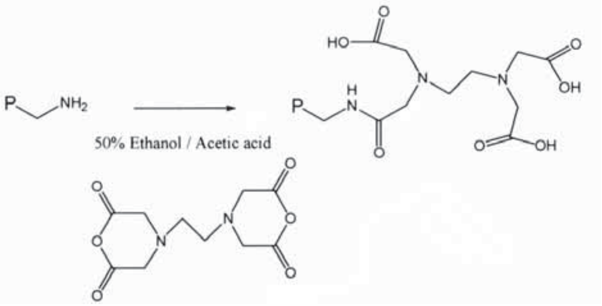
The influence of ligand structure on metal ion selectivity

A commonly accepted axiom in the analytical and surface science community is that tethering an active site to surfaces results in higher activity of that site whether it is for ion capture or catalysis [15]. We attempt to test this concept for metal ion capture here using the subject polyamine composites. By reacting the mono-anhydride of nitrilo-acetic acid (NTA) with either BP-1 or WP-1 we have made an amido-diacetate ligand with a two atom tether from the amine which we have named BP-NTA and WP-NTA (Scheme 1).



Scheme 1. Synthesis of BP-NTA and WPNTA. P=BP-1 or WP-1.

Using a similar approach we synthesized a tethered system with a higher number of coordinating groups by reacting ethylene diamine tetraacetic acid anhydride thus creating an amido triacetate ligand (Scheme 2).



Scheme 2. Synthesis of BP-ED and WPED. P=BP-1 or WP-1.

As expected considering the distribution of amines in the two polymers the composite BP-1 made from PAA loads more NTA and EDTA with amine modifications of 72 and 57% respectively while WP-NTA and WP-ED are only modified to the extent of 26 and 42% [9, 16]. Despite this BP-NTA and the WP-NTA have similar metal ion capacities. The pH profile batch capacities for these four composites for divalent and trivalent metals are shown in Figures 8-11.

It can be seen from the data in Figures 8-11 that except for the slightly lower capacities for the WP-ED relative to BP-ED the overall metal selectivity for each ligand type is not dependent on the nature of the polymer used. This is in sharp contrast to the case for BP-2 versus WP-2. This difference is likely due to the fact that in this series of composites each metal binding site is tethered and isolated and is therefore not influenced by the nature of the polymer to which the ligand is bound to any great extent. On the other hand the NTA ligand does show a better differentiation between the divalent metals particularly at higher pH values. This is most clearly manifested in the dynamic separation of copper from nickel at pH=2. This is illustrated in Figures 12 and 13 where it is shown that with BPED co-loading takes place while with BPNTA a clean separation of the two ions is accomplished. Thus, here again, as is the case for BP-2 versus WP-2 the ligand with lower denticity favors copper over nickel. This is born out by the similar binding constants for copper and nickel exhibited by EDTA itself (Table 1). On the other hand in the absence of copper the difference in binding constants between nickel and the other

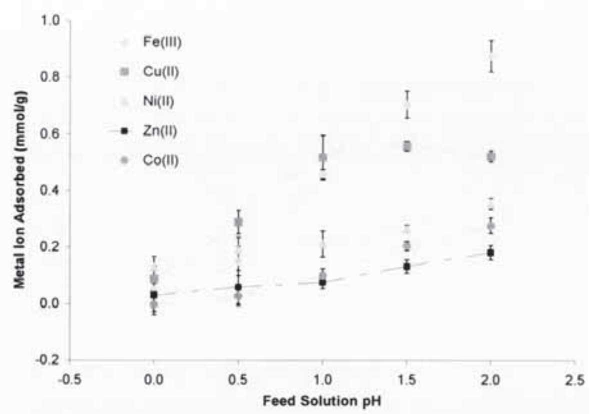


Fig. 3. Batch pH profiles of the divalent metal ions and ferric ion for WP-2. Solutions contained 1.5 g/L of the metal ion. 10 mL of solution was equilibrated with 0.10 g of composite.

