Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hughes, Mark A. and Rosenberg, Edward(2007) 'Characterization and Applications of Poly-Acetate Modified Silica Polyamine Composites', Separation Science and Technology, 42: 2, 261 — 283
To link to this Article: DOI: 10.1080/01496390601070141
URL: http://dx.doi.org/10.1080/01496390601070141

Separation Science and Technology, 42: 261–283, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390601070141

Characterization and Applications of Poly-Acetate Modified Silica Polyamine Composites

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Abstract: Silica polyamine composites made from silanized amorphous silica gel and a polyamine (polyallylamine (BP-1) and poly(ethyleneimine) (WP-1)) were functionalized with ethylenediamine-*N*, *N*, *N*′, *N*′-tetraacetic (EDTA) anhydride resulting in the modified composites BP-ED and WP-ED respectively. Successful immobilization of the poly-acetate ligand was confirmed by weight gain, IR and elemental analysis. The modified composites had ligand loading values of 0.78 mmol/g and 0.58 mmol/g respectively. Adsorption characteristics were investigated for BP-ED and WP-ED by pH profiles, time dependent isotherms, concentration dependent isotherms, and the Langmuir and Freundlich adsorption models. Metal ion capacities (mmol of metal adsorbed per gram of adsorbent) were shown to increase with pH for BP-ED and WP-ED, which is in contrast with silica gel modified with EDTA anhydride via amino propyl silane without the use of a polyamine where the opposite trend is observed. The adsorption of Ni(II), Zn(II) and Co(II) onto BP-ED and WP-ED was shown to fit the Langmuir adsorption model, which indicates a monolayer, non-cooperative metal ion uptake. For both composites the divalent metal ion selectivity is as follows: Cu(II) > Ni(II) >> Zn(II), Co(II) >> Mn(II). Also the trivalent metal ion selectivity is as follows: Fe(III) > Ga(III) >> Eu(III) > Al(III). This is in close agreement with reported formation constants for EDTA in solution. Breakthrough and recovery tests were carried out using a 5cc packed column. The separation and recovery of Ni(II) from Co(II) when BP-ED was challenged with a solution containing 1.5 mg/L of both metals resulted in an acidic strip solution of greater than 97% Ni(II) purity. Further, selective separation of Ni(II) from a solution containing low levels of Co(II) and Zn(II) and high level Fe(II) at pH = 1 was also achieved. Ni(II) was extracted at a flow rate of 0.1 column volumes per minute (0.5 mL/min) and recovered in greater

Received 15 May 2006, Accepted 5 October 2006
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than 90% purity by an acidic strip. Impurity in the strip was a consequence of Fe(II) oxidation to Fe(III). These tests demonstrate that well resolved separations of one divalent metal ion from one or more other divalent metal ions are possible through the use of EDTA anhydride modified silica polyamine composites with higher capacities than the previously reported amino propyl silane modified silica gel.

Keywords: Composite materials, polyamines, aminoacetate, metal ion separation

INTRODUCTION

The removal of heavy metal ions from aqueous solution can be achieved through the use of chelating materials. These materials have many advantages over conventional ion exchange materials that rely mainly on coulombic interactions between the functional group immobilized on the material and the metal ion to be extracted (1). Chelating materials coordinate in a multidentate fashion which allows for selective extraction from solutions at extreme pH, even when the metal ion in question is present at low concentrations. Chelating materials also have advantages over solvent extraction including the absence of hazardous solvents, interfacial crud buildup and the ability to extract metal ions to extremely low concentrations (2).

Chelating materials are often composed of a poly-dentate ligand immobilized upon a solid surface. In particular, cross linked polymeric resins (polystyrene, methyl methacrylate) and silica gels are commonly used as supports for such ligands (3). Several chelating materials produced in this manner are available commercially (4, 5). However, polymeric resins suffer from shrink/swell with changes in pH and do not tolerate high temperatures under optimal conditions (6). Chelating materials prepared by directly modifying an amino-propyl functionalized silica gel surface can suffer from degradation in the presence of base and insufficient mechanical stability (7). Recently, silica polyamine composite materials have been developed for the selective removal of heavy metal ions from aqueous streams (7–16). These composite materials consist of a polyamine grafted onto the surface of chloro-propyl functionalized mesoporous silica gel (Fig. 1). Subsequently the polyamine can be modified with an organic functional group with an affinity for one or more metal ions. The advantages of silica polyamine composites include the ability to tolerate higher operating temperatures (110°C compared with 70°C for polystyrene resins), improved stability with regards to radiolytic decomposition, superior mass transfer kinetics, and much longer usable lifetimes than their silica gel only and polystyrene based counterparts (6). A series of patented silica polyamine composites with excellent heavy metal ion extraction properties have been produced and are being made commercially available (15, 16).

The separation of divalent transition metals is made difficult by their physio-chemical similarities (17). EDTA is a chelating ligand with excellent

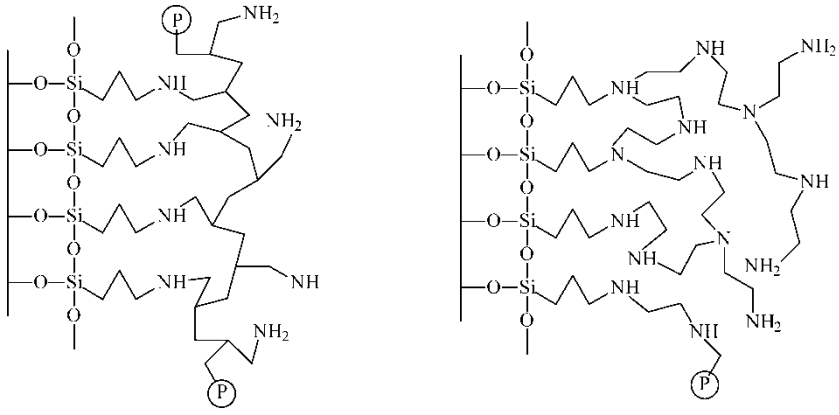


Figure 1. Approximate surface structure of BP-1 and WP-1 composites. BP-1 is made with PAA, which is a straight chain, water soluble, all primary amine polyamine (MW = 11,000). WP-1 is made with PEI, which is a branched chain, water soluble, polyamine with primary, secondary and tertiary amines in the ratio 35:35:30 respectively (MW = 1200). P indicates continuation of polyamine.

