

Metal Coordination and Selectivity with Oxine Ligands Bound to Silica Polyamine Composites

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ABSTRACT: A series of oxine ligands, 5-X, 8-OH-C₉H₆N (X = H, Cl, SO₃H) have been covalently bound to a silica gel polyamine composite made from a silanized amorphous silica xerogel and poly(allylamine) (BP-1) by the Mannich reaction. The resulting modified composites WP-4(X = H), CB-1(X = Cl), and SB-1(X = SO₃H) were characterized by elemental analysis, FTIR, and solid state CPMAS-¹³C-NMR. Using the analytical data before and after the ligand modification, the ligand loading could be estimated and in combination with metal ion capacities a metal to ligand ratio could be obtained. The composites WP-4 and CB-1 both showed ratios of approximately 1 : 1 while the sulfonate modified composite, SB-1, showed a metal to ligand ratio of 1 : 2. This is tentatively interpreted in terms of a zwitterionic oxine as the dominant species at pH = 2 where the sulfonic acid group is

ionized, the quinoline nitrogen is protonated and where two sulfonate groups on adjacent oxines bind a trivalent or divalent ion. All the modified composites show a clear selectivity for trivalent over divalent ions and a good selectivity for gallium over aluminum. The substituent groups on the oxine ligand have only a minor influence on these selectivity trends but SB-1 shows slightly better capture kinetics. The selectivity for gallium over aluminum is applied to the separation of gallium from aluminum, ferrous, and zinc in an acid ore leach of solid tailings obtained from a zinc mine using WP-4. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2855–2864, 2010

Key words: polyamines; composite materials; functionalization of polymers; selectivity; ion exchangers

INTRODUCTION

The consequences of increasing metal concentrations in surface and subsurface aqueous environments as a result of mining are not easy to anticipate due to the broad range of biogeochemical conditions and biological pathways in organisms.¹ To address this environmental problem, silica polyamine composites (SPCs) have been developed as one among many remediation technologies including organic polymer chelator resins and surface silanized silica gels.^{2–4} The SPCs combine the better capture kinetics and matrix rigidity of the surface modified silica gels with higher loading capacities of the polymer-based chelator resins. SPCs are composed of a silica gel support covalently bonded to linear or branched water soluble chelating polyamines.^{5–12} The SPCs are

synthesized via the following steps: acid washing of the silica gel surface, humidification, silanization with a mixture of methyltrichlorosilane (MTCS) and chloropropyltrichlorosilane (CPTCS), and finally addition of a polyamine and a modifying ligand (Fig. 1).⁵ SPCs show no shrinking or swelling, they withstand operating temperatures of up to 110°C, and have anticipated stability to radiolytic decomposition. They also exhibit long usable lifetimes due to their rigid macrostructure and the multipoint anchoring of the polymer.⁶ Previous studies on SPCs revealed that the usage of MTCS and CPTCS in a 7.5 : 1 ratio on modified silica gel gave improvements in metal ion capacities and mass transfer kinetics under low-pH aqueous extraction conditions.⁷ The improved metal selectivity capacity for a particular metal atom is thought to be caused by the greater availability of coordinating sites.⁷

The oxine ligand (8-hydroxy quinoline) has long been known to be a versatile functional group for complexing transition metal ions and in particular trivalent ions. The solvent extraction ligand, Kelex 100, is an alkyl modified oxine that has found extensive use in solvent extraction, particularly for the recovery of gallium from Bayer solutions produced in the aluminum refining industry.¹³ Several groups have reported the impregnation of Kelex 100 into polystyrene resins.¹⁴ Covalent binding of the oxine

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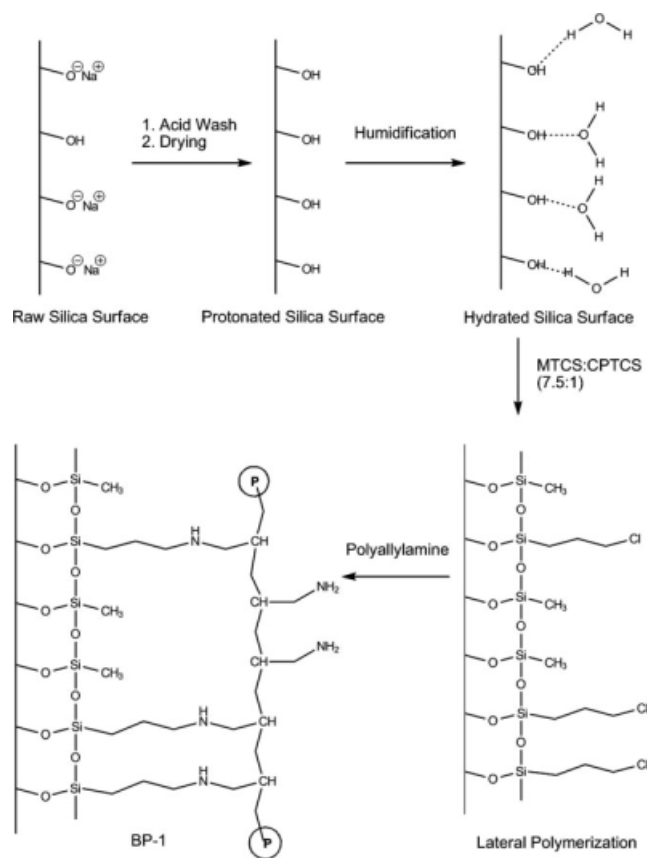


Figure 1 Scheme for synthesis of silica polyamine composites BP-1.

ligand to water soluble polymers,¹⁵ as well as polystyrene resins via azo linkages,¹⁶ Friedel-Crafts chemistry¹⁷ or copolymerization with resorcinol¹⁸ has been reported. Covalent bonding to aminopropyl functionalized silica gels via the diazotization method^{19,20} and the Mannich reaction^{21,22} has also been reported. Although some of these materials showed promise for sequestering metal ions in general, they had significant problems with mass transfer kinetics (organic polymers) or low capacities (silica gels). Furthermore, the selectivity of these oxine modified solid phase adsorbents for various metals was not well defined in previous work. Taking advantage of the hybrid properties of SPCs (*vide supra*), we have undertaken a study of covalent binding of a range of oxine ligands to this versatile surface using the Mannich reaction.

