# Synthesis and Characterization of Iron(III) Chelating Analogues of Siderophores on Organic Solid Supports

A. L. CRUMBLISS, J. M. GARRISON

*Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, N.C. 27706, U.S.A.*

C. R. BOCK, A. SCHAAF, C. J. BONAVENTURA and J. BONAVENTURA

*Marine Biomedical Center, Duke University Marine Laboratory, Pivers Island, Beaufort, N.C. 28516, U.S.A.*

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## Abstract

A series of iron(III)-selective chelating resins have been modeled after the structural features of the naturally occurring siderophore compounds with hydroxamate, catecholate and salicylate iron binding groups. Amberlite IRC-50 was derivatized via an acid chloride intermediate to produce poly(hydroxamic acid) (IRC-50 PHA/N-H and IRC-50 PHA/N-CH$_3$), poly(catecholate) (IRC-50 PEDA 2,3-DHBAD and IRC-50 PEDA 3,4-DHBA) and poly(salicylate) (IRC-50 PEDA 2-HBAD) chelating resins with enhanced iron(III) binding capacity. The poly(hydroxamic acid) IRC-50 PHA/N-CH$_3$ was produced in 57% yield, the highest conversion yet reported for such derivatizations. This is the first report of a catechol or salicylate derivatization of Amberlite IRC-50. The highest overall iron(III) binding capacities yet reported for poly(hydroxamic acid) modifications of commercially available polymer supports were obtained for IRC-50 PHA/N-H (1.75 mmol Fe/g dry resin) and IRC-50 PHA/N-CH$_3$ (1.52 mmol Fe/g dry resin). IRC-50 PHA/N-H was also found to be an effective iron chelator when tested at ambient environmental conditions. Selectivity for iron(III) was also determined by measuring $Fe^{3+}$ binding capacity in the presence of $Ca^{2+}$. UV–Vis spectroscopy with photoacoustic detection was used to assign the coordination environment of iron(III) in these chelating resins as bis-($FeL_2$) and tris-($FeL_3$) chelates. As an alternative synthetic approach, a poly(amidoxime) (PAO) chelating resin was synthesized by polymerization of appropriate monomers. Comparison between the two synthetic approaches showed that PAO bound a greater amount of iron(III) at flow-through column conditions, while IRC-50 PHA/N-H exhibited a greater iron(III) binding capacity at batch equilibration conditions.

## Introduction

Metal chelating resins are insoluble organic supports which contain functional groups capable of extracting metal ions from solution via complexation [1]. Because the alkali and alkaline earth metals occur in relatively high concentrations in natural waters, a desirable property of metal chelating resins having useful environmental or commercial application would be the ability to selectively bind the heavier transition, rare earth, and main group metal ions in the presence of calcium, magnesium, sodium, and potassium. The purpose of this study concerns the design and development of iron(III)-selective chelating resins; characterization of their iron(III) binding capacity, selectivity, and binding group-metal stoichiometry; and subsequent preliminary assessment of these resins' applicability to the removal of iron hydroxides from natural waters.

Ferric ion is a hard acid which coordinates strongly to ligands having functional groups made up of small, nonpolarizable, highly electronegative oxygen donor atoms (hard bases). The hydroxamate (**1**), catecholate (**2**), and salicylate (**3**) anions are such chelators which are known to form very stable six-coordinate tris complexes with iron(III) [2].
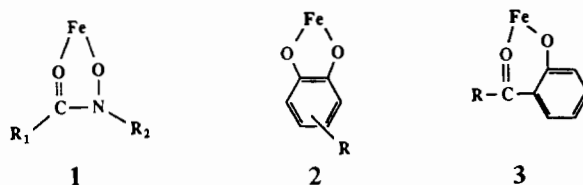