metal extraction capabilities from solutions at low pH. The ability of EDTA to selectively remove metal ions is a result of differences in the formation constants (K_{MY}) for soluble EDTA-metal ion complexes. For example K_{MY} for EDTA-Ni(II) complexes is 4.2×10^{18} which is greater than that for Fe(II) (2.0×10^{14}) or Mn(II) ($6.2. \times 10^{13}$). Thus EDTA will selectively chelate Ni(II) in the presence of Fe(II) or Mn(II). If a silica polyamine composite modified with EDTA anhydride possesses similar relative differences in formation constants when immobilized then it could be used to selectively extract Ni(II) from a solution containing Fe(II) and/or Mn(II). Previously, materials modified with EDTA anhydride, have shown promise for the selective separation and recovery of divalent transition metals such as Ni(II) from Co(II), Zn(II), and Mn(II) (18–20). The natural polysaccharide chitosan has been successfully modified with EDTA anhydride (18, 19). Metal capacities per gram of the resulting material were reported to be ~2 mmol/g at pH = 2, however to the best of our knowledge dynamic testing was carried out at reported flow rates no faster than 7.7 $cm^3\ hr^{-1}$ using columns requiring a large quantity of glass beads (18). Non-immobilized poly(allylamine) (PAA) has previously been modified with EDTA anhydride also, although selectivity in this form was reported to be poor (18). EDTA anhydride has also been reacted with functionalized silica gel through the use of amino-propyl silane (Silica-ED) (20). Silica-ED displayed only modest ligand loading per gram adsorbent (~0.3 mmol/g), hence only modest metal ion adsorption capacities (~22.3 mg/g Cu(II) and ~6.3 mg/g Ni(II) at pH = 1) (20). Further, although it is well known that the chelating ability of non-immobilized EDTA is

improved at higher pH, metal ion capacities for Silica-ED decrease as the challenge solution pH increases (20). The surface charge of silica gel becomes increasingly negative as pH increases, thus the electrostatic attraction between acetate groups of the immobilized ligand and surface hydroxyl groups becomes greater in magnitude. This microenvironmental effect suppresses the ability of the acetate ligands to complex metal ions as pH increases (20). Silica polyamine composites make use of a polymer matrix which may shield a pendant ligand from the charged surface allowing increased capacities at increased pH. Also, immobilized polyamines contain a large quantity of amine sites per gram of composite ($2 \sim 4$ mmol/g) which may promote increased ligand loading and therefore metal ion capacities.

We have previously reported the silica polyamine composite BP-1 made from PAA and chloropropyl silanized amorphous silica gel. This composite has been successfully modified with 2-picolyl, phosphonic acid and 8-hydroxyquinoline ligands (10, 21, 22). We have also reported the composite WP-1 made from poly(ethyleneimine) (PEI) and chloropropyl silanized amorphous silica gel. WP-1 was successfully functionalized with acetic acid and 8-hydroxyquinoline ligands (11, 22). We report here the modification of BP-1 and WP-1 with EDTA anhydride. The ligand was attached to the composites by way of the acid catalyzed aminolysis of EDTA anhydride resulting in an ethylenediaminetriacetic acid acetamide ligand (20). Although both PAA and PEI are water soluble polyamines they differ substantially in structure. PAA is an all primary amine straight chain polymer (MW = 11,000) whereas PEI is a branched chain polymer with primary, secondary, and tertiary amines in the ratio 35:35:30 (MW = 1,200). The adsorption characteristics of the resultant materials (BP-ED, WP-ED) for several divalent and trivalent ions were investigated by pH profiles, time dependant isotherms, concentration dependant isotherms and Langmuir and Freundlich plots. Comparisons with other EDTA modified materials reported in the literature are made throughout. Further, the selective removal of Ni(II) from other transition metals in a synthetic solution based on actual mine leach solutions is demonstrated.

EXPERIMENTAL SECTION

Materials

Silica gel (267 Å pore diameter, 2.82 mL/g pore volume, 84.7% porosity, 422 m^2/g surface area) was obtained from INEOS enterprises Ltd., UK (previously Crosfield UK) and was sieved to 100–150 microns. All chemicals were reagent grade and were purchased from ALDRICH Co. Metal solutions were prepared by dissolving the appropriate quantity of the sulfate salt in deionized water. Solution pH was adjusted from intrinsic with 0.05 M, 2.0 M

or 4.5 M H_2SO_4. Stripping and recovery was achieved with 4.5 M H_2SO_4. Metal standards for AA analysis were also obtained from ALDRICH Co.

Methods

Infrared characterization of modified composites was carried out with a Thermo-niclet 633 FT-IR spectrophotometer. Elemental analysis (Carbon, Hydrogen, Nitrogen) was conducted at Schwarzkopf Microanalytical Laboratory, N.Y. The error in elemental analysis was reported as no more than 0.3% absolute. Batch experiments were conducted in a Precision Scientific 360 shaker bath (Precision Scientific, Inc., Chicago, IL). Dynamic experiments were conducted with a 5cc column fashioned from a disposable syringe fitted with frits at both ends. Columns were packed dry and fed challenge solution by a variable-flow FMI Lab Pump model QG150 (Fluid Metering Inc., Syosset, N.Y.). Metal ion concentrations were determined via a Flame Atomic Absorption (FAA) method using a S2 FAA Spectrometer from SOLAR, UK. Error bars are included where the error is deemed significant relative to the absolute measurement.

SYNTHESIS OF EDTA MODIFIED COMPOSITE

The synthesis of BP-1 (poly(allylamine) grafted onto chloro-propyl functionalized amorphous silica gel) and WP-1 (poly(ethyleneimine) grafted onto chloro-propyl functionalized amorphous silica gel) have been reported elsewhere (15, 17). For the modification of BP-1 and WP-1 with EDTA anhydride (Fig. 2) 25 g of BP-1/WP-1 (containing 75 mmoles of amines) was mixed with 50 g (195 mmoles) of EDTA anhydride in 250 mL of 50% acetic acid/ethanol solution in a 500 mL flask equipped with an overhead stirrer. The reaction mixture was heated to 70°C for 24 hrs. The flask was

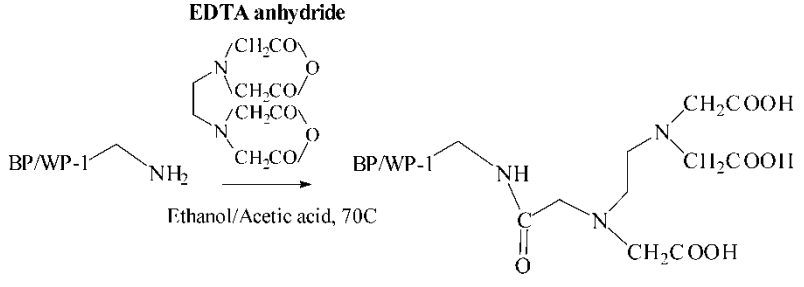


Figure 2. Acid catalyzed aminolysis. BP-ED and WP-ED are prepared from the reaction of EDTA anhydride with the appropriate composite precursor. The result is a pentadentate ethylenediaminetriacetic acid acetamide.

cooled and the product was filtered. The resulting composite was washed once with 75 mL of water, once with 75 mL of 4 M NH_4OH, three times with 75 mL of water, once with 75 mL of 50% acetic acid/ethanol, three more times with 75 mL of water, twice with 75 mL of methanol and dried to a constant mass at 70°C. IR spectra of BP-ED and WP-ED show amide and carboxylic adsorptions at 1638 cm^{-1} and 1747 cm^{-1} respectively for the resultant ethylenediaminetriacetic acid acetamide ligand. Weight gain after 24 hrs drying: BP-ED 20.2%, WP-ED 14.6%. See Table 1 for elemental analysis.

pH Profiles

pH profiles were acquired for several divalent and trivalent metals. The pH of the challenge solutions was adjusted with sulfuric acid. Metal concentrations in challenge solutions were 1 g/L. Batch extraction tests were conducted by adding 0.2 g of EDTA modified composite (BP-ED/WP-ED) to 20 mL of 25 mM aqueous acid metal solution at selected pH values. To ensure equilibrium, the metal ion and BP-1/WP-1 mixtures were placed in a shaker bath. After 24 hrs the mixtures were allowed to settle. Each supernatant was extracted and diluted with 2% nitric acid for analysis.

