

NEW FUNCTIONAL POLYMERS AS SORBENTS FOR THE SELECTIVE RECOVERY OF TOXIC HEAVY METALS FROM ACID MINE DRAINAGE¹

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Abstract: By a new synthetic technique, macroporous crosslinked polystyrene resin was functionalized with ligands containing sulfur, nitrogen, and/or oxygen atoms. Preliminary studies indicate that when added to a synthetic acid mine drainage (AMD) solution, some of these functional polymers were capable of selectively binding zinc without becoming "fouled" by iron. Elution of the loaded resins with acid to recover the zinc was also possible. The greatest selectivity for zinc was obtained with functional groups that contained only electronically "soft" nucleophilic centers such as sulfur and nitrogen, and not oxygen atoms, which are electronically "hard" (and prefer such "hard" electrophiles as magnesium, aluminum, or iron cations). The performance of some of these new materials exceeded that of the commercial ion-exchange resins tested with respect to capacity and selectivity.

Additional Key Words: ion-exchange resins, chelating resins, zinc, iron.

Introduction

Acid mine drainage poses a serious environmental problem (Ritcey 1989). The standard treatment, liming to neutralize the AMD and precipitate the metals, followed by disposal of the resultant sludge (MacDonald et al. 1989), does not enable metal recovery. Metal values are lost as metal hydroxides in the sludge, which is considered hazardous waste. A method enabling metal recovery would have the benefit of providing some revenue to offset the costs of treatment and disposal as well as decreasing the sludge volume and toxicity.

If toxic heavy metals could be selectively removed, the solution of remaining Fe⁺², Fe⁺³, Al⁺³, Mg⁺² etc. could then be used as a source of ferric chloride and alum, which could then be used in municipal wastewater treatment. Untreated AMD has been used successfully as a coagulating agent in laboratory experiments (Rao et al. 1992).

It is possible to selectively extract metals of choice using ion-exchange or chelating resins. The present work is directed toward exploring the potential use of new polystyrene-based chelating resins for the selective and economical recovery of zinc from AMD. This preliminary work studied the uptakes of zinc, iron and magnesium, with the primary concern being selectivity for zinc over iron.

An ion-exchange resin consists of a chemically-inert polymer matrix, such as polystyrene ("Ps"), with a functional group attached to the polymer backbone. The functional group may be anionic, such as sulfonate, with a cationic counter-ion (e.g., Ps—SO₃⁻Na), or cationic, such as a quaternary amine, with an anionic counter-ion (e.g., Ps—CH₂NMe₃⁺Cl). It is the counter-ion that can be exchanged for ions of like charge in solution. Being quite unselective, the application of ion-exchange resins has been limited to the bulk removal of all dissolved metals. A spent resin would be regenerated by eluting off the accumulated metals, using solutions of acids (e.g., hydrochloric or sulfuric), salts (e.g., brine), or soluble complexing agents (e.g., EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriaminepentaacetic acid)), to recover the desired metals in concentrated solution. The resin could then be reused in the treatment process.

This project uses chelating resins, which can also be referred to as a type of ion-exchange resin. The functional group on the polymer is a chelant. Chelation (Greek *chelae* = "claw") takes place when the lone-pair electrons of several electron-donating heteroatoms (O, N, S: "Lewis bases") in the chelant, are able to coordinate (bond)

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simultaneously to an electron-acceptor (metal cation: a "Lewis acid"), forming a stable complex, a chelate. Chelants are multidentate ligands; monodentate ligands have only one place of attachment to the metal. Chelants can be very selective for specific ions, according to the identities, numbers, and positions of the coordinating heteroatoms in the chelant, and the overall structure of the chelant. Though relatively inert towards such non-targeted ions as Ca^{+2} , Mg^{+2} or Na^{+1} , current commercial chelating resins are less able to discriminate between transition metals, such as zinc and iron ions.