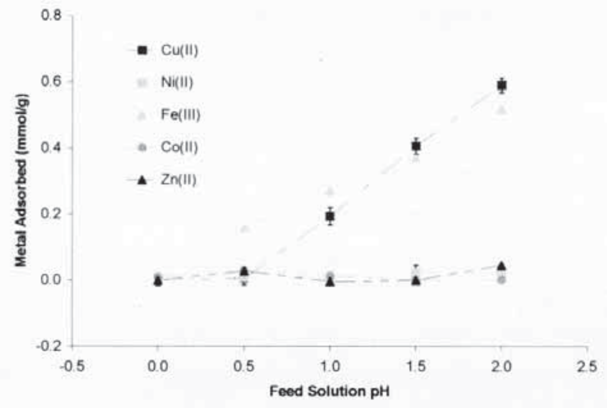


Fig. 4. Batch pH profiles of the divalent metal ions and ferric ion for BP-2. Conditions same as for Figure 3.

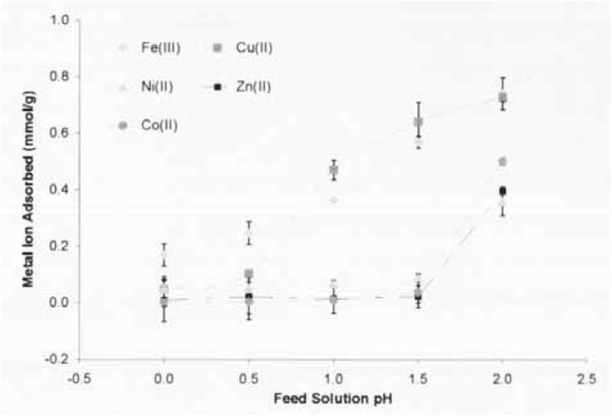


Fig. 5. Batch pH profiles of the divalent metal ions and ferric ion for IRC 748. Conditions same as for Figure 3.

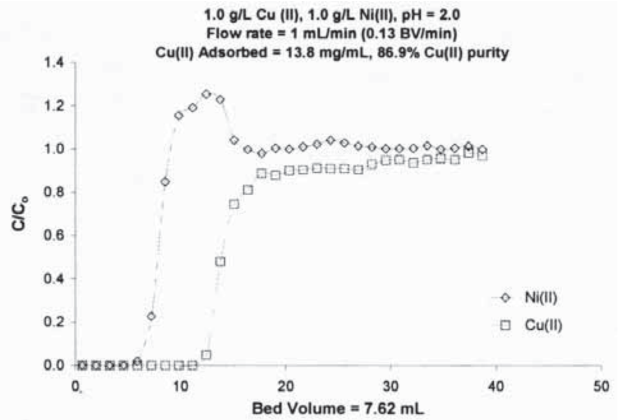


Fig. 6. Dynamic separation of copper from nickel with WP-2.

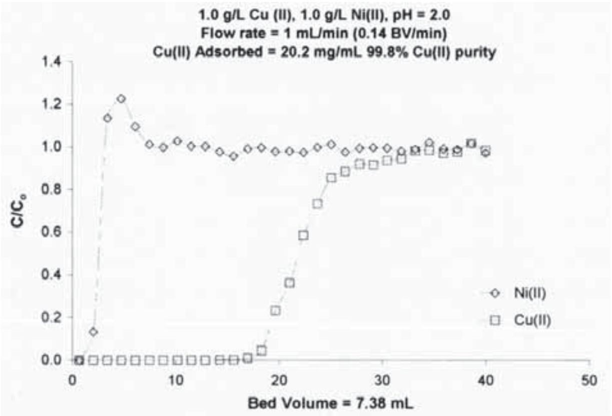


Fig. 7. Dynamic separation of copper from nickel with BP-2.