Furthermore, it has been well established that the hydroxamic acid and catechol moieties are the chelating functionalities present in many naturally occurring iron(III)-specific chelating agents known as siderophores [3–6]. Siderophores are synthesized by microorganisms to solubilize iron from the environment via complexation and transport it to the cell [3–7]. Thus, it is reasonable to model iron(III) chelating resins, whose purpose it is to selectively solubilize iron hydroxides from aqueous media, after the structural features of iron(III)-specific chelating agents (siderophores) already provided by nature to serve a similar purpose.
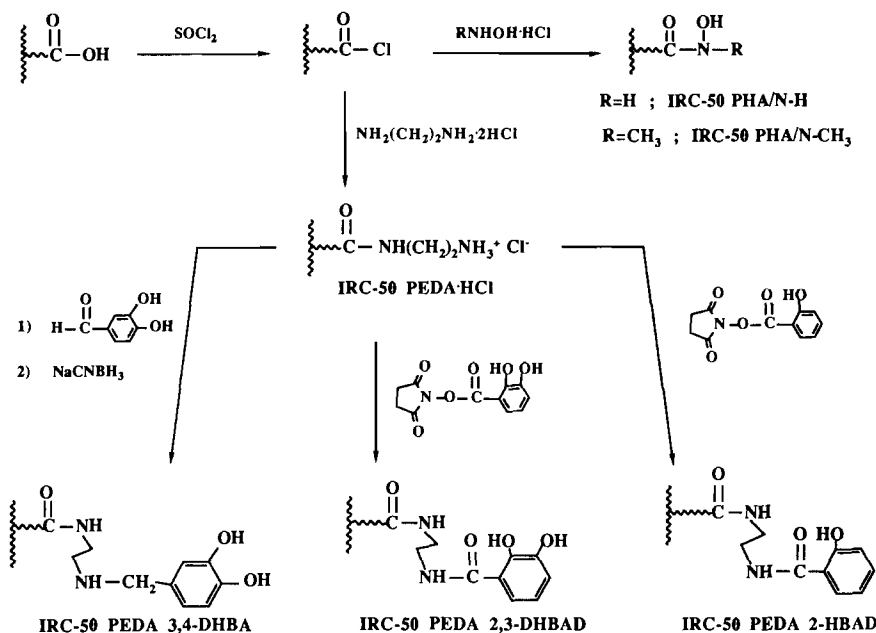
Fig. 1. Preparative scheme for poly(hydroxamic acid), poly(catechol), and poly(salicylic acid) derivatizations of Amberlite IRC-50.

In general there are two main approaches by which chelating resins can be synthesized. One approach involves the polymerization of appropriate monomers to form a solid polymer support containing the desired chelating functionality. This is the approach that has been taken by many workers in the synthesis of a poly(amidoxime) (PAO) resin which also contains a significant number of hydroxamic acid groups [8]. The second approach is to chemically modify (derivatize) existing polymer supports to contain the chelating functional group of interest. This approach has been previously attempted by a number of workers in the case of poly-(hydroxamic acid) (PHA) modifications with only limited success [9–11].

Both of these synthetic approaches were utilized in the development of the iron(III) chelating resins characterized in this study. Optimization of the preparative techniques for PHA modification of Amberlite IRC-50 has been achieved by derivatizing the resin under extremely anhydrous conditions while making full use of current synthetic methods for hydroxamic acid monomers (Fig. 1) [12–15]. The first poly(catechol) (IRC-50 PEDA 2,3-DHBAD and IRC-50 PEDA 3,4-DHBA) and poly(salicylic acid) (IRC-50 PEDA 2-HBAD) modifications on Amberlite IRC-50 are reported as well. Finally, a poly(amidoxime) (PAO) resin was synthesized and characterized for its iron(III) binding capacity in order to determine which synthetic approach was most effective in producing an iron(III)-specific chelating solid support.