Mass Transfer Kinetics

Adsorption isotherms were obtained for WP-ED and BP-ED as a function of time. Using the batch method described previously samples of each composite were fed with a 20 mM Ni(II) solution at pH = 1. The supernatant was sampled several times over the following 24 hrs. Samples diluted and preserved in 2% HNO_3 solution before FAA analysis. The fraction of metal adsorbed was calculated by equation (1), where C_o is the initial Ni(II) concentration in the feed solution and C_t is the Ni(II) concentration of the supernatant at a time t.

$$(C_o - C_t)/C_t \quad (1)$$

Table 1. Elemental analysis data and ligand loading for BP-1, WP-1 and the corresponding EDTA anhydride modified BP-ED and WP-ED. Error in elemental analysis is ±0.3%

	C mmol/g	H mmol/g	N mmol/g	C/N	EDTA mmol/g
BP-1	11.23	27.2	2.86	3.93	—
BP-ED	14.41	28.8	3.36	4.29	0.76
WP-1	10.75	26.7	3.11	3.46	—
WP-ED	14.55	29.4	3.66	3.98	0.56

Concentration Dependent Isotherms

In order to assess the applicability of the Langmuir and Freundlich adsorption models to BP-ED and WP-ED metal chelation, concentration dependant adsorption isotherms were acquired. Isotherms were obtained by batch experiments as described in the previous experimental section. Metals investigated included Ni(II), Zn(II) and Co(II). Metal ion concentration was varied, pH was held constant (pH = 1), and each sample was shaken for 48 hrs to ensure equilibrium. Langmuir and Freundlich parameters were obtained from the appropriate linear regressions for Ni(II), Co(II) and Zn(II) for both BP-ED and WP-ED. The details of these models are described in section on Langmuir and Freundlich Adsorption Isotherms.

Column Separation and Concentration of Metal Ions

Breakthrough experiments and subsequent stripping were carried out as follows: Each flow test required 5 mL of BP-ED composite (~2.6 g). BP-ED was packed into the 5cc column. The 5cc column, fitted with a frit at both ends, received flow from a variable flow FMI Lab Pump, Model QG150 from Fluid Metering Inc., NJ, and USA. The flow rate was held constant at 0.5 mL/min (0.1 column volume/min). Each column of BP-ED was conditioned as follows: 20 mL water, 30 mL 4.5 M H_2SO_4 and 100 mL water. Two experiments were conducted:

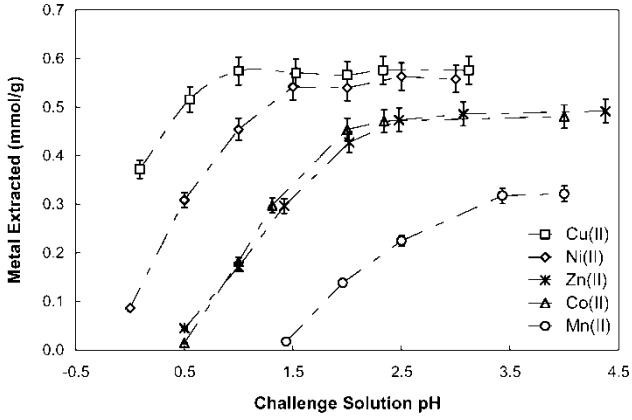
1. BP-ED was challenged with 100 mL of an aqueous solution containing 1.0 g/L Ni(II) and 1.0 g/L Co(II).
2. BP-ED was challenged with 150 mL of an aqueous solution containing 2.00 g/L Fe(II), 0.8 g/L Ni(II), 0.1 g/L Zn(II) and 0.1 g/L Co(II).

Columns were then rinsed with 20 mL water, stripped with 30 mL 4.5 M H_2SO_4. Eluent fractions were collected in 5 mL aliquots beginning with the first 5 mL of challenge solution. The fractions were preserved with HNO_3 and analyzed by FAA. Experiment 2 underwent four consecutive cycles to test for reproducibility.

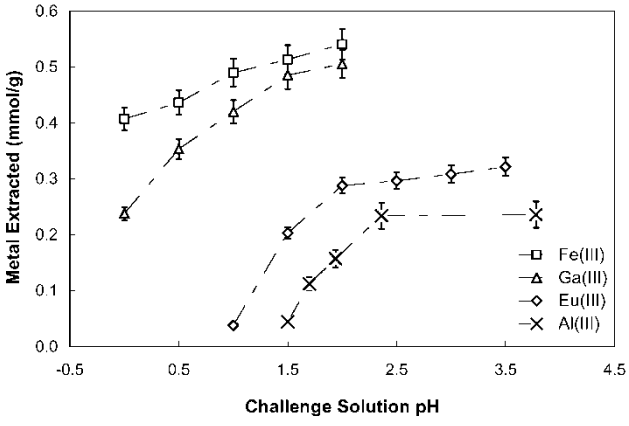
RESULTS AND DISCUSSION

Adsorption pH Dependence

pH profiles for BP-ED and WP-ED for both divalent and trivalent metals are displayed in Figs. 3 and 4 respectively. The dependence of metal ion adsorption on pH is clearly illustrated. It is evident that BP-ED and WP-ED behave similarly with regard to pH. However, BP-ED has higher capacities in most



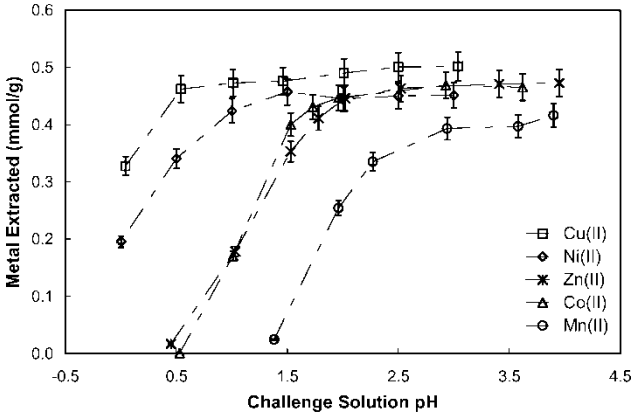
(a)