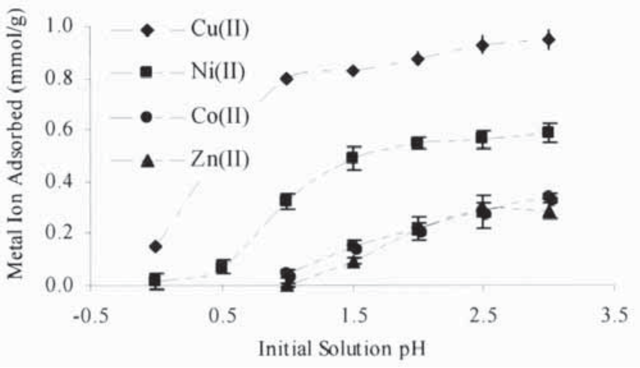


Fig. 8. pH profile batch capacities for BPNTA for the divalent metals. Challenge solutions contained 1.5 g/L of each metal. 0.1 g of composite was equilibrated with 10.0 mL of solution.

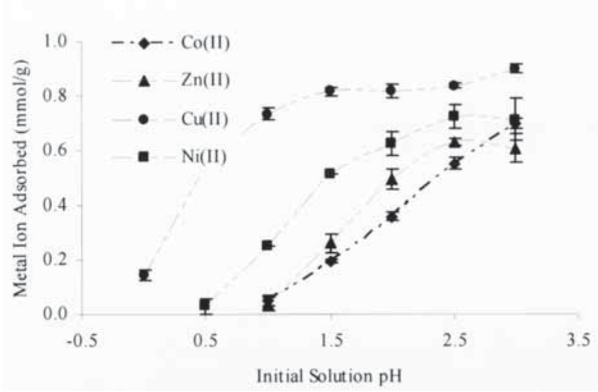


Fig. 9 pH profile batch capacities for the divalent metals for WP-NTA. Conditions the same as for Figure 8.

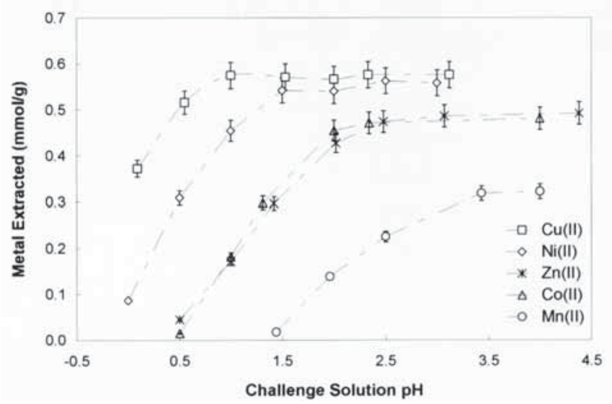


Fig. 10. pH profile batch capacities for the divalent metals for BP-ED. Conditions are the same as for Figure 8.

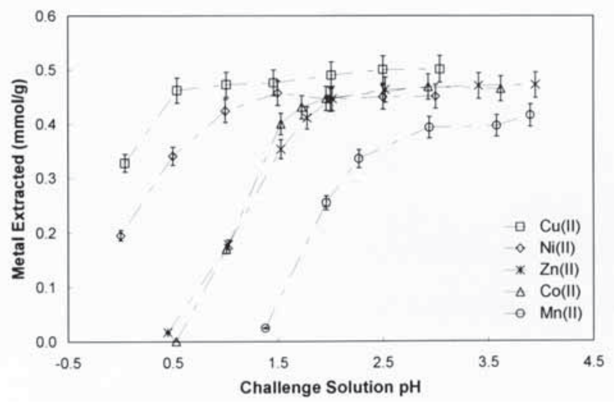


Fig. 11 pH profile batch capacities for the divalent metals for WP-ED.