## Experimental

### Preparation of Chelating Resins

#### Poly(hydroxamic acid) chelating resins (IRC-50 PHA/N-H, IRC-50 PHA/N-CH₃; Fig. 1)

Amberlite IRC-50 (Rohm and Haas) was dried *in vacuo* with heating (75 °C) for 2 days to constant weight (*ca.* 30 g) and placed in a reaction flask equipped with a reflux condenser and addition funnel. Thionyl chloride (120 ml; Aldrich) was added slowly over a 30 min period and then sufficient DMF (*ca.* 2.5 ml; Fisher Scientific) was carefully added to catalyze the reaction. The reaction mixture was allowed to stir under reflux conditions for 4–5 h. The resulting modified resin was filtered, washed 4–5 times with 100 ml portions of Na distilled ether, immediately dried *in vacuo* to a constant weight and stored *in vacuo* over $P_2O_5$/NaOH desiccants. Anhydrous conditions and an inert atmosphere were maintained throughout the course of the reaction.

Coupling of the Amberlite IRC-50 acid chloride resin to hydroxylamine hydrochloride and *N*-methyl-hydroxylamine hydrochloride was accomplished by the following procedure. Hydroxylamine hydrochloride (320 mmol; 22.24 g; Eastman) and sodium bicarbonate (480 mmol; 41.32 g; Fisher Scientific) were placed in a previously dried, $N_2$ flushed reaction flask equipped with mechanical stirrer, $N_2$ inlet-outlet, and solid phase addition funnel. About 75 ml of Na distilled ether were added and the mixture

allowed to stir under $N_2$ at $-78\,^{\circ}$C for 1 h. The acid chloride resin (320 mmol) was then added slowly to the stirring mixture by means of the solid phase addition funnel over a 1 h period. The reaction was then allowed to stir for 12–24 h as the temperature of the reaction flask reached ambient. The reaction mixture was filtered, washed with three 100 ml portions of distilled water, followed by ether, and dried *in vacuo* to constant weight either in the presence of $P_2O_5$/NaOH or under slight heat (*ca.* 55 °C). The same procedure was employed when coupling the acid chloride resin to $N$-methylhydroxylamine hydrochloride (385 mmol; 32.16 g; Aldrich) in the preparation of IRC-50 PHA/N-CH$_3$.

### Poly(catechol) and poly(salicylate) chelating resins (IRC-50 PEDA 3,4-DHBA, IRC-50 PEDA 2,3-DHBAD and IRC-50 PEDA 2-HBAD; Fig. 1)

Ethylenediamine hydrochloride (324 mmol; 43.14 g; Sigma) which had been previously dried *in vacuo* to constant weight was used in the preparation of Amberlite IRC-50 PEDA·HCl. The procedure employed was the same as that described for the coupling of the Amberlite IRC-50 acid chloride resin to hydroxylamine hydrochloride, except that the resulting IRC-50 PEDA·HCl resin was washed with three 100 ml portions of a 0.1 M HCl solution to ensure the formation of the amine hydrochloride salt on the derivatized resin.

In the preparation of poly(ethylenediamine 3,4-dihydroxybenzylamine) (IRC-50 3,4-DHBA), 3,4-dihydroxybenzaldehyde (165.2 mmol; 22.82 g; Aldrich) was placed in a reaction flask which had been previously oven-dried and flushed with Ar gas. Methanol (magnesium distilled; 100 ml) was added to the reaction flask with stirring and slight heat until the 3,4-dihydroxybenzaldehyde had dissolved. IRC-50 PEDA·HCl (165.2 mmol; 27.20 g) was placed in a solid phase addition funnel attached to the reaction apparatus. Sodium cyanoborohydride (297.56 mmol; 18.70 g; Sigma) was then added to the reaction flask and the IRC-50 PEDA·HCl quickly added. The reaction mixture was stirred and allowed to reflux at 60–65 °C for 18–24 h. The resulting resin was filtered, washed with three 100 ml portions of methanol, a 25 ml portion of propanol, a 25 ml portion of ether, and dried *in vacuo* in the presence of $P_2O_5$/NaOH to constant weight (yield 32.5 g).