We report here the synthesis and characterization of SPC materials WP-4, SB-1, and CB-1 prepared by reaction of the immobilized polymer amine groups in the PAA containing composite BP-1 with 8-hydroxy quinoline, 5-sulfonic acid-8-hydroxy quinoline, and 5-chloro-8-hydroxy quinoline respectively, using the Mannich reaction (Fig. 2). The goal of this study was to understand how substitution affects transition metal selectivity, mass transfer kinetics,

and coordination mode of the oxine ligand bound to the SPC surface. We also exploit the observed selectivity for trivalent over divalent transition metals of WP-4 for recovery of gallium from a leach solution of zinc mine tailings containing aluminum, ferrous, and zinc and for the dynamic separation of nickel from ferric ion.

EXPERIMENTAL SECTION

Materials

Silica gel (267 Å average pore diameter, 2.82 mL/g pore volume, 84.7% porosity, 422 m²/g surface area) was obtained from INEOS Enterprises Ltd., UK, or Qing Dao-Meigao, China, and sieved to 150–250 microns. All chemicals were reagent grade and purchased from Sigma-Aldrich Co. and EMD Chemicals Inc. Stock solutions of Al(III), Ga(III), Fe(III), Ni(II), and Cu(II) were prepared using aluminum sulfate hydrate (Al₂(SO₄)₃·xH₂O), gallium nitrate hydrate (Ga(NO₃)₃·xH₂O), ferric sulfate hydrate (Fe₂(SO₄)₃·xH₂O), nickel sulfate hexahydrate (NiSO₄·6H₂O), and cupric sulfate pentahydrate (CuSO₄·5H₂O), respectively. Solution pH was adjusted from the intrinsic pH, where necessary, using sulfuric acid and sodium hydroxide. Metal Standards for AA analysis were obtained from Sigma-Aldrich and Fisher Scientific Co.

METHODS

Infrared characterization of modified composites was carried out with a Thermo Nicolet Nexus 670 wFT-IR spectrophotometer as KBr pellets. Solid state ¹³C CPMAS spectra were obtained on a Varian NMR Systems 500 MHz spectrometer at 125 MHz with a spinning speed of 15 KHz. ¹³C chemical shifts are reported relative to external tetramethyl silane. Elemental analyses (carbon, hydrogen, nitrogen, chloride, sulfur) were conducted by Schwarzkopf Micro-analytical Laboratory, Woodside, NY and Galbraith Laboratories Inc., Knoxville, TN.

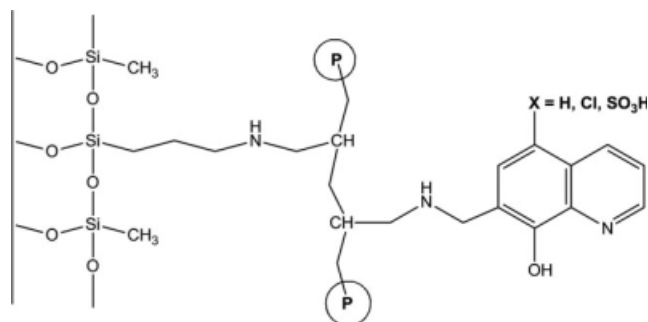


Figure 2 Schematic of the covalent binding of 8-hydroxy quinoline to BP-1.

Batch capacity experiments were conducted in 20 mL vials and agitated on a Precision Scientific 360 shaker bath (Precision Scientific, Inc., Chicago, IL). Dynamic experiments were conducted with a borosilicate glass column (Ominfit[®] Bio-Chem Valve Inc.). The column was then slurry packed and the challenge solution was fed by a variable-flow FMI Lab Pump model QG150 (Fluid Metering Inc., Syosset, NY). Metal concentrations were determined via a flame atomic absorption (FAA) method using a S2 FAA Spectrometer from SOLAAR. The samples that were above the calibration range of the FAA were diluted using a solution mixture of 2%/2% – HNO₃/KCl. A nitrous oxide/acetylene flame was used to analyze aluminum and gallium. The dilutions for FAA and AES were done in triplicate and standards were analyzed after every 10 samples. The standards for aluminum, gallium, iron, nickel, copper, calcium, magnesium, and manganese were obtained from Fisher Scientific Co. Error bars are included where the error is deemed significant relative to the absolute measurement. The starting composite BP-1 was synthesized by previously published procedures.^{5,7,8}

Characterization of the synthesized composites was achieved by elemental analysis, KBr infrared pellet and ¹³C CPMAS solid state NMR. These data confirm the presence of the desired functional groups and allow an estimate of the degree of conversion from the starting amine functionalities.

Synthesis of BP-1-8-hydroxyquinoline (WP-4) via Mannich reaction¹¹

Ten grams of BP-1 was mixed with a reagent solution of 50 mL aqueous formaldehyde (38.0%) and 1 mL glacial acetic acid (17.4M) in a 250 mL flask. The suspension was stirred for 1 h at room temperature and filtered. The composite was then washed with 100 mL of ethanol and filtered. The aforementioned procedure was repeated three times. Ten grams of 8-hydroxyquinoline (98%) and 100 mL of methanol were added and stirred for 24 h at 60°C. In addition, the solution was adjusted to pH 9 by adding tetramethyl ammonium hydroxide (25 wt % solution in methanol) dropwise. After the completion of the aforementioned step, the composite was washed one time with methanol, one time with 1M NH₄OH, three times with distilled water, three times with 2M H₂SO₄, three times with distilled water, two times with acetone and dried at 70°C. Mass gain of WP-4 was 38%.