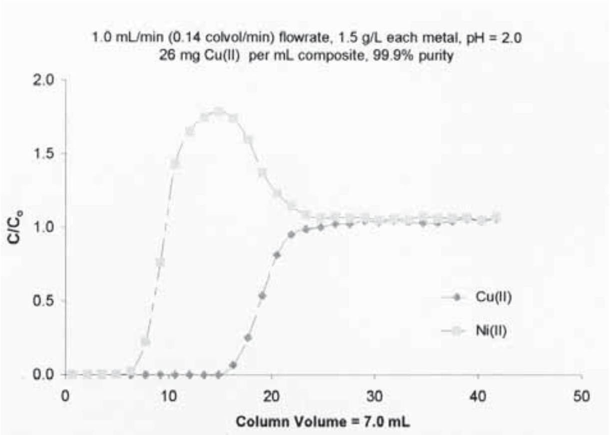


Fig. 12. Dynamic copper-nickel separation using BP-NTA showing the clean separation at pH=2.

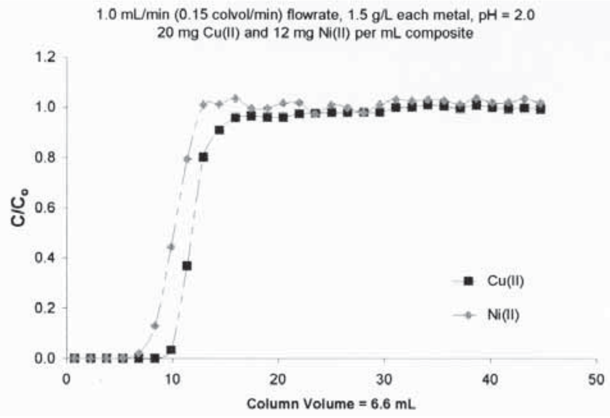


Fig. 13. Dynamic copper-nickel separation showing co-loading at pH=2 with BP-ED.

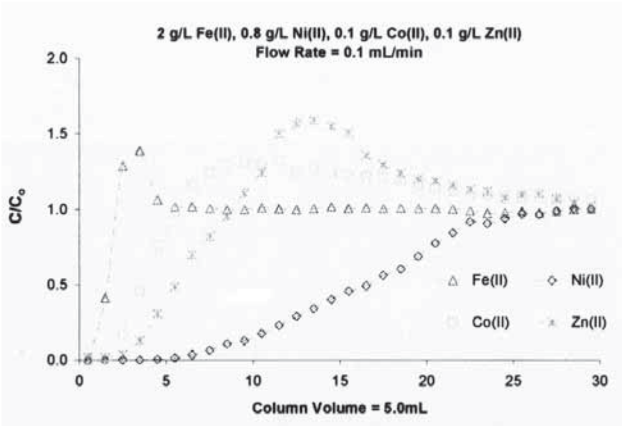


Fig. 14. Separation of nickel from cobalt, zinc and ferrous using BP-ED at pH =1.

divalent metals (Table 1) allows for the clean separation of nickel from cobalt, zinc and ferrous ion. This illustrated in Figure 14 using a mock solution that contains the divalent metals in relative concentrations similar to that found in laterite ores after removal of copper [14]. The nickel strip is greater than 90% pure and the only contaminant is iron [9]. Separate studies have shown that this iron is ferric iron due to ferrous to ferric oxidation during loading. Addition of a low concentration of oxalic acid to the feed suppresses the oxidation and strips of 99% purity are obtained. Finally it should be noted that the NTA and EDTA composites show high affinities and selectivity for trivalent metals. These results are reported elsewhere [9,16].