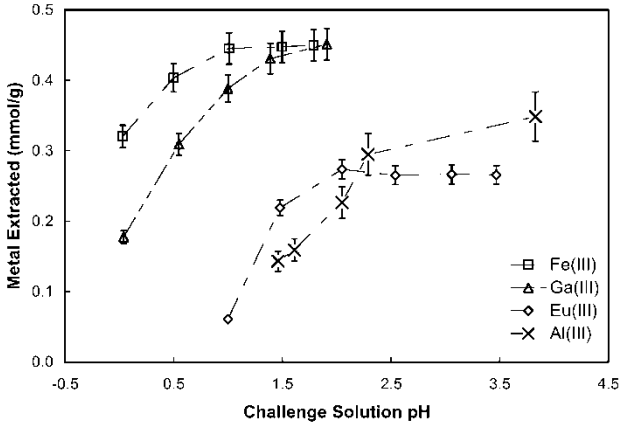
(b)

Figure 3. pH profiles for metal adsorption onto BP-ED, (a) Divalent metals, (b) Trivalent metals. Equilibration time: 48 hrs. 0.2 g of composite was challenged with 20 mL of feed solution. All metal ion concentrations were 1.5 g/L.

cases. Over the pH range studied the divalent metal ion capacity (mmol/g) of BP-ED and WP-ED increases with increasing pH until a point is reached after which the adsorption capacity is constant. This is a trend in agreement with chitosan modified with EDTA anhydride but not with that found for Silica-ED (18, 20). This leads to the conclusion that the polyamine matrix must create a great enough distance between immobilized ligands and surface



(a)



(b)

Figure 4. pH profiles for metal adsorption onto WP-ED, (a) Divalent metals, (b) Trivalent metals. Equilibration time: 48 hrs. 0.2 g of composite was challenged with 20 mL of feed solution. All metal ion concentrations were 1.5 g/L.

silanols so that there is no suppression of metal ion capacity by surface-ligand interactions for either BP-ED or WP-ED. This demonstrates a further advantage of silica polyamine composites over chelating materials prepared with functionalized silica gel but without the use of a polyamine (e.g. Silica-ED). Also, metal ion adsorption capacities per gram of chelating material are substantially higher for BP-ED than for Silica-ED. The Cu(II)

capacity at pH = 1 is ~36.5 mg/g for BP-ED compared with ~22.3 mg/g for Silica-ED. The Ni(II) capacity at pH = 1 is ~26.8 mg/g compared with ~6.3 mg/g for Silica-ED (20). Based on the batch pH profile data the order of selectivity for both BP-ED and WP-ED for divalent metal ions is: Cu(II) > Ni(II) >> Zn(II),Co(II) >> Mn(II), which is in agreement with that reported for both Silica-ED and chitosan EDTA chelating materials (19, 21). This trend is also in good agreement with the formation constants (K_{YM}) for EDTA-metal ion complexes, indicating that the pendant ligand closely models EDTA behavior in solution.

It is apparent from Figs. 3 and 4 that each divalent metal pH profile has two distinct regions:

1. A lower pH range in which solution acidity is great enough for protons to compete with metal ions for adsorption sites thus preventing maximum metal uptake capacities.
2. A higher pH range in which metal uptake is limited by the extent of ligand loading per gram and the relative stability of the resulting EDTA metal complex.

For both BP-ED and WP-ED the highest metal ion capacities for Zn(II), Co(II), and Mn(II) over the pH range studied are not as large as Cu(II) and Ni(II) capacities. This is due to lower formation constants of the complexes formed between these metal ions and the pendant ligands.

Calculations based upon elemental analysis yield a ligand loading of ~0.74 mmoles/g for BP-ED and ~0.58 mmoles/g for WP-ED (Table 1). The highest metal ion capacities for Cu(II) for BP-ED and WP-ED are 0.58 and 0.56 mmol/g respectively indicating that a fraction of the ethylenediaminetriacetic acid acetamide ligands are unavailable for coordination. It is possible that some ligands have attached to two polymer amine sites through two acetamide linkers leaving only two acetate groups available for coordination per ligand. This can only be confirmed by solid state NMR. Interestingly, elemental analysis of the precursors BP-1(poly(allylamine) and WP-1(poly(ethyleneimine)) indicates a larger quantity of polymer amines per gram for WP-1 than for BP-1 (Table 1). However BP-1 has a greater ligand loading, thus the PAA polymer must have more accessible amines. 30% of all PEI amines are tertiary and cannot be modified with EDTA. Also 35% of PEI amines are secondary and the steric bulk of two alkyl groups may hinder modification by the large EDTA ligand. PAA contains all primary amines that are not obstructed during subsequent functionalization hence higher ligand loading. Most importantly, the differences in the adsorption of Ni(II) and Co(II), Zn(II) at pH ~ 1, support the possibility of a column chromatography style separation of Ni(II) from Co(II) and/or Zn(II) with either BP-ED or WP-ED. Further, since Ni(II) is not appreciably chelated at very low pH (pH < 0.5) the recovery of sequestered Ni(II) from BP-ED/WP-ED may be possible using an acidic strip solution.

Figures 3(b) and 4(b) display pH profiles for four trivalent metal ions. Based on these data the order of selectivity for both BP-ED and WP-ED for trivalent ions is: Fe(III) > Ga(III) >> Eu(III) > Al(III). This is also in agreement with the K_{MY} values for the soluble EDTA-metal ion complexes. Similar to the divalent metal ion profiles there are two regions for each profile as described previously. Fe(III) and Ga(III) both reach a maximum metal uptake value of 0.54 and 0.51 mmol/g respectively for BP-ED and 0.45 mmol/g for both metals for WP-ED. Adsorption by WP-ED utilizes a larger fraction of the pendant ligands again indicating that a relatively large portion of BP-ED ligands may not be participating in metal ion coordination. Both BP-ED and WP-ED composites have a relatively low affinity for Al(III) at low pH (negligible below pH 1.25), therefore selective complexation of Ga(III) or Fe(III) from a pH = 1 solution containing high Al(III) concentrations was proposed. Dynamic column experiments demonstrated successful adsorption of Ga(III) in the presence of Al(III) (99.9% purity on the column), however, because Ga(III) is readily adsorbed from solutions at pH < 1 it was not possible to recover all of the adsorbed metal and regenerate the material even with highly acidic (4.5 M H_2SO_4) strip solutions (92% recovery).