Elemental Analyses: BP-1: 10.05% C, 2.09% H, 2.43% N

WP-4: 20.47% C, 2.57% H, 3.22% N

IR spectra (KBr pellet) for WP-4: 3433(m) (νN–H), 2959–2838 (m) (νC–H, aliphatic), 1733(w) (aromatics),

1636(m) (νN–C), 1458(m) (νSi–CH₂), 1377(m) (νSi–CH₃), 1105(s) (νSi–O), 801(m) (νN–H) cm⁻¹

¹³C-NMR (CPMAS, δ) for WP-4: –6.09 (Si–CH₃), 8.47 (Si–CH₂), 29.16 (CH₂ polyamine), 47.80 (NH–CH₂), 118.71–143.48 (aromatic)

Synthesis of 5-chloro-8-hydroxyquinoline (CB-1) and 5-sulfonic acid-8-hydroxyquinoline, (SB-1) via Mannich reaction¹⁰

BP-1 (10 g) was mixed with a reagent solution of 50 mL aqueous formaldehyde (38.0%) and 1 mL glacial acetic acid (17.4M) in a 250-mL flask. The suspension was stirred for 1 h at room temperature and filtered. The composite was then washed with 100 mL of ethanol and filtered. The aforementioned procedure was repeated three times. Five grams of 5-Chloro-8-Hydroxyquinoline (95%) or 5 g of 8-Hydroxyquinoline-5-Sulfonic acid (98%) and 200 mL of ethanol were added and stirred for 24 h at 70°C. In addition, the solution was adjusted to pH 9 by adding tetramethyl ammonium hydroxide (25% wt solution in methanol) dropwise. After the completion of the aforementioned step, the composite was washed once with ethanol (pH 9), once with 1M NH₄OH, three times with distilled water, three times with 2M H₂SO₄, three times with distilled water, two times with acetone, and dried at 70°C. The mass gain for CB-1 and SB-1 were 10.5 and 17.5%, respectively.

Elemental Analyses: BP-1: 11.91% C, 2.45% H, 2.42% N, 0.64 % Cl

CB-1: 17.51% C, 2.24% H, 2.85% N, 2.54% Cl

SB-1: 15.48% C, 2.21% H, 2.52% N, 2.90% S

IR spectra (KBr pellet) for CB-1: 3437(m) (νN–H), 2960–2838 (m) (νC–H, aliphatic), 1733(w) (aromatics), 1636(m) (νN–C), 1458(m) (νSi–CH₂), 1383(m) (νSi–CH₃), 1108(s) (νSi–O), 807(m) (νN–H) cm⁻¹

¹³C-NMR (CPMAS, δ) for CB-1: –6.35 (Si–CH₃), 7.82 (Si–CH₂), 16.37 (CH₂ aliphatic), 28.70 (CH₂ polyamine), 117.19–146.14 (aromatic)

IR spectra (KBr pellet) for SB-1: 3437(m) (νN–H), 2960–2838 (m) (νC–H, aliphatic), 1733(w) (aromatics), 1647(m) (νN–C), 1457(m) (νSi–CH₂), 1383(m) (νSi–CH₃), 1108(s) (νSi–O), 799(m) (νN–H) cm⁻¹

¹³C-NMR (CPMAS, δ) for SB-1: –6. (Si–CH₃), 8.27 (Si–CH₂), 17.23 (CH₂ aliphatic), 32.36 (CH₂ polyamine), 123.86–151.54 (aromatic)

Concentration dependent isotherms

The Langmuir adsorption model was applied to ferric binding on WP-4. Isotherms were obtained using batch experiments as described in the experimental section. Ferric binding was investigated at pH 2. Each sample was shaken for 48 h to ensure complete

equilibration. Langmuir parameters were obtained from the appropriate linear regressions for Fe(III).

Kinetic study

Kinetics studies were performed on the composites: WP-4, SB-1, and CB-1. To three separate vials, 0.1 g of each composite was added. Ten milliliters of a 1.5 g/L Iron (III) solution at pH 2 was then added to each vial. The tests were performed for a 24 h period and the samples were removed from the shaker at 10, 20, 30, 60 min and 2, 4, 6, 12, 24 h. After the samples were removed from the shaker, a small aliquot (20 μ L) of the solution was extracted and diluted in a solution mixture of 2%/2% – HNO₃/KCl. Fe(III) concentration at each time interval was determined with FAA/AES and plotted over time.

Column breakthrough testing

The iron (III) and nickel (II) breakthrough experiment and subsequent stripping were carried out by packing a 5 cc column with WP-4 (2.5 g). A frit was attached at both ends of the column and challenge solutions were run through the column using a variable-flow pump. The flow rate was held constant at 0.5 column volume/min. The column was conditioned as follows: 10 mL water, 15 mL pH 1.5 water adjusted with H₂SO₄. One hundred milliliters of challenge solution (1.25 g/L of Fe and 0.4 g/L of Ni at pH 1.5) was ran through the column. The same column was rinsed with 10 mL pH 1.5 water, eluted with 25 mL 2M H₂SO₄, and finally rinsed with 10 mL of water. The rinse water used in all the aforementioned cases was deionized water. Eluent fractions were collected in 10 mL aliquots beginning with the first 10 mL of challenge solutions. The fractions were preserved with 2% HNO₃ and analyzed by FAA and/or AES.