Table 1.
Binding constants of the divalent metals and ferric ion with EDTA

Metal Ion	K_{MY}
Fe(III)	1.3×10^{25}
Cu(II)	6.3×10^{18}
Ni(II)	4.2×10^{18}
Zn(II)	3.2×10^{16}
Co(II)	2.0×10^{16}
Fe(II)	2.1×10^{14}

Further comparisons with polystyrene resins

Wall Effects

It is obvious that part of the sharper separations achieved with silica polyamine composites relative to polystyrene analogs is due to their smaller particle size. This is of course part of the explanation but it is also due, in our view, to the higher porosity and more hydrophilic nature for the composites versus polystyrenes. It is well known that that if the bed diameter is less than 30 times the particle size than wall effects will be important and this will negatively impact capture kinetics [17]. In our prior work on cobalt nickel separations using the silica polyamine composite CuWRAM and the polystyrene product M-4195 the work was done in a 10 mm diameter column and the CuWRAM particle size was 0.200 mm while the M-4195 was .320 mm in diameter [11].

This puts the M-4195 experiments right on the border line where wall effects could be important. We therefore went ahead and repeated the M-4195 cobalt-nickel separations using a 25 mm column. The results of these experiments are shown in Figures 15-17. It can be seen that although loading in the larger column is somewhat slower the overall capture kinetics as measured by the slope of the breakthrough line and the purity of the strip remain basically unchanged. The issue of wall effects being a major contributor to the differences in performance between the silica polyamine composite CuWRAM and M-4195 are laid to rest.

Copper-ferric ion separations

In our previous work we also compared the performance of M-4195 with CuWRAM for copper-ferric ion separations.

This comparison was really not appropriate because there is now available a polystyrene resin that is much more effective for copper-ferric ion separations, XFS 43084 [18]. We report here a comparison of this resin with CuWRAM for copperferric separation and a comparison of the two materials with regard to chloride retention which is sometimes an important issue in copper extraction applications.

The batch pH profile batch capacity data for CuWRAM and XFS 43084 are shown in Figures 18 and 19.

It can be seen that both materials have the ability to separate copper from the other metals at pH=1.0 or above. However, CuWRAM has the ability to perform these separations even down at pH=0. This is a distinct advantage. However at pH=2 XFS 43084 is still selective for copper while for CuWRAM the selectivity almost disappears. In this sense the two materials are complimentary.

Dynamic copper-ferric separations are illustrated in Figures 20 and 21.

Both materials performed well under the conditions of the test. The strip purities ere identical at 99.3% but CuWRAM showed a slightly higher capacity of 20g/mL versus 17.9 g/mL for XFS 43084. Both materials stripped well. As usual the silica polyamine showed a sharper breakthrough a factor that becomes critically important at faster flow rates.

Chloride retention is sometimes important in copper recovery because the presence chloride in the copper strip can cause problems in the electroplating of copper where liberation of chlorine can compete with water oxidation at the anode. A simple way to overcome this problem is to wash the copper loaded column with sodium sulfate. In order to examine this problem for both CuWRAM and XFX 43084 we loaded 10 mL columns of the two materials with 1.6 g/mL copper solutions spiked with 400 ppm of chloride as the sodium salt. The columns were then washed with 40 mL of 15 g/L sodium sulfate and then stripped the column in the usual manner. We found that the CuWRAM retained 23% of the chloride ion loaded while the XFS 43084 retained none. We attribute this difference to the fact that the picolyl ligand in the polystyrene resin has a hydroxypropyl group attached to the picolyl nitrogen and it is likely that this group takes up a coordination site on the coordinated copper ion thus hindering chloride coordination to the copper. It is likely that further washing with sodium sulfate of the CuWRAM column would remove the remaining chloride but this kind of extensive washing would probably not prove to be practical. Introduction of an hydroxyl alkyl group into the CuWRAM structure is a better approach and these studies are currently underway in our laboratories.