Succinimido 2,3-dihydroxybenzoate and succinimido 2-hydroxybenzoate were prepared according to a literature procedure [16]. Succinimido 2,3-dihydroxybenzoate was coupled to IRC-50 PEDA·HCl according to a literature procedure [16] in which IRC-50 PEDA·HCl (86.14 mmol; 20.59 g) was placed in a dry reaction flask along with 30 ml of 5% aqueous THF solution. Triethylamine (86.14 mmol; 12.0 ml) was pipetted into the stirring solution and 70 ml of 5% aqueous THF solution added. Succin-

imido 2,3-dihydroxybenzoate (48.37 mmol; 12.15 g) dissolved in THF (50 ml) was then added dropwise over a 45 min period and the reaction allowed to stir for 71 h. The resulting resin was filtered, washed with THF, dried by suction, and dried *in vacuo* to constant weight (yield 29.60 g). The procedure for coupling 2-hydroxybenzoate to IRC-50 PEDA·HCl was the same as that described above for succinimido 2,3-dihydroxybenzoate.

### Poly(amidoxime) chelating resin (PAO)

The procedure reported by Vernon [8] was followed using 4-methyl-2-pentanone as the ketone component. The reaction mixture consisted of the following monomer mole fractions: styrene (0.025), divinylbenzene (0.021), ethylacrylate (0.184), and acrylonitrile (0.846). The final product was washed several times with water (70 °C), superficially dried by suction, and dried at 50 °C to constant weight. Ethylacrylate was assumed to be quantitatively converted to hydroxamic acid. Acrylonitrile was assumed to be converted to hydroxamic acid and amidoxime groups with the relative proportion of the latter being estimated from nitrogen elemental analysis. Reasonable agreement between calculated and experimental analysis was obtained for a polymer having the following composition (mole fraction): styrene (0.025), divinylbenzene (0.021), acrylic acid hydroxamate (0.682), acrylic acid amidoxime (0.272).



**PAO**
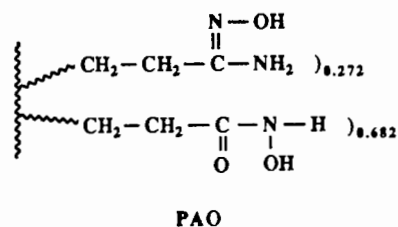
### Iron(III) Binding Capacity

Iron binding was measured by flow-through column and batch equilibration techniques. For the column technique, samples of each resin were dried at 105–110 °C to constant weight to determine water content. Fresh 2–10 g samples of each resin were allowed to equilibrate with deionized water for at least 30 min. Samples were rinsed with 0.1 M HCl (Fisher Scientific) before loading into glass columns of 0.7 to 1.2 cm I.D. These resins were treated with 10 mM FeCl$_3$ (Fisher Scientific) at pH 2.5, with or without 0.6 M CaCl$_2$·2H$_2$O (Fisher Scientific), at a flow rate of 4–5 ml/min. Samples of effluent were checked periodically by atomic absorption spectroscopy (AAS) until iron uptake had ceased. The columns were rinsed and backwashed with deionized water to remove any precipitated iron, then eluted with 4 M HCl at 4–5 ml/min. Iron eluted was mea-

sured either by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 5000 atomic absorption spectrophotometer, or spectrophotometrically using a Hewlett Packard 8451A diode array spectrophotometer using 1,10-phenanthroline monohydrate (Aldrich) as an indicator [17]. Calcium eluted was measured by AAS.

Iron(III) binding capacity was determined in a batch equilibration mode by measuring equilibrium iron uptake (C) at pH 2.5 with varying $Fe^{3+}$ concentrations ($[Fe^{3+}]$). These batch equilibrations produced uptake isotherms that fit the Langmuir relationship [18, 19].