The breakthrough capacity (BC, the total mole quantity of metal ion adsorbed by each gram of composite under flow conditions) was calculated according to

$$BC = [(C_o V_F) - (C_f V_{FR})]/m_c \quad (1)$$

where C_o (mM) represents the initial metal ion concentration of the feed solution, and V_F (L) is the volume of metal ion feed solution fed through the column. C_f (mM) is the total metal ion concentration in the eluent, which includes the eluent from the treated metal ion feed solution and the subsequent water rinse. V_{FR} (L) is the volume of the feed and rinse solutions combined. m_c (g) is the mass of silica polyamine composite packed into the column. V_C , the volume of the SPC in the column (mL), can be substituted for m_c in eq. (1) to obtain a value for BC in the units of mmol/mL.

Recovery of gallium from zinc mine tailings

Experimental testing of the WP-4 for gallium recovery in the presence of aluminum, excess zinc and ferrous ion was done with a sample of solid zinc tailings provided by Pasminco Zinc, Clarksville, TN. The ore was leached using the oxidized pressure leach reported by Anderson et al.²³ The solution produced contained the metal concentrations shown in Table V. Before separation, the solution was treated with zinc dust to ensure that all of the iron was present as ferrous and the concentration of zinc in Table V includes zinc dissolved during this pretreatment. The separation was performed in a 25 mL column containing 18.6 grams of WP-4 at a flow rate of 0.2 column volumes per minute. The columns were stripped and collected using 25 mL of 4M sulfuric acid.

RESULTS AND DISCUSSION

Characterization of WP-4, CB-1 and SB-1

The three new polyamine composites reported here WP-4, containing the 8-hydroxy quinoline functional group, CB-1, containing the 5-chloro, 8-hydroxy quinoline functional group, and SB-1 containing the 5-sulfonic acid, 8-hydroxy quinoline functional group were all synthesized by a two step Mannich reaction modified from the literature procedure used for aminopropyl silanized silica gel.²¹ Methanol was used in the synthesis of WP-4 because it is more soluble in this solvent than in ethanol. The reactions for making CB-1 and SB-1 were done in the slightly higher boiling solvent ethanol because they are expected to be less reactive than the unsubstituted 8-hydroxy quinoline.

Solid state NMR data are consistent with the proposed composite formulations WP-4, SB-1, and CB-1. All three composites show the expected aromatic resonances in the range of 128–143 ppm as well as the aliphatic resonances associated with the PAA and the silane anchors. The methyl resonance for the methyl silanized sites is observed at –6.0 ppm for all three composites. The solid state NMR cannot specify the position of attachment of the polymer to the quinoline ring but previous work on related systems using the same synthetic pathway specified the 7' position.^{21,22} Elemental analyses of WP-4, SB-1, and CB-1 show higher carbon and nitrogen content in all the composites. The higher carbon and nitrogen content indicates successful modification of amines with 8-Hydroxyquinoline, 8-Hydroxyquinoline-5-Sulfonic acid, and 5-Chloro-8-Hydroxyquinoline ligands. In Table I, the percentage composition data was converted to mmol/g. On the basis of the chlorine and sulfur analyses, CB-1 has a ligand

TABLE I
Elemental Analysis Data and Ligand Loading for BP-1, SB-1, and CB-1. Error in elemental analysis is $\pm 0.3\%$.

	C (mmol/g)	H (mmol/g)	N (mmol/g)	Cl (mmol/g)	S (mmol/g)
BP-1	9.92	24.31	1.73	0.18	–
SB-1	12.89	21.92	1.80	–	0.90
CB-1	14.58	22.22	2.03	0.72	–

loading of 0.54 mmol/g and SB-1 has a ligand loading of 0.90 mmol/g. A different sample of BP-1, made from a different commercial silica gel, was used to prepare WP-4 and the ligand loading can be estimated by calculating the difference in nitrogen content, before and after reaction, taking into account the observed mass gain, thereby giving a value of 0.54 mmol/g (Table II). In the specific case of SB-1, it is possible that any amines not modified by the formaldehyde could react with the sulfonic acid group to give a sulfonamide. However, it should be pointed out that the reaction with the 5-sulfonic acid-8-hydroxyquinoline takes place under basic conditions where the quinoline ring has a -2 charge, not a situation conducive to attack by a nucleophile. Also the known efficiency of the formaldehyde step and the high degree of ligand loading are inconsistent with a predominant reaction at unmodified amines after the formaldehyde addition.^{21,22}

pH profile for WP-4

Equilibrium batch tests were performed to evaluate the capacity of WP-4 for adsorption of iron (III) in the pH range of 0–2 based on the observed selectivity of the 8-hydroxy quinoline for trivalent over divalent ions (*vide infra*). Solutions (10 mL) containing 1.5 g/L of ferric iron were shaken with 0.1 g of the composite for 24 h. The batch capacities for ferric iron are shown in Table III. Maximum ferric iron capacity occurs at pH 2 while the minimum ferric iron capacity occurs at pH 0. Above pH = 2 ferric precipitation becomes a problem. An interesting point to note is the adsorption of Fe (III) ions to the 8-hydroxyquinoline ligand of WP-4 (0.16 mmol/g) at pH 0. The phenol and quinoline nitrogen in 8-hydroxy quinoline have pKa values of 9.70 and

4.9, respectively,²⁴ while the corresponding values for the immobilized oxine ligand on amino propyl silica gels are 9.2 and 2.9.²² Therefore at pH 0, the phenol and quinoline nitrogen will be protonated. The significant adsorption of Fe (III) ions at pH 0 indicates that the 8-hydroxyquinoline ligand displays binding affinity for Fe (III) ions even under fairly acidic conditions.