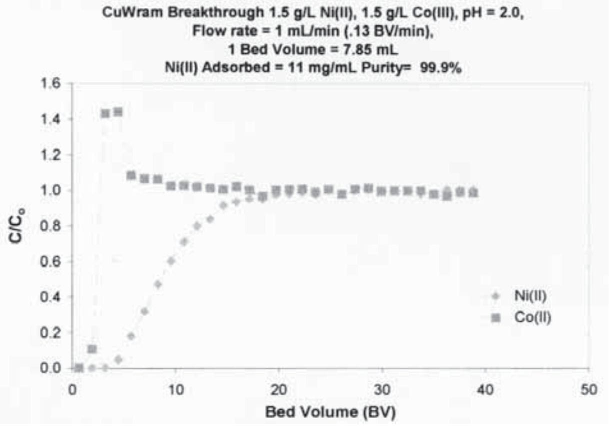


Fig. 15. Nickel-cobalt separation with CuWRAM in a 10 mm diameter column.

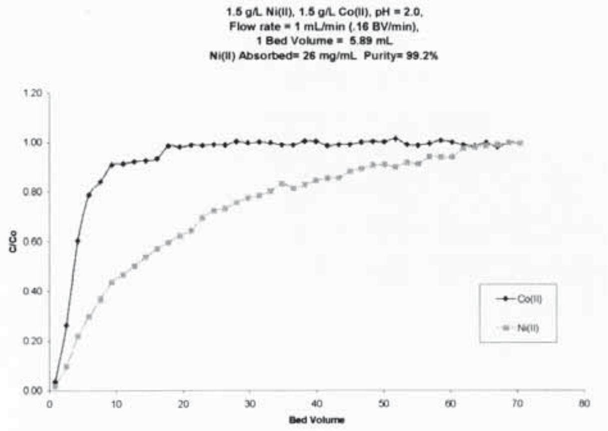


Fig. 16. Nickel-cobalt separation using M-4195 run to full breakthrough in a 10 mm column.

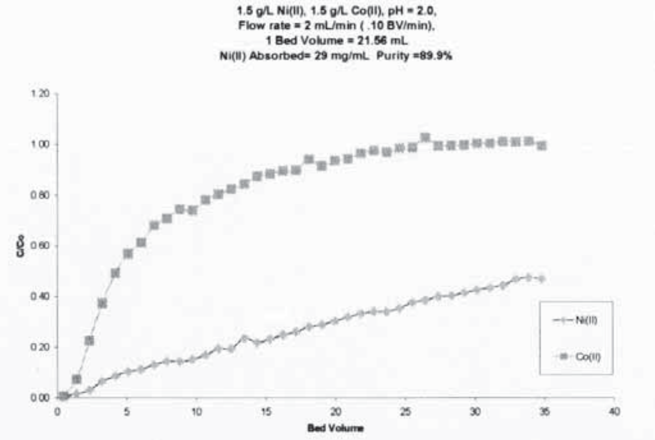


Fig. 17. Nickel-cobalt separation using m-4195 in a 25 mm column (Not run to full breakthrough so purity is not optimized)

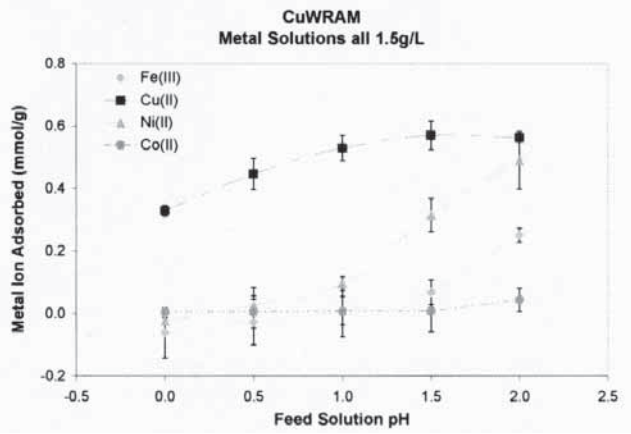


Fig. 18. pH profile batch capacities for CuWRAM for ferric, copper, cobalt, nickel.