The principle determining selectivity of the chelating groups that is used in the present work is hard/soft formalism (Mackay and Mackay 1989). Metal ions are classified as hard or soft "Lewis acids" and the electron-donating heteroatom(s) of the ligand (functional group) as hard or soft "Lewis bases". A heteroatom is a soft (Lewis) base if it is polarizable and is a hard base if it is nonpolarizable. Sulfur and phosphorus are polarizable and therefore soft, nitrogen is slightly soft, and oxygen is harder. A metal ion is a soft (Lewis) acid if it has easily polarizable electrons, or has a low charge, while a hard metal ion has high charge or valence electrons which are not polarizable. The "HSAB" (Hard-Soft-Acid-Base) rule states that soft bases tend to form complexes with soft acids, and hard bases tend to form complexes with hard acids.

Fe^{+3} is hard and not readily complexed with a soft ligand, while Zn^{+2} is relatively soft and can be complexed with a soft ligand. Resins containing soft ligands are potentially selective for the removal of zinc, leaving ferric ions in solution. The chelating groups of interest will have sulfur and possibly nitrogen in them. Since oxygen-containing chelants have a tendency to complex iron, these should be avoided. Although harder than Zn^{+2} , Fe^{+2} is slightly soft, so interference may occur. Ligands that prefer to bind zinc over iron are also likelier to bind other soft cations, such as cadmium, lead, mercury, silver, copper, gold, etc. Table 1 lists some common hard and soft acids and bases.

Table 1. Common Lewis acids and bases.

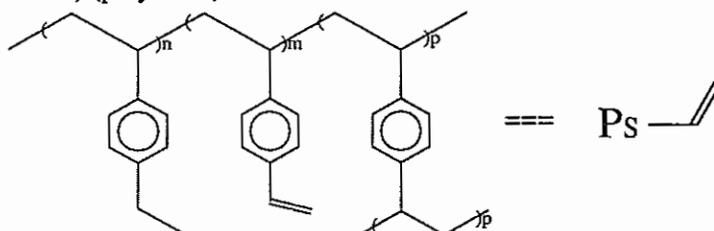
Hard bases	Soft bases	Hard acids	Soft acids
O, F	N, P, S	Na^{+1} , Fe^{+3} , Ca^{+2} , Al^{+3} , Mg^{+2}	Fe^{+2} , Zn^{+2} , Ni^{+2} , Cd^{+2} , Pb^{+2} , Cu^{+2} , Hg^{+2} , Pt^{+2} , Au^{+1} , Ag^{+1}

Ion-exchange and chelating resins are easy to handle, nontoxic, safely transportable, and can be regenerated repeatedly for multiple reuse. The ideal resin should be easy and inexpensive to manufacture; have a high affinity, capacity, and selectivity for the target cation(s); be easy to recover, regenerate, and recycle; and be mechanically and chemically stable to the conditions of its use and regeneration. Crosslinked polystyrene is a proven inert and stable matrix for ion-exchange resins and other functional polymers for many applications. The design for a zinc-versus-iron-selective sorbent thus depends on the choice of an appropriate chelating functional group. As well as being selective for the metal(s) of choice, it is important to have chelating functional groups that are nonhydrolyzable (stable to acid) and that are strongly bonded to the polymer backbone, so that they are not removed during usage.

Experimental Work

Synthetic Techniques

Radical Suspension Polymerization of Divinylbenzene. Using standard methodologies (Gao et al. 1993), macroporous beads of poly(divinylbenzene), also called (vinyl)polystyrene, were prepared. The resins were characterized using Fourier transform infrared (FTIR) spectrometry to determine the degree of functionalization (C_f , the number of residual double bonds (vinyl groups) in mmol per gram of resin) (Bartholin et al. 1981). The chemical structure of poly(divinylbenzene) (polyDVB) follows:



Functionalization of Poly(Divinylbenzene). It is possible to attach different functional groups to the vinyl group of the poly(divinylbenzene) using different methodologies. The method used in this study is radical-catalyzed

anti-Markovnikov addition of thiols (Gao et al. 1993). It creates a stable connection of the functional group to the polystyrene backbone through a two-carbon-unit bond. It is through the sulfide-functionality that the functional group is chemically attached to the polyDVB. The functional capacity of the resin (C_f , the number of functional groups in mmol per gram of resin) was found using elemental sulfur analysis. The following scheme shows the functionalization of poly(divinylbenzene) using thiol-containing compounds. (AIBN is 2,2'-azobis-(isobutyronitrile), a radical initiator).