Equilibrium batch tests for WP-4, SB-1, and CB-1 on mixed metal solutions

Previous reports on the metal adsorption properties of covalently immobilized oxine ligands focused primarily on the divalent transition metal ions.^{13–20} Therefore, equilibrium batch tests were performed to evaluate the selectivity of WP-4, SB-1, and CB-1 for divalent versus trivalent cations. Solutions (10 mL) containing two different cations were shaken with 0.1 g of a composite for 24 h at pH 2. Solutions containing 2 g/L each of Cu (II) and Fe (III) were evaluated first. Cu (II) and Fe(III) ions co-loaded on all the composites. WP-4, SB-1, and CB-1 loaded a total of 0.46, 0.44, 0.58 mmol of Cu (II) and Fe (III) ions per gram of composite, respectively (Table IV). Selectivity factors for Fe (III) over Cu (II) were 2.8, 2.6, and 4.3 for WP-4, SB-1, CB-1, respectively.

In another batch test with 2 g/L of Al(III) and Ga(III) at pH 2.3, selectivity of the composites toward chemically similar trivalent ions were determined. Analogous to the Cu(II) and Fe(III) batch, co-loading of Al(III) and Ga(III) ions occurred. WP-4, SB-1, and CB-1 loaded a total of 0.48, 0.58, 0.47 mmol of Al(III) and Ga(III) ions per gram of composite, respectively. Selectivity factors for Ga(III) over Al(III) ions for WP-4, SB-1, and CB-1 were 8.6, 1.8, and 2.3 respectively (Table IV). WP-4 showed a much higher selectivity for Ga(III) over Al(III) than

TABLE II
Elemental Analysis Data and Ligand Loading for BP-1 and WP-4

	C (mmol/g)	H (mmol/g)	N (mmol/g)
BP-1	8.37	20.73	1.73
WP-4	17.04	25.50	2.30

Error in elemental analysis is $\pm 0.3\%$.

TABLE III
Iron (III) Batch Capacities at Various pH for WP-4

pH	Fe(III) capacity- mg/g (mmol/g)
0.0	9.1 \pm 0.0 (0.16)
0.5	17.0 \pm 0.1 (0.30)
1.0	21.9 \pm 0.2 (0.39)
1.5	23.7 \pm 0.1 (0.42)
2.0	25.9 \pm 0.2 (0.46)

TABLE IV
Mixed Metal Batch Tests, Selectivity Ratios and Metal to Ligand Ratios WP-4, SB-1, CB-1

SPC	pH	Capacity-mg/g (mmol/g)		Selectivity factor	Metal to ligand ratio		
		Cu(II)	Fe(III)		Cu(II)	Fe(III)	
2 g/L of Cu(II) and Fe(III)	2	WP-4	7.6 ± 0.1(0.12)	19.0 ± 0.1(0.34)	2.8	0.22	0.62
		SB-1	8.0 ± 0.1(0.13)	17.4 ± 0.2(0.31)	2.4	0.14	0.34
		CB-1	6.9 ± 0.1(0.11)	26.1 ± 0.2(0.47)	4.3	0.20	0.87
2 g/L of Al(III) and Ga(III)	2.3	WP-4	1.4 ± 0.0(0.05)	30.3 ± 0.3(0.43)	8.6	0.10	0.79
		SB-1	5.8 ± 0.2(0.21)	26.0 ± 0.3(0.37)	1.8	0.23	0.41
		CB-1	3.8 ± 0.0(0.14)	23.0 ± 0.4(0.33)	2.3	0.26	0.61
1 g/L of Ni(II) and Fe(III)	2	WP-4	0.5 ± 0.0(0.01)	25.3 ± 0.2(0.45)	45	0.02	0.83
		SB-1	0.3 ± 0.0(0.01)	20.1 ± 0.2(0.36)	36	0.01	0.40
		CB-1	0.4 ± 0.0(0.01)	25.4 ± 0.2(0.45)	45	0.02	0.83

the other two composites. The selectivity for Ga (III) over Al (III) displayed by WP-4 can be explained by a larger ionic radius for Ga (III) (76 p.m.) than Al (III) ions (67.5 p.m.).

The last batch test was conducted at pH 2 consisting 1 g/L Ni (II) and Fe (III). All the composites were selective for Fe (III) over Ni (II) ions. WP-4, SB-1, and CB-1 displayed selectivity factors of 45, 36, and 45 for Fe (III) over Ni (II) ions, respectively. The sum of Fe (III) and Ni (II) ions to ligand ratio for WP-4, SB-1, and CB-1 are 0.85, 0.41, and 0.85 respectively. As expected from the Irving-Williams series copper has a much stronger binding constant for most nitrogen containing ligands than nickel leading to the higher selectivity factors for the trivalent ferric ion.²⁵

Using the estimates of ligand loading obtained from elemental analyses and the total metal loadings for the three mixed solutions in Table IV, we are able to get metal to ligand ratios to gain some insight into the coordination mode of the various metal ions tested. In the case of WP-4 and CB-1, the combined metal to ligand ratios are in the range 0.84–1.07 suggesting that each metal atom is bound to one ligand (Table IV). The metal ions would likely be in an octahedral environment with the oxine ligand occupying two *cis*-sites, and the remaining coordination sites being taken up by water or the anions present in the solution depending on the metal salt used in the batch experiments (Fig. 3). One possible exception would be copper, which likes to adopt a square planar structure and would have only two ligands *trans*- to the oxine nitrogen and oxygen. Most interestingly, the metal to ligand ratios for SB-1 are in the range of 0.41–0.64 suggesting that two oxine ligands are bound to each metal ion. Considering that the relative pK_a values for the sulfonic acid group and the quinoline nitrogen are 1.6 and 4.9, respectively, it seems reasonable to propose that at pH = 2 the quinoline nitrogen would be

fully protonated and the sulfonic acid group would be mostly in the anionic form. In the case of the neutral CB-1 and WP-4, the binding constants for the metals are competitive with N-protonation (in part due to the chelate effect). However, in the case of SB-1, metal adsorption could take place via simple electrostatic interaction with two neighboring anionic sulfonate groups (Fig. 3). It is expected that there would be more sites on SB-1 with neighboring