To reduce processing time in industrial applications a chelating material with good mass transfer kinetics is necessary. Figure 5 compares the time required to reach equilibrium for both BP-ED and WP-ED. Equilibrium for each material is reached at ~800 minutes. Although both materials have

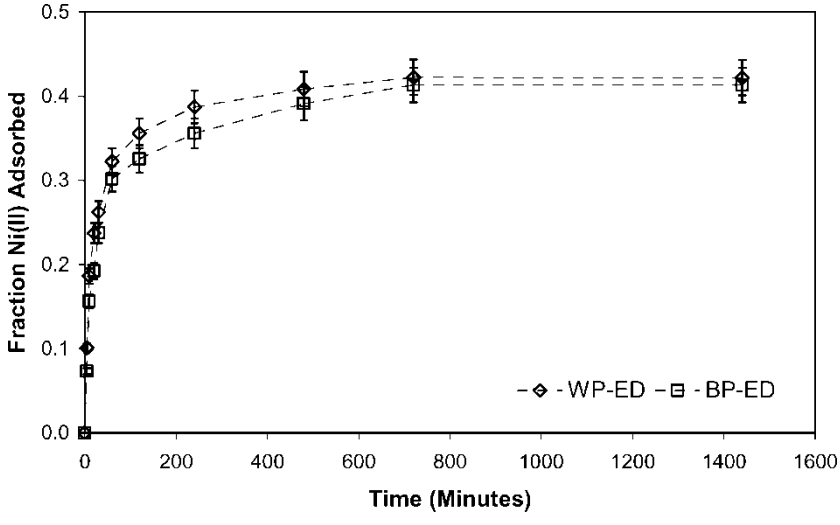


Figure 5. Time dependent adsorption isotherms for Ni(II) onto BP-ED and WP-ED at pH = 1.0.2 g of composite was challenged with 20 mL of feed solution (20 mM Ni(II)).

very similar equilibrium capacities WP-ED adsorbs Ni(II) more quickly than BP-ED at pH = 1. After 2 hrs WP-ED has adsorbed ~92% of that adsorbed at 24 hrs. At the same time BP-ED had adsorbed ~86% of that adsorbed at 24 hrs. It has already been established here that BP-ED has greater capacities in general than WP-ED, however, since most industrial dynamic extraction applications are terminated at 10% breakthrough capacity to improve efficiency, WP-ED may have equal or greater metal ion capacities (mmol/g) than BP-ED at this point. Improvements in mass transfer kinetics, all other factors being equal, are primarily due to a larger equilibrium constant for the adsorption process.

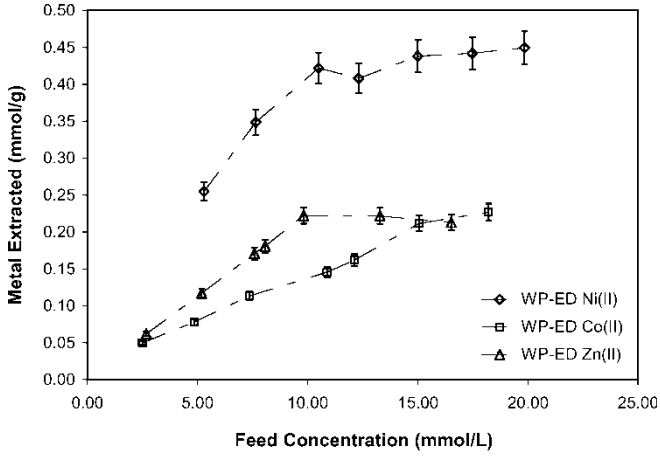
Langmuir and Freundlich Adsorption Isotherms

Concentration dependant isotherms for BP-ED and WP-ED are reported in Figs. 6a and 6b respectively. These data reconfirm that at pH = 1 BP-ED and WP-ED have a greater affinity for Ni(II) relative to Zn(II) and Co(II). These plots also show that the metal ion adsorption characteristics of BP-ED and WP-ED at pH = 1 are quite similar. Interestingly there are differences in the adsorption capacities of Zn(II) and Co(II) at low concentrations. This suggests that the separation of each of these metals from Ni(II) may be different. To further investigate the adsorption of each of these three metals at pH = 1 onto BP-ED and WP-ED the concentration dependant data were fitted to the theoretical Langmuir and empirical Freundlich models. The Langmuir adsorption model for the relationship between the concentration of a metal ion adsorbed onto a material and the concentration of a metal ion remaining in solution at equilibrium assumes that adsorption occurs as a monolayer on a homogenous surface without interactions between metal ions (23). The Langmuir model provides an estimate of the theoretical quantity of surface sites available for adsorption (Q_m) and the driving force for the adsorption process (b) for the coordination of a metal ion onto the chelating surface. The full derivation of the Langmuir equation can be found elsewhere (24). In the rearranged Langmuir equation:

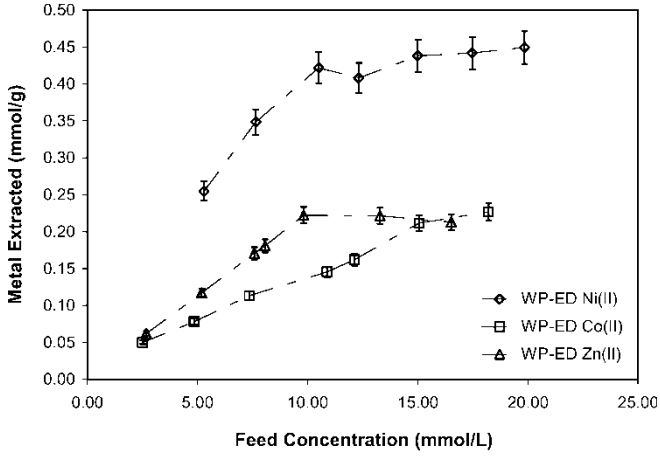
$$1/Q_e = 1/Q_m b C_e + 1/Q_m \quad (2)$$

C_e represents the concentration of metal ions in solution at equilibrium (mg/L) and Q_e is the concentration of metal ions adsorbed onto the composite (mg/g). Q_m can be calculated from the y intercept of the straight line for a plot of 1/Qe vs. 1/Ce. The constant b can be derived from the slope of the same straight line ($1/Q_m b C_e$) (23).

The Freundlich adsorption model is an empirically derived model that describes the relationship between the concentration of metal ions in solution at equilibrium (C_e) and the concentration of metal ions adsorbed onto the composite (Q_e) at low metal ion concentrations (23). The equation



(a)



(b)

Figure 6. Concentration dependent adsorption isotherms for Ni(II), Zn(II), and Co(II) onto (a) BP-ED and (b) WP-ED. pH = 1. Equilibration time: 48 hrs. 0.2 g of composite was challenged with 20 mL of feed solution.

is exponential in nature:

$$Q_e = AC_e^{1/n} \tag{3}$$

where the constant A is defined as the adsorption coefficient representing the quantity of metal adsorbed (mg/g) at unit equilibrium concentration. The value 1/n is a measure of the surface heterogeneity. Values of 1/n above

one indicate cooperative adsorption whereas a value below one indicates normal Langmuir (monolayer and non-cooperative) adsorption. A plot of log Q_e vs. log C_e allows the calculation of the parameters A and $1/n$ from the y intercept and slope of the linear regression respectively (23).