Simulated Acid Mine Drainage

The study used a synthetic AMD solution of composition like that of "les Mines Gallen" AMD (table 2). It was prepared by dissolving calculated amounts of metal sulfates, and sodium arsenite (for arsenic), in 1L of water, and adjusting the pH to 2.1. The AMD was flushed twice a week with nitrogen to minimize the oxidation of Fe^{+2} to Fe^{+3} .

Table 2. Composition of "synthetic" AMD.

Metal ion concentration	Fe^{+2}	Fe^{+3}	Cu^{+2}	Zn^{+2}	Al^{+3}	Mn^{+2}	Mg^{+2}	Cd^{+2}	As^{+3}
g/L.....	2.70	3.52	0.04	3.06	0.70	0.03	0.64	0.01	0.01
mmol/L.....	48.3	63.0	0.63	46.8	25.9	0.55	26.0	0.09	0.13

Treatment Procedure and Analysis

A weighed quantity of resin was put into a 10 mL polyethylene bottle, 5 mL of AMD was added, and the contents were mixed at room temperature using a platform shaker. After the required time of shaking, the contents were allowed to settle; centrifuging when necessary. 5 μL of solution was withdrawn, diluted to 10 mL (dilution factor of 2000), and analyzed for Fe, Zn, and Mg by atomic absorption spectrometry. The amount of resin to be tested, corresponding to 0.25 mmol of functional groups (fg), was calculated from a knowledge of the functional capacity (C_f) of that resin, using formula 1. Due to limited quantities of resin, some resins tested had less than 0.25 mmol of functional (chelating) groups.

$$\text{Mass of the resin (g)} = (0.25 \text{ mmol}) / (C_f \text{ mmol fg/g}) \quad (1)$$

In the first set of experiments, 5 mL of AMD was treated using this method, and analyses for the metals were conducted after 1, 2, 4, 6, and 22 h to establish the time required to reach equilibrium. This would then be used as the treatment time in the remaining experiments. In the second set of experiments, 5 mL of unoxidized AMD (containing both ferrous (+2) and ferric (+3) ions) was used to measure the metal uptake by the resins. A third set of experiments was conducted, identical to the second, but in which the ferrous ion was oxidized to the ferric state by treatment with a stoichiometric amount of hydrogen peroxide before the AMD's treatment with the resin. The fourth set of experiments involved attempting to extract the adsorbed zinc from selected resins. Currently, only sulfuric acid has been used, though other eluents are planned. The resin, previously treated with 5 mL of AMD, was rinsed with distilled water to remove any residual AMD, then soaked in 20 mL of 4 M sulfuric acid for a few minutes. The amount of metal that was released by the resin was then measured.

The resins were evaluated using the following criteria. The **weight capacity**, C , or loading, which is the amount of metal ion (mg or mmol) adsorbed by 1 g of dry resin, was calculated. The adsorption of metal ions was indirectly measured using the difference of the initial and final concentrations of the metals in solution (measured using atomic adsorption spectrometry). The **distribution coefficient**, D , measures the partitioning of the metal between the resin and the solution. A solution-dependent value, D was found by dividing the capacity (mmol/g resin) by the equilibrium concentration (mmol/mL) (equation 2). The selectivity of the resins for zinc over iron was determined by calculating the **separation factor**, $S_{\text{Zn/Fe}}$ (equation 3). Also solution-dependent, it is the ratio of the distribution coefficient for zinc to that of iron. When it is high, the resin is selective for zinc; when it is low, the resin is selective for iron. The goal of this project is to develop resins with a high selectivity for zinc over iron.

$$D \text{ (mL/g)} = C \text{ (mmol } M_1/\text{g resin)} / [M_1 \text{ (aq) (mmol/mL)}] \quad (2)$$

$$S_{\text{Zn/Fe}} = D_{\text{Zn}}/D_{\text{Fe}} = \frac{C \text{ (mmol Zn/g resin)} \times [\text{Fe (aq)}]}{C \text{ (mmol Fe/g resin)} \times [\text{Zn (aq)}]} \quad (3)$$

Results

Equilibrium Time

The metal uptake from unoxidized AMD by some resins over time was measured (table 3). There was no significant increase in metal uptake after 2 h. Consequently, all later tests used a treatment time between 4 and 6 h.