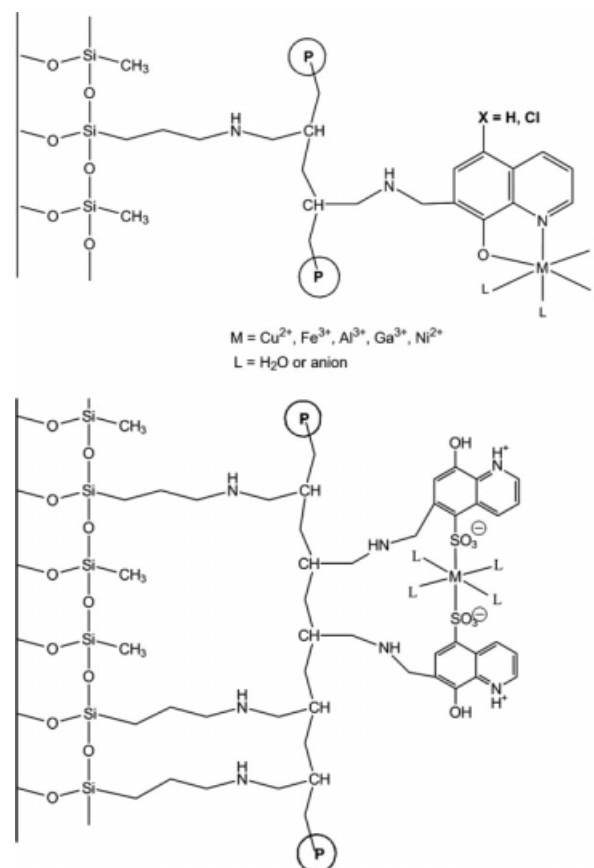


Figure 3 Mode of metal coordination to (a) WP-4 and CB-1; (b) Mode of metal coordination in SB-1.

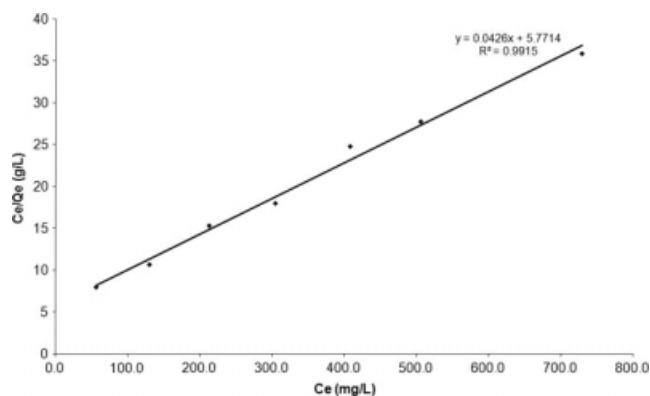


Figure 4 Fe(III) Langmuir plot for WP-4 at pH 2.

oxine ligands based on the higher ligand loading for this composite relative to CB-1 and WP-4 (0.90 versus 0.54 mmol/g). Thus, in the case of SB-1 the anionic sulfonate group interferes with ligand binding rather than enhancing the rate of adsorption as has been previously reported for sulfonic acid groups on polystyrene resins with phosphonic based co-ligands.²⁶

Langmuir adsorption isotherms

The Langmuir sorption model determines the relationship between the concentrations of surface adsorbed species to the number of active sites on that surface at equilibrium. If an adsorption process follows this model then it can be concluded that adsorption takes place as a monolayer on a homogeneous surface without interactions between the adsorbed species. The rearranged linear version of the Langmuir equation is shown in eq. (2).

$$C_e/Q_e = C_e/Q_m + 1/Q_m K_{ads} \quad (2)$$

where C_e represents the concentration of metal ions in solution at equilibrium (mg/L), Q_e is the concentration of metal ions adsorbed onto the composite (mg/L), Q_m is the measure of the maximum capacity of the adsorbent (mg/g) and K_{ads} is the intensity of adsorption (L/g).

Q_m can be calculated from the slope of the straight line plot of C_e/Q_e vs C_e . The constant K_{ads} can be derived from the slope and the intercept of the same straight line ($1/Q_m K_{ads}$). If the plot of eq. (2) is linear then Q_m provides an estimate of the active sites and K_{ads} gives an estimate of the driving force or the equilibrium constant for the process.

The Langmuir concentration dependent isotherm for ferric iron on WP-4 at pH 2 is reported in Figure 4. The Langmuir model fits the sorption of ferric iron by WP-4 very well, $R^2 = 0.9915$. In addition, the model provides information regarding the intensity

of the sorption process (K_{ads}) as well as an approximation of the theoretical number of sorption sites on the surface (Q_m). The value of K_{ads} for WP-4 is 0.007 L/g and the value of Q_m is 24 mg/g at pH 2. The values of K_{ads} and Q_m values reported here are similar to the values obtained for cation binding by similar silica polyamine composites ($K_{ads} = 0.012$ L/g and $Q_m = 21\text{--}44$ mg/g for Ni^{2+} cations with an EDTA ligand on silica polyamine composite).¹⁰