$$C^{-1} = (C_m K_c)^{-1} [Fe^{3+}]^{-1} + C_m^{-1}$$

Plots of $C^{-1}$ *versus* $[Fe^{3+}]^{-1}$ were linear and yielded values of the conditional equilibrium constant, $K_c$, and ferric ion capacity ($C_m$) at pH 2.5. The batch equilibrations were carried out with a series of solutions in flasks on a shaker. The series of $Fe^{3+}$ solutions (5–50 ppm) at pH 2.5 was prepared by dilution of a stock solution (1000 ppm $Fe^{3+}$ in 0.05 M HCl) followed by adjustment of the pH with dilute HCl and solid $NaHCO_3$. Accurately weighed samples of the resin (0.1 g) were added to each of the solutions (450 ml) and the flasks agitated on the shaker. Solution pH was readjusted as necessary. Aliquots were removed with time and analyzed for $Fe^{3+}$ by either AAS or by the 1,10-phenanthroline method [17]. Once iron(III) uptake had ceased, the resin beads were filtered off, water washed and extracted with 5 N HCl to remove the $Fe^{3+}$ which was analyzed as before.

*Physical Characterization Methods*

A Princeton Applied Research (PAR) model 6001 photoacoustic spectrometer (PAS) was used to obtain UV–Vis spectra of ferrioxamine B and iron(III) bound to solid samples of modified polymer supports (see Fig. 2). The spectrum of each sample was referenced to carbon black and S/R recorded. A modulation frequency of 41 Hz was employed to prevent thermal saturation of the samples except in the case of PAO where a modulation frequency of 79 Hz was employed due to this resin's high iron binding capacity. All PAS spectra were also obtained at a higher modulation frequency as a check that thermal saturation was not taking place at 41 Hz or 79 Hz.

Fourier transform infrared spectra with photoacoustic detection (FT-IR–PAS) were obtained using an IBM model 9195 spectrometer. All resin samples were referenced to carbon black and S/R recorded. A mirror velocity of 0.059 cm/s and an optical velocity of 0.236 cm/s was employed making the resolution of each spectrum 8 cm$^{-1}$ after 512 transients had been accumulated.
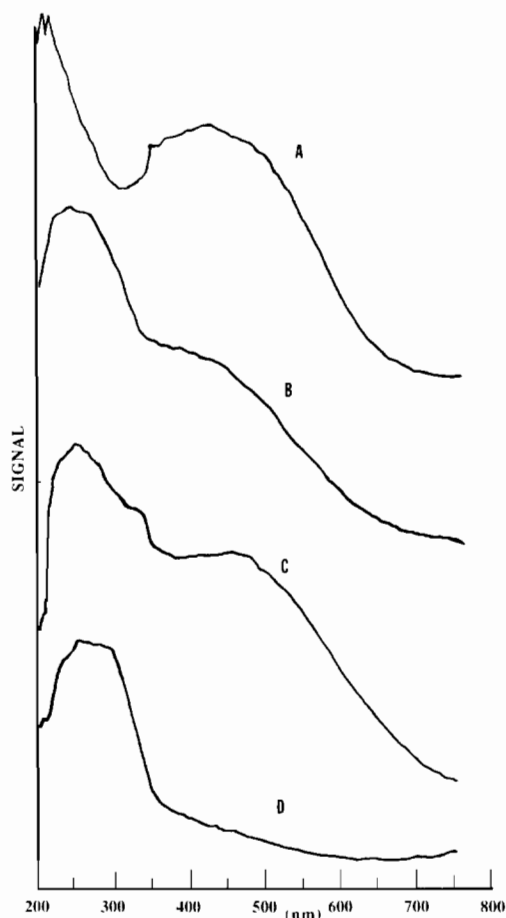


Fig. 2. UV–Vis–PAS spectra of microcrystalline ferrioxamine B perchlorate pentahydrate (A), IRC-50 PHA/N-H and IRC-50 PHA/N-CH$_3$ before (D) and after (B and C, respectively) treatment with 10 mM FeCl$_3$; pH 2.5. Spectra are vertically offset for clarity.

Elemental analysis (C, H, N) on modified and unmodified solid polymer supports was obtained by MHW Laboratories, Phoenix, Arizona, The N/C ratios obtained from the elemental analysis results (see Table I) were used as criteria for % conversion to the modified forms of the resin since the unmodified resin contained no nitrogen.