Table 3. Metal uptake over time from 5 mL unoxidized AMD by two resins.

Resin	Quantity, g	Time, h	Fe uptake, C, mmol/g	Zn uptake, C, mmol/g	Mg uptake, C, mmol/g
1	0.625	1	0.01	0.07	0.03
		2	0.02	0.10	0.04
		4	0.02	0.10	0.04
		6	0.02	0.10	0.04
		22	0.02	0.10	0.04
2	0.250	1	0.13	0.19	0.05
		2	0.16	0.26	0.07
		4	0.18	0.27	0.07
		6	0.18	0.27	0.07
		22	0.18	0.27	0.07

Recovery of Zinc

Two resins were treated with 20 mL of 4 M sulfuric acid in order to recover the adsorbed zinc (table 4).

Table 4. Zinc recovery from two spent resins.

Resin	Amount of resin, dry weight, g	Amount of Zn adsorbed, mg	Amount of Zn released, mg	Recovery, %
19 ¹	0.22	5.90	5.00	84.7
19 ²	0.22	5.88	5.00	85.0
20 ¹	0.20	6.47	5.20	80.4
20 ²	0.20	5.88	5.00	85.0

¹ AMD with Fe⁺² and Fe⁺³.

² AMD with Fe⁺³.

Selectivity of Resins for Zinc over Iron

The distribution coefficients, ratios of zinc to iron capacity, and separation factors (Zn-Fe) for each resin tested was calculated ($S_{Zn/Fe} = D_{Zn}/D_{Fe}$) (table 5). A large $S_{Zn/Fe}$ means that the resin is selective for zinc over iron. The asterisks (*) indicate an extremely high $S_{Zn/Fe}$, whose exact value is somewhat uncertain.

Discussion

Equilibrium Time

As can be seen in table 3, the time for zinc uptake to reach its maximum was between 2 and 4 hours, depending on the resin. As a result, all tests had between 4 and 6 hour treatment times, which is estimated to have allowed all systems sufficient time to reach equilibrium.

Zinc Recovery From Resins

Two resins, 19 and 20, previously treated with AMD were regenerated by soaking for a few minutes in 20 mL of 4 M sulfuric acid (table 4). More than 80% recovery of the zinc from the loaded resins was possible. Further tests will include determining the removal of other adsorbed metal ions, as well as determining any changes to the resin. Other eluents will be tested, such as distilled water, solutions of chelating agents such as EDTA or DTPA, hydrochloric

acid, and brine. It may not be necessary to use concentrated acid. Another method of metal recovery from the resins could be electroelution (Martins, 1993).

Table 5. Distribution coefficients, capacity ratios and Zn-Fe separation factors ($S_{Zn/Fe}$).

Resin	D_{Zn} , mL/g mixed Fe ⁺² -Fe ⁺³	D_{Zn} , mL/g Fe ⁺³ only	D_{Fe} , mL/g mixed Fe ⁺² -Fe ⁺³	D_{Fe} , mL/g Fe ⁺³ only	C_{Zn}/C_{Fe} mixed Fe ⁺² -Fe ⁺³	C_{Zn}/C_{Fe} Fe ⁺³ only	$S_{Zn/Fe}$ mixed Fe ⁺² -Fe ⁺³	$S_{Zn/Fe}$ Fe ⁺³ only
1	2.3	NA	0.2	NA	4.2	NA	10.0	NA
2	6.3	6.1	1.7	0.5	1.6	5.3	3.7	12.6
3	7.7	NA	3.1	NA	1.0	NA	2.5	NA
4	8.9	NA	2.2	NA	1.7	NA	4.2	NA
5	5.0	5.7	3.2	1.4	0.7	1.8	1.6	4.2
6	3.9	NA	1.8	NA	0.9	NA	2.1	NA
7	6.8	NA	4.5	NA	0.6	NA	1.5	NA
8	3.9	2.8	1.9	0.4	0.9	3.0	2.1	7.1
9	4.4	4.7	4.1	6.2	0.5	0.3	1.1	0.8
10	7.5	7.8	2.1	1.7	1.5	2.0	3.6	4.7
11	5.0	5.3	0.7	1.4	3.1	1.6	7.4	3.7
12	13.6	10.8	10.1	2.7	0.6	1.7	1.4	4.0
13	9.4	NA	5.9	NA	0.7	NA	1.6	NA
14	7.7	14.1	10.4	8.9	0.3	0.7	0.7	1.6
15	9.1	NA	6.7	NA	0.6	NA	1.4	NA
16	15.3	16.9	5.4	6.1	1.2	1.2	2.8	2.8
17	8.5	7.6	2.4	0.5	1.5	6.8	3.6	16
18	15.6	16.1	6.2	1.9	1.1	3.5	2.5	8.4
19	9.6	10.3	0.8	4.6	5.0	0.9	11.9	2.2
20	10.5	10.1	0.1	0.2	36	21	87*	50*
21	4.4	3.7	4.1	2.9	0.4	0.5	1.1	1.3
22	0.8	3.3	1.5	5.6	0.2	0.2	0.5	0.6
23	8.7	9.4	2.6	4.0	1.4	1.0	3.3	2.3
24	2.6	2.2	4.2	4.2	0.3	0.2	0.6	0.5
25	3.0	2.3	0.1	0.1	15	12	37*	29*
26	5.5	5.9	0.1	0.1	18	19	42*	45*
27	NA	11.4	NA	14.8	NA	0.3	NA	0.8