Table 2 summarizes the Langmuir and Freundlich constants for BP-ED and WP-ED for Ni(II), Zn(II) and Co(II). The applicability of these models can be determined by analysis of the R^2 values for the Langmuir and Freundlich plots seen in Figs. 7 and 8. It is evident that, although both the theoretical and empirical models adequately describe the adsorption of these divalent metals on both chelating materials, the Langmuir model better fits the data. The $1/n$ Freundlich parameter for all cases is between 0 and 1 confirming Langmuir type adsorption throughout. The Langmuir constant *b* describes the driving force for the adsorption process. It is evident that the order of intensity is: Ni(II) $\gg$ Zn(II), Co(II) for both chelating materials. This indicates a higher K_{MY} for the immobilized EDTA-Ni(II) complex supporting the possibility of the separation of Ni(II) from a mixture of the three with either composite. The maximum number of adsorption sites (Q_m) is greater for BP-ED for all three metals which is logical in light of the increased ligand loading and superior capacities. However, the Langmuir parameters indicate that WP-ED consistently has a greater affinity (*b*) for all three divalent metals at pH = 1. The increase in the Langmuir parameter *b* for WP-ED explains the small improvement in mass transfer kinetics for WP-ED demonstrated in the section titled "Adsorption pH Dependence". The increased adsorption parameters also explain the participation of a greater fraction of WP-ED ligands compared to BP-ED ligands in the adsorption of all metal ions studied.

Interestingly the Q_m value for Zn(II) is higher than for Ni(II) for both BP-ED and WP-ED ($\sim$40% for both composites). Q_m is a measure of the

Table 2. Adsorption model parameters of Ni(II), Zn(II), and Co(II) onto BP-ED and WP-ED. Solution pH = 1, equilibration time was 48hrs and sample to solution ratio was 1:10

	Langmuir			Freundlich		
Metal	Q_m (mg/g)	b (L/g)	R^2	A (mg/g)	1/n	R^2
BP-ED						
Ni(II)	30.96	12.2×10^{-3}	0.99	4.06	0.31	0.91
Zn(II)	44.05	1.2×10^{-3}	0.96	0.35	0.61	0.84
Co(II)	21.23	1.7×10^{-3}	0.98	0.10	0.74	0.99
WP-ED						
Ni(II)	26.39	87.0×10^{-3}	0.93	11.83	0.1	0.89
Zn(II)	38.31	1.3×10^{-3}	0.96	0.59	0.3	0.99
Co(II)	18.42	3.3×10^{-3}	0.98	0.12	0.7	0.81

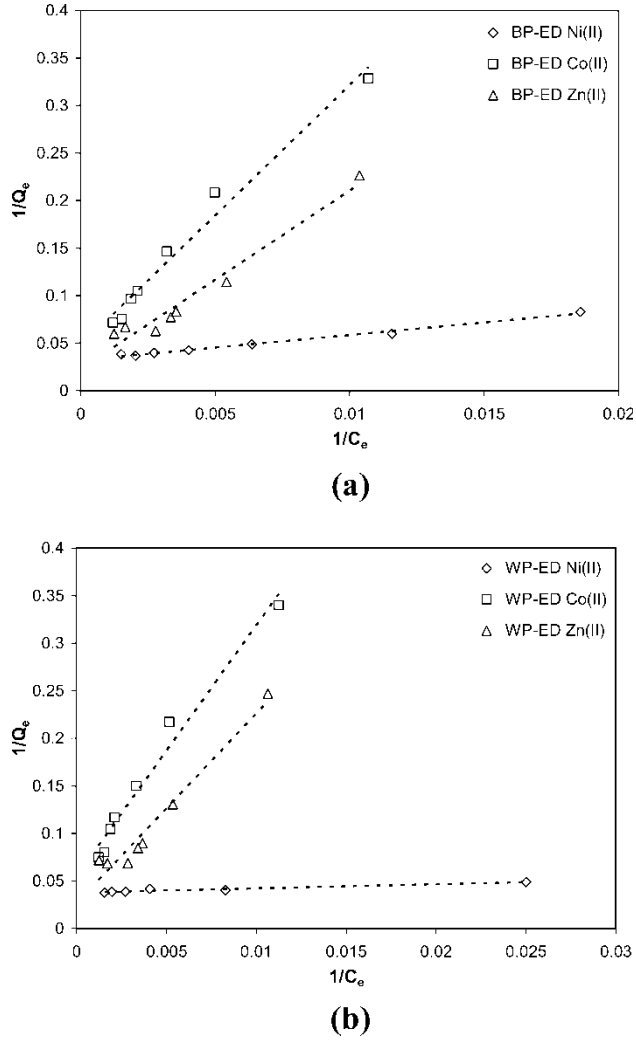


Figure 7. Langmuir plots for Ni(II), Zn(II), and Co(II) (a) BP-ED and (b) WP-ED.

maximum theoretical number of coordination sites available. This infers that the maximum possible metal uptake for Zn(II) should be higher than for Ni(II). However, Zn(II) capacities at pH = 1 are much lower than that for Ni(II). This can be explained by the smaller value of the Langmuir parameter *b* for Zn(II) (∼10 times smaller for BP-ED and ∼67 times smaller for WP-ED) in comparison to that for Ni(II). Therefore, the stability constants for Ni(II) coordination will be much larger than for Zn(II) coordination. Co(II) and Zn(II) as discussed above display similar adsorption characteristics, but the Langmuir parameters show differences in the nature of the adsorption of

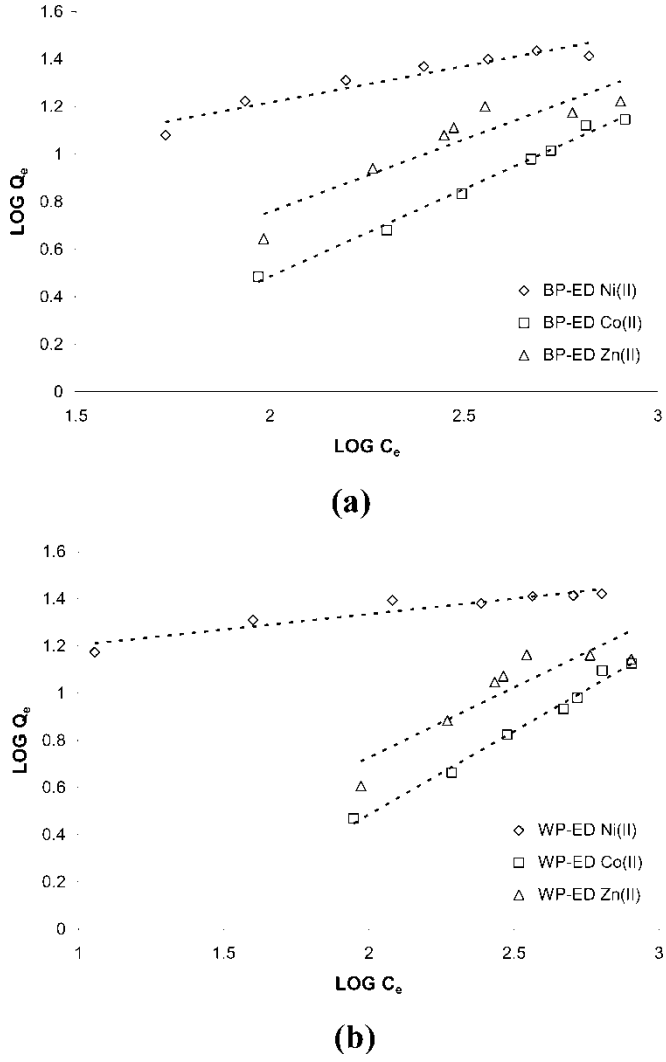


Figure 8. Freundlich plots for Ni(II), Zn(II), and Co(II) (a) BP-ED and (b) WP-ED.

these metals onto both BP-ED and WP-ED. Zn(II) has substantially more theoretical adsorption sites, although this is counterbalanced by higher values of *b* for Co(II), resulting in similar pH profiles for Co(II) and Zn(II).