Kinetic study

In an attempt to gain a better understanding of the impact of the substituent groups on the kinetics of adsorption in SB-1 and CB-1 versus WP-1 their adsorption of Fe (III) was monitored with time. The adsorption profiles reveal that maximum loading of all three composites is reached within 2 h [Fig. 5(a)]. Within first 25 min, SB-1 and CB-1 showed a slightly faster rate of adsorption of Fe (III) ions than WP-4 [Fig. 5(b)]. Thus the substitution of sulfonate or chloride has little influence on the rate of adsorption even though the mode of binding of the metal ions in SB-1 is quite different than the other two composites. Overall, the time to reach full loading of metal ion for these composites is very similar to that observed for composites containing more lipophilic

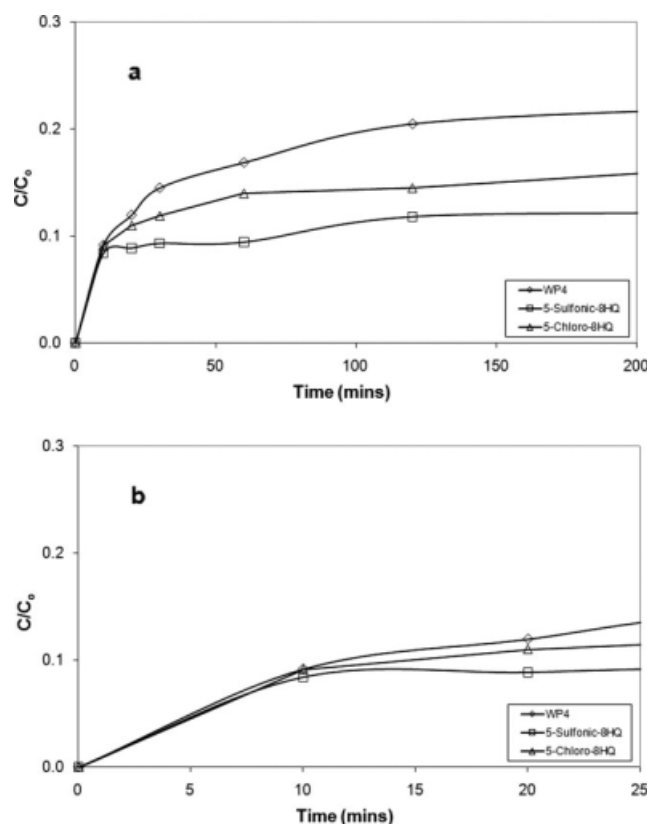


Figure 5 Mass transfer kinetics graph of WP-4, CB-1 and SB-1: (a) $t = 0$ to 200 min and (b) $t = 0$ to 20 min.

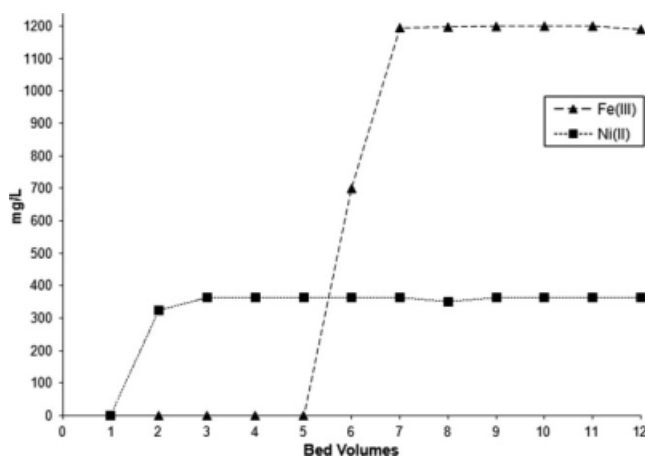


Figure 6 Ni(II) and Fe(III) breakthrough for WP-4.

modifying ligands.²⁷ This demonstrates that even with the rather large hydrophobic oxine ligands on the surface of the composite the rapid mass transfer kinetics associated with these materials is not significantly affected.

Breakthrough results for WP-4

In general, column studies provide a better description of how a material will perform in an actual application relative to batch experiments. Given the excellent selectivity for ferric over nickel observed with WP-4 a dynamic separation of nickel from iron was attempted. The breakthrough profile of WP-4 is shown in Figure 6 was done on an aqueous solution containing 1.25 g/L of Fe (III) and 0.4 g/L of Ni(II) at pH 1.5 using a 5 cc column containing 2.5 g of WP-4. At a rate of 0.5 column volumes per minute, the breakthrough graph illustrates the selective removal of ferric from nickel. Fe(III) was observed after 5 bed volumes but Ni(II) was detected in the effluent almost instantly. Fe(III) effluent concentration reached the feed concentration after 8 bed volumes. Using eq. (1), breakthrough capacity for WP-4 was calculated to be 11 mg/g or 0.20 mmol/g. Iron can be removed and the material regenerated by the use of 2M sulfuric acid. The resulting solutions were 99.9% pure with respect to iron. This represents an excellent way to separate nickel and ferric ion and

TABLE V
Metal Profile of Pasmenco Challenge Solution

Element	Concentration (mg/L)
Aluminum	1944
Gallium	2191
Germanium	200
Iron (as ferrous)	36980
Zinc	5381

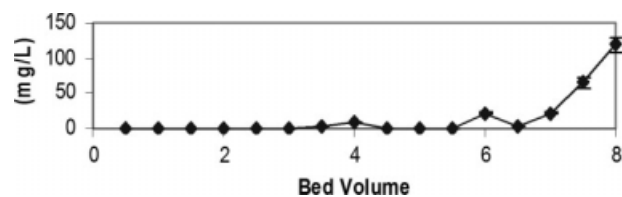


Figure 7 Gallium breakthrough curve for the separation of gallium from the zinc mine waste solution at pH = 2.1 with WP-4.

should have practical applications in the specialty steel industry for recovery of nickel from pickling solutions and in certain ore leach hydrometallurgical circuits.