* Notably large values with potentially large associated error; see text. NA--not available

Uptake of Metals and Selectivity

The resins were evaluated using the calculated separation factor, $S_{Zn/Fe}$ (table 5). Table 6 ranks some resins tested with regard to their separation factor. These results are for resins tested using the oxidized AMD. The symbol C_f is the functional capacity in mmol fg/g. As some of the final (equilibrium) iron concentrations were close and possibly equal to the initial concentration, within the detection limits of the atomic absorption method used to measure them, error on the large $S_{Zn/Fe}$ values marked with an asterisk (*) is itself quite large; more accurate values will be obtained in future experiments by measuring bound metals directly, following digestion of the polymer, instead of by difference as was done here. The structure of the functional group is given, with the point of attachment to the polymer through the sulfur. A comparison between the most selective resin, **20**, and some commercial resins tested is given in table 7.

The predominant trend in comparing the selectivities of each resin when treated with AMD containing the slightly soft ferrous ion (unoxidized AMD) and when treated with the oxidized AMD (no ferrous ion, all iron existed as the harder ferric ion) was that the selectivity ($S_{Zn/Fe}$ value) tended to increase (table 5). The increase of selectivity ($S_{Zn/Fe}$) when the AMD was oxidized was significant for the following resins, with as much as a five-fold increase, **17**, **18**, **8**, **2**, **12**, and **5**. Resin **19**, on the other hand, had a much better zinc selectivity using unoxidized AMD.

As a control, polyDVB, the "non-chelating" precursor to the chelating resins, was also tested. Resin **16** consisted of "inert" vinyl groups; these may have hydrolyzed to alcohol groups under aqueous acid conditions. The $S_{Zn/Fe}$ for resin **16** was not changed when oxidized AMD was used ($S_{Zn/Fe}$ 2.8).

Table 6. Ranking of resins based on separation factor ($S_{Zn/Fe}$).
(5 mL oxidized AMD used, 6 h equilibrium time)

Resin	Structure of functional group (Ps-SR)	C_f , mmol/g	$S_{Zn/Fe}$	C_{Zn} , mg/g	C_{Fe} , mg/g
20		0.11	50*	31	1
26		0.81	45*	18	<1
25		0.28	29*	7	<1
17		0.56	16	23	3
18		1.93	8.4	49	12
16		2.29	2.8	52	38
23		0.12	2.3	29	25
19		1.15	2.2	32	29
21		0.38	1.3	11	18
9		0.70	0.8	14	39
22		0.32	0.6	10	35
24		0.01	0.5	7	26

* Notably large values with potentially large associated error; see text.

As indicated by the "top three" resins (**20**, **26** and **25**, whose $S_{Zn/Fe}$'s were respectably high, table 5), it may be unnecessary to oxidize the AMD before treatment with the resins.