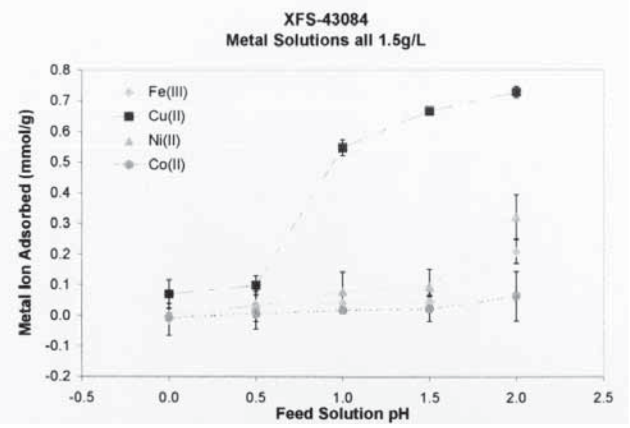


Fig. 19. pH profile batch capacities for XFS for ferric, copper, cobalt, nickel.

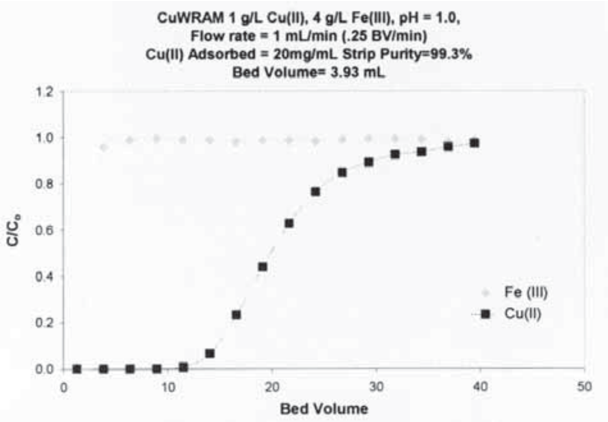


Fig. 20. Breakthrough curve for copperferric separation at pH=1.0 using CuWRAM.

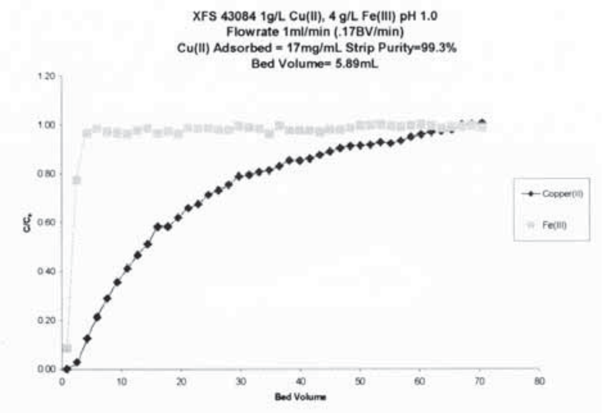


Fig. 21. Breakthrough curve for copperferric separation at pH=1.0 using XFS 43084.

Conclusions

The studies on the acetate modified silica polyamine composites reported here have uncovered two important features of these chelator materials:

1. Polyamine structure can have profound influence on the selectivity of acetate modified composites when the acetate groups are directly bound to the amines on the polymer.
2. Tethering the acetate group via an amide bond leads to composites with isolated coordination sites where the polymer structure has little influence on metal selectivity but where the coordination properties of the ligand determine metal binding affinities.

The reported comparisons with polystyrene analogs show that wall effects make a minimal contribution to the overall properties of the materials under the conditions examined so far. The silica polyamine composite and the polystyrene analog, XFS 43084 are both effective for separating copper from other metals commonly found in acidic ore leaches but have slightly different operational pH ranges. The sharper separation kinetics observed with CuWRAM were not important in the current study but would be more important at faster loading rates. The polystyrene resin showed much cleaner removal of chloride from adsorbed copper when washed with sodium sulfate. To date the collaboration between Purity systems

Inc. (www.puritysystemsinc.com) and the University of Montana has resulted in the design and synthesis of nine new chelator materials it is our hope that these new composites will make a significant contribution to separations science in the near future.

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