**Results and Discussion**

*Preparation and Characterization of Chelating Resins*

Two main approaches were taken in the synthesis of iron-selective chelating organic solid supports: (1) the derivatization of an existing macroreticular resin to contain the hydroxamic acid, catechol, or salicylic acid chelating moieties, and (2) the polymerization of appropriate monomers to produce a macroreticular resin containing amidoxime and hydroxamic acid functional groups. The synthetic

TABLE I. Elemental Analysis and Percent Conversions of Chelate Modified Resins

| Resin abbreviation | Calculated[a] (%) | | | Found[a] (%) | | | Conversion[b] (%) |
|---|---|---|---|---|---|---|---|
| | C | N | H | C | N | H | |
| IRC-50 PHA/N-H | 47.52 N/C = 0.2498 | 13.85 | 6.98 | 47.07 N/C = 0.08760 | 4.81 | 6.94 | 35 |
| IRC-50 PHA/N-CH₃ | 52.16 N/C = 0.2000 | 12.17 | 7.88 | 42.72 N/C = 0.1138 | 5.67 | 6.57 | 57 |
| IRC-50 PEDA 3,4-DHBA | 62.38 N/C = 0.1538 | 11.19 | 7.25 | 51.17 N/C = 0.03954 | 2.36 | 6.77 | 26 |
| IRC-50 PEDA 2,3-DHBAD | 59.08 N/C = 0.1538 | 10.60 | 6.10 | 57.34 N/C = 0.04111 | 2.75 | 8.10 | 27 |
| IRC-50 PEDA 2-HBAD | 62.89 N/C = 0.1538 | 11.28 | 6.50 | 59.07 N/C = 0.04455 | 3.07 | 8.29 | 29 |

[a]N/C = (% N/14.01 amu)/(% C/12.01 amu).    [b]% Conversion = $(N/C)_{found}/(N/C)_{calc}$.

approach to derivatizing Amberlite IRC-50 to produce a poly(hydroxamic acid) (IRC-50 PHA/N-H and IRC-50 PHA/N-CH₃), poly(catechol) (IRC-50 PEDA 3,4-DHBA and IRC-50 PEDA 2,3-DHBAD) and poly(salicylic acid) (IRC-50 PEDA 2-HBAD) is shown in Fig. 1. Previous reports of hydroxamic acid conversions of Amberlite IRC-50 [10] and Zeo-Karb 226 [11] resulted in poor yields due to acid chloride conversion procedures. This led to increased attention being given to the second approach described above in that the resins had higher metal binding capacities and greater resistance to decomposition by strong acid or base [1]. However, in the present study resin derivatization has been optimized. FT-IR-PAS spectra of the acid chloride intermediates show no absorption bands for unreacted carboxylic acid groups and complete conversion to the acid chloride ($1801$ cm$^{-1}$) and acid anhydride ($1786$, $1763$ cm$^{-1}$). FT-IR–PAS spectra of IRC-50 PHA/N-H and PHA/N-CH₃ indicate a predominant carbonyl stretch in the region normally found for hydroxamic acids near $1640$ cm$^{-1}$ [20].

Percent conversions based on elemental analyses for IRC-50 resin hydroxamic acid, salicylic acid and catechol derivatizations are given in Table I. These data compare favorably with related literature reports [9–11] for poly(hydroxamic acid) derivatization of commercially available resins (*ca.* 30–40%). The 57% conversion obtained in this work for IRC-50 PHA/N-CH₃ represents the highest yield yet reported for a hydroxamate derivatized resin.