Separation of Transition Metals

Results to this point clearly demonstrate the possibility of separating Ni(II) from Co(II) by a chromatographic column separation in which a column of

the BP-ED or WP-ED material is fed with a solution containing 1.0 g/L of both metals in a sulfate matrix at pH = 1. Figure 3(a) displays the breakthrough profiles of nickel and cobalt under the conditions described in detail in the experimental section of this paper. BP-ED was chosen for separation experiments because of its greater capacities when compared to WP-ED. It has been established that BP-ED has a preference for nickel over cobalt. Therefore, although the composite loads cobalt in the initial stages of the breakthrough the nickel displaces almost all of the cobalt by the conclusion of the experiment (Fig. 9(a)). This is in agreement with the information derived from the Langmuir plots and the K_{MY} values for the free EDTA-Ni(II) (4.2×10^{18}) and EDTA-Co(II) (2.0×10^{16}) complexes. The Co(II) concentration in the eluent quickly exceeds the cobalt concentration of the challenge solution then slowly decreases until it is almost at the feed concentration of 1.0 g/L. This is indicative of a metal that has an affinity for the ligand but cannot remain on the material due to the presence of a competing metal (Ni(II)) whose coordination has greater stability. The column color was initially pink but gradually turned to green as the cobalt is replaced with nickel. After 20 column volumes (100 mL) the purity of nickel on the column was ~97%. At this point the Co(II) eluent concentration had not yet decreased to the Co(II) concentration in the challenge solution and the Ni(II) concentration in the eluent had not increased to the concentration of Ni(II) in the challenge solution. Therefore increasing the length of the experiment to 25–30 column volumes (125–150 mL of challenge solution) would increase the purity of Ni(II) on the column (>99%). Figure 9(b) shows the strip profile for both nickel and cobalt. 100% stripping was achieved with strong acid (4.5 M H_2SO_4) at a flow rate of 0.5 mL/min resulting in an acidic strip solution of ~97% nickel purity. Of interest is a comparison of the flow rates used in these experiments (0.5 mL/min through a 5 mL column) with that reported in the literature for chitosan modified with EDTA anhydride for a Ni(II)/Co(II) separation (3.92 mL/hr through a 20–30 mL column) (19). The porous nature of the silica gel, the hydrophilicity of the polymer matrix and the fact that the chelating sites are on the surface and highly accessible conspire to allow BP-ED to effectively operate at 0.1 CV/min, whereas the gelatinous EDTA-chitosan system requires much slower flow rates.

Quite often industrial leach solutions containing high levels of nickel also contain high levels of trivalent iron as well as appreciable levels of copper, zinc and cobalt. Typically such solutions are passed over elemental iron to cement out the copper. This is an efficient and profitable process as copper cement is of reasonable value. As a consequence of the cementation process the iron is reduced to the ferrous form. In order to test the chelating ability of BP-ED to separate Fe(II), Zn(II) and Co(II) from Ni(II) in a solution containing these metal in ratios similar to those found in acid leaches, a solution containing 2 g/L Fe(II), 0.8 g/L Ni(II), 0.1 g/L Zn and 0.1 g/L Co(II) in a sulfate matrix at pH = 1 was prepared. This solution was fed to a 5cc column of

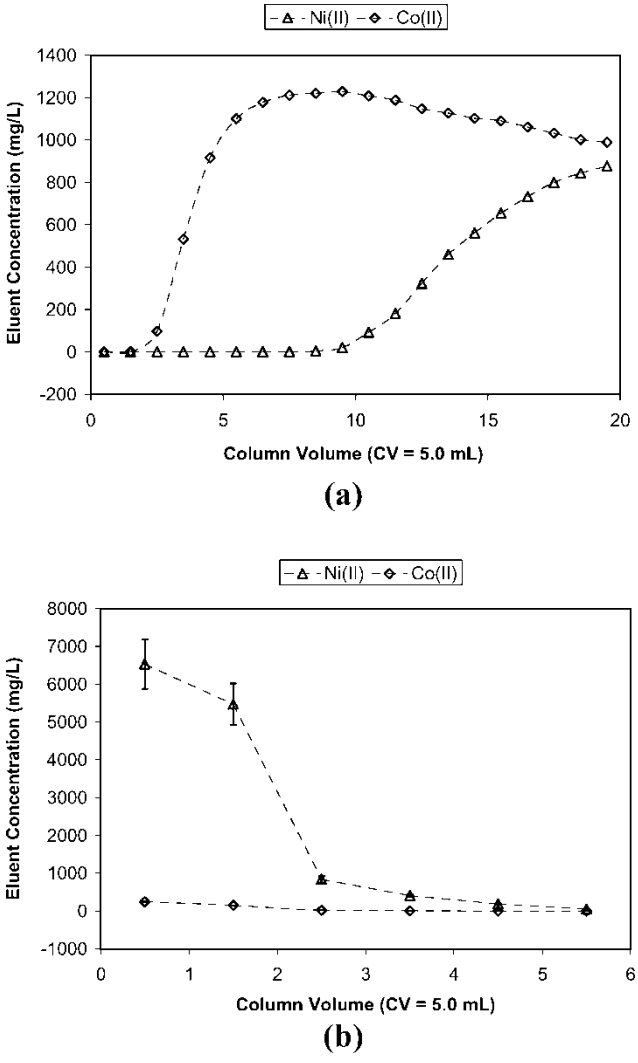


Figure 9. Ni(II)/Co(II) column separation using BP-ED. Column volume = 5 mL. Column mass = 2.8 g. Flow rate = 0.05 mL/min. pH = 1. Feed concentration of Ni(II) = 1 g/L. Feed concentration of Co(II) = 1 g/L, 100 mL. 4.5 M H_2SO_4 strip solution, 30 mL. (a) Eluent concentration upon feeding as a function of the volume of challenge solution passed through the column. (b) Eluent concentration upon stripping as a function of the volume of strip solution passed through the column.