Recovery of gallium from zinc mine tailings

Given the selectivity of WP-4 for gallium over aluminum observed in the batch data presented earlier, it would be useful to test a real multicomponent metal solution containing gallium. Gallium batch capacities at pH = 2.3 were 22.47 ± 0.13 , 24.50 ± 0.24 , and 26.07 ± 0.17 mg. We decided to use WP-4 because of the higher selectivity factor observed for this SPC. A sample of solid ore tailings from a zinc mine in Gordonsville, TN was received from Pasmenco Zinc, an Australian mining company, which has a zinc mine located in Gordonsville, Tennessee. This waste product was found to contain large amounts of iron, zinc, gallium, and a small amount of germanium. As both gallium and germanium are quite valuable, removal and concentration of both metals using the silica gel polyamine technology seemed worth pursuing. The first step was to dissolve the metals into solution using the nitrogen catalyzed pressure leach developed by Anderson et al.²³ The oxidized pressure leach involves the use of a sulfuric acid medium at elevated temperatures and pressures to which a small amount of nitric acid is added. This provides the powerful oxidant NO^+ which promotes the oxidation of the sulfides. This solution is filtered to remove elemental sulfur and provides the dissolved metals in a sulfate matrix. The total reaction

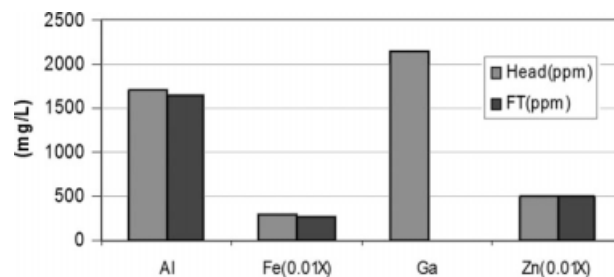


Figure 8 Bar graph of flow through versus feed for gallium recovery from zinc mine waste solution using WP-4.

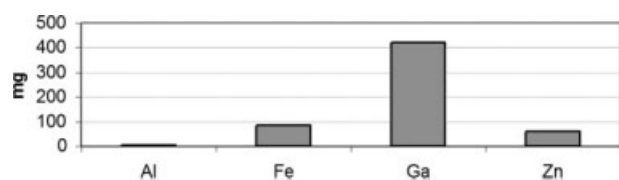
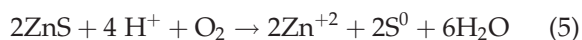
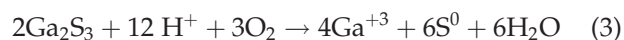


Figure 9 Strip composition for gallium recovery from zinc mine waste solution using WP-4.

for the dissolution of metals into solution can be summarized by the following reactions:



Zinc powder was added prior to running the breakthrough test to ensure that all the iron present was in the ferrous form because ferric ion is known to bind to WP-4.

The testing of WP-4 was carried out in a 25-mL syringe column. The solutions contained germanium, gallium as well as zinc, aluminum, and iron (Table V). The pH of the solution was adjusted to 2.1 as this proved to be the optimal pH for gallium recovery. Gallium breakthrough for WP-4 does not occur until seven bed volumes using a flow rate of 0.2 column volumes per minute (Fig. 7). WP-4 was very selective for gallium removal from aluminum, ferrous, and zinc. The silica gel composite passed the other metals while retaining all the gallium (Fig. 8). There was some co-loading of ferrous and zinc as seen from the strip of the column after breakthrough (Fig. 9) but considering the large excess of these metals selectivity can be considered good. Most importantly, the selectivity for gallium over aluminum is very good and the strip solution could be directly electrolyzed to give a ball of pure gallium as the only reduced species.²⁸ The strip contained 410 mg of gallium in the 25 mL strip or 16.4 g/L. This constitutes a concentration factor of 7.5 and a gallium capacity of 22 mg/g of gallium. The metal selectivity ratios relative to the three other metals present in the solution for WP-4 are given in Table VI. Thus, it would appear that WP-4 could

TABLE VI
Metal Selectivity Ratios for the WP-4 Recovery of Gallium from a Waste Ore Leach

Gallium to metal ratio	Ratio
Aluminum	92.41
Iron	4.87
Zinc	6.81

provide an effective material for recovering gallium from acidic zinc tailings solutions containing significant amounts of gallium. We did not analyze the strip or the flow through for the small amount of germanium in the feed solution. Subsequent studies with WP-4 showed that the germanium does co-load with the gallium and that this composite showed some selectivity for germanium.²⁹ It is possible that with further column engineering that this selectivity could be used to separate the two metals. Apparently the contamination of gallium by germanium did not interfere with electrolysis of the gallium as mentioned earlier.

CONCLUSIONS

The three oxine modified composites reported here all showed significant selectivity for ferric ions over the divalent copper and nickel. In the case of nickel and ferric ion, this selectivity was good enough to afford a good separation of nickel from ferric under dynamic flow conditions. All three composites also showed selectivity for the larger trivalent ion gallium over aluminum and in the case of the unsubstituted oxine ligand in WP-4 the selectivity factor was sufficient to allow an adequate separation of gallium from aluminum and a large excess of divalent iron and zinc. Although the separation was not perfect, it was sufficient to allow isolation of pure gallium by subsequent electrolysis.

The substituent groups on the oxine ligand had little effect on the kinetics of metal uptake and all three composites showed uptake rates very similar to previously reported SPCs.²⁷ The sulfonic acid substituent did have a profound influence on the mode of metal ion coordination based on the estimated metal to ligand ratios (Table IV) and we interpret this in terms of metal binding to anionic sulfonic acid groups on adjacent oxine groups (Fig. 3) in the low-pH range examined.

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