*Iron(III) Binding Capacity and Characterization*

The iron binding capacities at flow-through column conditions for the hydroxamic acid, catechol and salicylic acid resin derivatives are given in Table II in the presence and absence of $Ca^{2+}$. Also included for comparison purposes are the corresponding data

TABLE II. Iron Binding Capacity in Flow-through Columns

| Resin abbreviation | $Fe^{3+}$ capacity[a] (mmol/g dry) | $Ca^{2+}$ capacity[b] (mmol/g dry) |
|---|---|---|
| IRC-50 | 0.56[c] 1.27[d] | 0.004[d] |
| IRC-50 PHA/N-H | 1.75[c] 2.02[d] | 0.013[d] |
| IRC-50 PHA/N-CH₃ | 1.52[c] 1.48[d] | <0.01[d] |
| IRC-50 PEDA 3,4-DHBA | 0.37[c] 0.12[d] | <0.02[d] |
| IRC-50 PEDA 2,3-DHBAD | 0.86[c] 0.88[d] | 0.002[d] |
| IRC-50 PEDA 2-HBAD | 1.11[c] 0.96[d] | 0.002[d] |
| PAO | 3.95[c] 3.53[d] | 0.06[d] |

[a]Estimated uncertainty ≤0.02 mmol/g dry. [b]Estimated uncertainty ≤0.005 mmol/g dry. [c]Resin loaded with 10 mM FeCl₃, pH 2.5. [d]Resin loaded with 10 mM FeCl₃, 0.6 M CaCl₂, pH 2.5.

for the underivatized resins and PAO. These results show that hydroxamic acid derivatization of the Amberlite IRC-50 resin enhances its iron binding capabilities, both in the presence and absence of $Ca^{2+}$. Comparison of results obtained for the phenol and catechol derivatizations suggests that a salicylate mode of bonding to iron(III) as shown in 3 is operative. IRC-50 PEDA 3,4-DHBA, in which such a bonding mode is not possible, exhibits an iron(III) binding capacity which is less than the underivatized resin. The optimum form of the derivatized resins investigated appear to be the hydroxamate based

TABLE III. Iron Binding Capacity in Batch Equilibration

| Resin abbreviation | $C_m{}^a$ | $K_c{}^b \times 10^3$ |
|---|---|---|
| IRC-50 | 0.38 | 3.5 |
| IRC-50 PHA/N-H | 1.2 | 6.1 |
| IRC-50 PEDA 2,3-DHBAD | 0.66 | 2.3 |
| PAO | 0.85 | 4.6 |

[a]Resin capacity (mmol Fe/g dry). [b]Conditional equilibrium constant (1/mol).

IRC-50 PHA/N-H and IRC-50 PHA/N-CH$_3$, which represent the highest overall iron(III) binding capacities yet reported for poly(hydroxamic acid) modifications of commercially available resins [9–11].

IRC-50 PHA/N-H was also flow-tested at ambient environmental conditions using high iron content well water ([Fe] = 13 ppm; [Ca$^{2+}$] = 0.8 ppm; pH 6.4). Flow velocities and column preparation were the same as that used to obtain the data listed in Table II. Iron binding was found to be 3.16 mmol/g dry resin and Ca$^{2+}$ was 0.05 mmol/g dry resin. The enhanced iron binding over those data presented in Table II may partially be due to surface adsorption of polymeric hydroxides. This value does, however, correspond to a single iron atom bound to each resin hydroxamate group, according to the elemental analysis given in Table I. These data confirm the feasibility of utilizing such derivatized resins in natural waters.

The PAO resin showed the largest overall iron(III) flow-through column capacity of all the resins tested in the absence and in the presence of calcium (Table II). However, the Ca$^{2+}$ binding capacity was also enhanced.

A hydroxamic acid and salicylate-catecholate derivatized resin were also tested for iron binding capacities along with PAO by a batch equilibration method (Table III). All performed better than the underivatized IRC-50 resin. However, in contrast to the flow-through column method, IRC-50 PHA/N-H out performed PAO. This may be attributed to differences in the Fe$^{3+}$(aq) concentrations employed in the two methods. Column conditions were favorable to both the kinetics and thermodynamics of ferric ion uptake because the resin was continuously exposed to a constant Fe$^{3+}$(aq) concentration. On the other hand, much lower Fe$^{3+}$(aq) concentrations (5–50 ppm) were employed in the batch technique and these concentrations were decreasing with time due to ferric ion uptake by the resin.