BP-ED at 0.5 mL/min in order to selectively capture Ni(II) when multiple metal ions are present. A plot of the eluent metal concentrations (mg/L) as a function of column volume eluted is displayed in Fig. 10(a). Clearly the BP-ED column has only a slight affinity for Fe(II), Zn(II) and Co(II) relative

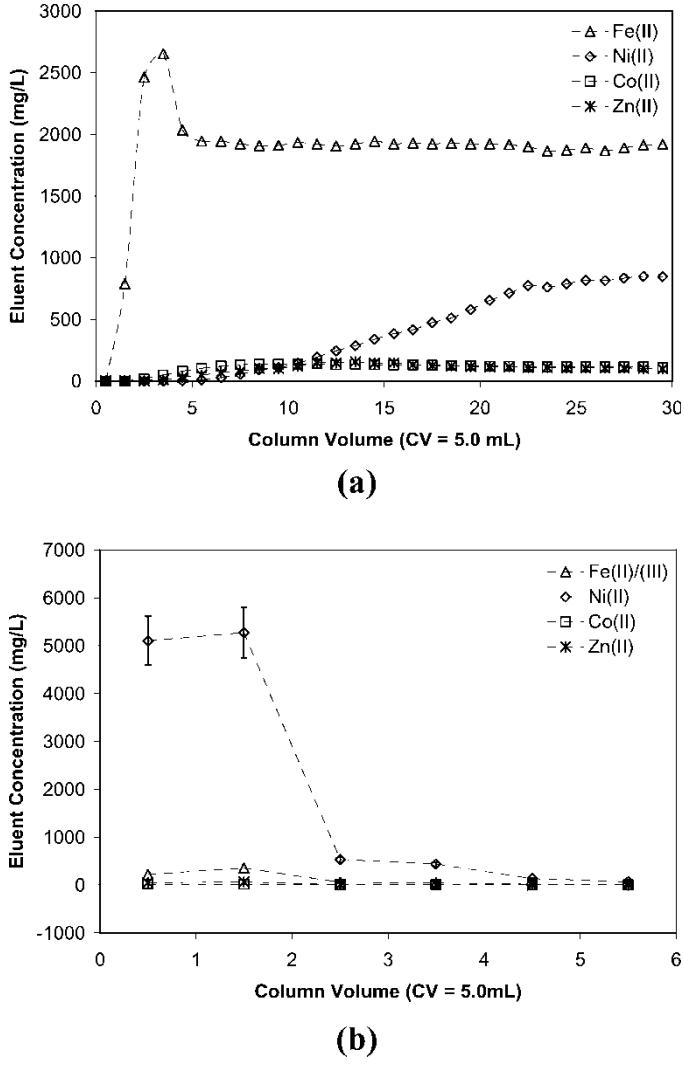


Figure 10. Ni(II)/Co(II) column separation using BP-ED. Column volume = 5 mL. Column mass = 2.8 g. Flow rate = 0.05 mL/min. pH = 1. Feed concentration of Ni(II) = 1 g/L. Feed concentration of Co(II) = 1 g/L, 100 mL. 4.5 M H_2SO_4 strip solution, 30 mL. (a) Eluent concentration upon feeding as a function of the volume of challenge solution passed through the column. (b) Eluent concentration upon stripping as a function of the volume of strip solution passed through the column.

to Ni(II) which is extracted selectively. The eluent concentrations of Fe(II), Zn(II) and Co(II) exceed the concentration of each metal ion in the feed solution as Ni(II) outcompetes all three metals. The eluent concentration of each then returns to the concentration of the challenge solution indicating

Table 3. Metal ion concentration (mmol/g) in 4.5 M H_2SO_4 strip solutions for 4 consecutive load strip cycles

Cycle	Fe(II)/(III) (mmol/g)	Zn(II) (mmol/g)	Co(II) (mmol/g)	Ni(II) (mmol/g)	Ni(II) Purity %	TOTAL (mmol/g)
1	0.025	0.0044	0.0012	0.39	92.8	0.42
2	0.034	0.0022	0.0010	0.37	90.8	0.41
3	0.038	0.0017	0.0011	0.37	90.2	0.41
4	0.043	0.0019	0.0009	0.37	89.1	0.42

that the separation is complete. However, as the extraction proceeds a small portion of composite turns to brown non-uniformly at the bottom of the column indicating oxidation of Fe(II) to Fe(III). Ferric iron is chelated readily by the BP-ED. The formation complex for an EDTA-Fe(III) complex (1.3×10^{25}) in solution is much greater than that of Ni(II) thus it should successfully compete for BP-ED adsorption sites. Figure 10(b) demonstrates the strip profile of BP-ED when the fully loaded column is fed 30 mL of 4.5 N H_2SO_4. The purity of nickel in the strip is greater than 90% (Table 3). The contaminant metal is iron most likely in the trivalent form as ferrous iron was easily pushed off of the column by Ni(II). Isolated oxidation is most likely due to imperfections in the frit material, non-uniform composite packing, or to surface catalyzed oxidation by adsorbed oxygen. This may allow air pockets to form in areas close to the inlet thus promoting the likelihood of oxidation in these locations. Repeating this multi-element experiment yielded similar results each of the four times (Table 3). The brown composite appears in a similar position in all four cycles reinforcing the conclusion that oxidation is caused by imperfections in the column rather than by the BP-ED material. Slurry packing, the use of a pulse-less pump, degassing of the challenge solution, re-engineering of the column, and the introduction of a reducing agent into the challenge solution are options for alleviating the problem of oxidation. In this way Ni(II) purity should approach 99.9%.

CONCLUSIONS

Adsorption and separation of divalent and trivalent metal ions by EDTA immobilized on silica polyamine composites BP-1 and WP-1 was investigated and the following conclusions were drawn:

1. Silica polyamine composites prepared using PAA and PEI can be reacted with EDTA anhydride to produce a pentadentate ligand attached to the surface by an acetamide functional group. In comparison, ligand loading was greatest for the linear all primary amine PAA most likely due to the presence of secondary and tertiary amines in PEI

2. The resulting composites have the ability to extract several divalent and trivalent metals down to very low levels and have a particular affinity for Fe(III), Ga(III), Cu(II), and Ni(II). In contrast to Silica-ED, metal ion capacities increase with increasing pH for BP-ED and WP-ED. This must be a consequence of the polyamine which removes the ligand far enough from the silica surface so that electrostatic interactions are negligible.
3. The differences between BP-ED and WP-ED include greater ligand loading for the former but when concentration dependent capacity data is fitted to the Langmuir model for monolayer adsorption WP-ED has larger *b* parameters for Ni(II), Zn(II), and Co(II) which explains the similarity in their adsorption capacities of the two different composites.
4. BP-ED can be used to separate Ni(II) from Fe(II), Co(II), and Zn(II) other transition metals when Cu(II) is not present yielding solutions of high Ni(II) purity. Higher flow rates are possible with BP-ED than that reported in the literature for other EDTA modified materials (18–20). Although the oxidation of ferrous iron to ferric is a concern, this may be eliminated by use of a superior column, the introduction of a reducing agent, or degassing the water medium.

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