Since the selectivity of resin **20** was so good, future resins could be based on the aminoethanethiol functionality and derivatives thereof. The syntheses of these ligands, such as by an established method (Luhowy and Meneghini 1973), will be advantageous in this work.

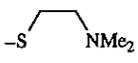
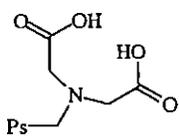
The presence of a sulfonate group ($-SO_3^-$), as in resins **19**, **22**, **23**, and the commercially-available **12** and **13**, will make the resin more water-swallowable, which can increase the efficiency of the resin.

Some resins (e.g., **19**, **20**, and **26**) were derived from known chelating agents. They all had excellent selectivity for zinc over iron; other heavy metals not analyzed in this study may have been adsorbed as well. These resins outperformed the commercial resins studied in terms of selectivity for zinc. Resins **21** and **24**, also based on known chelating groups, did not perform as well as hoped.

Analogous of the ligands of some of the more successful resins, such as **17**, **19**, **20**, **25**, and **26**, will be studied. They may be closely related, varying by substitution of a group or atom, for example, an amine for a thiol, or other nitrogen- or sulfur-containing entities. One possibility is to study the effect of the substitution of the sulfur by a nitrogen in the ring of the group from **26**; another possibility is to study the effect of replacing the amine by a thiol in **25**. The effects of ligands containing mostly sulfur, some sulfur and some nitrogen, or mostly nitrogen will be contrasted. The effect of ring-containing ligands will be studied. Ligands that are multidentate, ringed structures will also be studied; examples are sulfur- or nitrogen-containing analogs of crown ethers.

The commercial resins, **12**, **13**, **14**, **15** and **27** had low selectivities (table 5). The selectivity of **27**, as well as the capacity, strongly favored iron uptake from oxidized AMD, as would be expected for a carboxylate-containing chelating group. In comparison to the commercial resins, resins **17**, **18**, **20**, **25**, and **26** had better selectivities (oxidized AMD). Resin **20** had the best selectivity for zinc, and comparable capacity (31 mg Zn/g), despite the low amount of functional groups per gram of polymer ($C_f = 0.11$). Increasing the functionality would increase the capacity, probably surpassing those of commercial resins.

Table 7. Comparison of best experimental resin (**20**) with commercial resins.
(5 mL oxidized AMD used, 6 hour equilibrium time)

Resin	Structure of functional group	C_f , mmol/g	$S_{Zn/Fe}$	C_{Zn} , mg/g	C_{Fe} , mg/g
20		0.11	50*	31	1
12	Ps-SO ₃ ⁻ Na (commercial Dowex 50X8-100)	1.7	4.0	33	17
14	Ps-CH ₂ NMe ₃ ⁺ Cl (commercial Amberlyst)	NA	1.6	43	55
27		0.7	0.8	35	92
	(commercial Chelex-100)				

* Notably large values with potentially large associated error; see text. NA--not available

Application

A treatment process using chelating resins could consist of three stages: production of the resin by a commercial chemical manufacturer, application of the resin at the AMD site, and regeneration of the resin with metals recovery, done either on- or off- site. Resin particles could be loaded into inert plastic (polypropylene) mesh bags, which would be lowered into the AMD pond or waste stream and allowed to become saturated with metal ions, then pulled out and regenerated. The bag of regenerated resin could then be dumped back into the AMD pond for reuse. Removal of metals from an AMD solution could make it easier to recover sulfuric acid through electro-osmosis. It may be possible to make the polymer into other forms such as hollow fibers or membranes.

Conclusions

These exploratory investigations using synthetic chelating resins have shown that certain polymer-supported functional groups can serve to selectively recover zinc from synthetic AMD. Further investigations should enable the development of resins with high zinc capacities and affinities for the maximum selective recovery of zinc, leaving iron in solution. The detoxification of AMD, along with the recovery of zinc and related metals, could then be possible.

Future Work

Further work will be done in the following areas: design and synthesis of resins, testing of resins, and possible costs and application. Testing methods will use larger quantities of resins, preconditioned with sulfuric acid (pH 2), exposed to a large excess of AMD or acidic metal-containing solutions. Atomic absorption spectrometry and elemental analysis will be used to measure the metal uptakes of all metals in AMD. Methods of regeneration will be examined.

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