UV–Vis–PAS spectra were obtained of iron bound to various modified resins at flow-through column conditions in order to detect the presence and stoichiometry of iron(III)-hydroxamate, catecholate and salicylate complexes. The solution $\lambda_{max}$ values for iron(III) complexes which contain these

TABLE IV. UV–Vis–PAS of Chelate-resin Bound Iron

| Resin abbreviation | $\lambda_{max}$ (nm) | L/Fe$^{3+}$ $^a$ |
|---|---|---|
| IRC-50 PHA/N-H | 410 | 3:1 |
| IRC-50 PHA/N-CH$_3$ | 455 | 2:1 |
| IRC-50 PEDA 3,4-DHBAD | 520 | 3:1 |
| IRC-50 PEDA 2,3-DHBAD | 475 | 3:1 |
| IRC-50 PEDA 2-HBAD | 460 | 2:1 |

[a]Ratio bidentate chelate group to Fe$^{3+}$ based on $\lambda_{max}$ values; see text.

bidentate chelating groups are diagnostic of metal-binding group stoichiometry as follows (L = bidentate chelate group). Hydroxamates: FeL$_3$, 400–440; FeL$_2$, 460–480; FeL, 500–515 nm [21]. Catecholates: FeL$_3$, 480–495; FeL$_2$, 560–570; FeL, 700 nm [22, 23]. Salicylates: FeL$_3$, 425; FeL$_2$, 460; FeL, 510 nm [24]. The applicability of these solution spectral interpretations to solid state surface spectra may be seen by considering the UV–Vis–PAS spectrum of microcrystalline ferrioxamine B, a hexadentate iron(III)–siderophore complex with three coordinated hydroxamate groups. This spectrum is shown in Fig. 2 and has a distinct $\lambda_{max}$ at 425 nm in agreement with the corresponding solution spectrum [25]. Also shown in Fig. 2 are the PAS spectra of IRC-50 PHA/N-H and IRC-50 PHA/N-CH$_3$ before and after treatment of the resins with 10 mM FeCl$_3$ at pH 2.5.

Table IV lists the values of $\lambda_{max}$ determined by UV–Vis–PAS on samples of iron(III) bound to the chelate modified Amberlite IRC-50 resins. Based on these $\lambda_{max}$ values, an interpretation of the mode of iron(III) binding as a mono, bis or tris chelate complex is made. At a constant pH of 2.5, one might expect that only the mono (FeL) chelate complex would be formed on the modified solid supports since the chelation of iron(III) by hydroxamate, catecholate or salicylate groups, which requires the dissociation of one or two protons, would be suppressed. The results shown in Table IV, however, clearly indicate that there is a greater tendency to form bis (FeL$_2$) and tris (FeL$_3$) chelate complexes. This is probably due to the fact that there are a relatively large number of chelating groups chemically bound to the resin in close proximity. It appears that the ligand stoichiometry of iron(III) bound to the chelate modified organic solid supports is dictated by the number of available chelating units per iron and the relative orientation of these chelating groups to one another within the polymer matrix.

## Conclusions

The preparative conditions for the poly(hydroxamic acid) modification of Amberlite IRC-50 have

been optimized. A 57% conversion to form IRC-50 PHA/N-CH$_3$ represents the highest value reported in the literature thus far. The values of 1.75 and 1.52 mmol Fe/g dry resin for the IRC-50 PHA/N-H and IRC-50 PHA/N-CH$_3$ resins, respectively, are the highest iron(III) capacities yet reported for poly-(hydroxamic acid) modifications of commercially available resins [1, 9—11]. Iron(III) chelation in the presence of Ca$^{2+}$ has also been demonstrated. The derivatization of IRC-50 has also been carried out to include catechol and salicylic acid chelating groups, the first such derivatizations to be reported. Surface spectroscopic results suggest that bis and tris iron(III) chelate complexes are formed on the resin surface. The chelating resins described here may have useful environmental applications in the selective removal of iron from aqueous media.

## Acknowledgements

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