

## Sorption behavior of environmentally relevant metal cations of 4-vinylpyridine based resins

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### Summary

Sorption behavior of resins based on 4-vinylpyridine and N,N'-dimethylacrylamide and 2-acrylamidoglycolic acid as comonomers, compared with the crosslinked homopolymers, towards Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) was studied at different pHs depending on the metal ion. Some resins show that from pH = 1.0 or 2.0 Hg(II), Cr(III), and Cd(II) were sorbed significantly from an aqueous solution of 1.0 g/L. Hg(II) and Cr(III) were eluted significantly in acidic media.

### Introduction

The rising cost of disposal fees, more stringent regulations, and the value of some recoverable metals have encouraged all metal waste generators to consider processes and plant designs for zero metal discharge. This in turn requires that valuables and/or toxic metal ions be selectively recovered from often dilute process effluents and concentrated in relatively pure form to permit resale, reuse or recycle. The combination of low concentration goals for toxic heavy metal ions such as Pb(II) and Cd(II) and selectivity requirements is out of the practical range most conventional treatment technologies and sets challenging goals for metal separations technologies under developments.

According to that, chelating resins have many practical applications in water treatment, environmental protection, chemical analysis, etc. The synthesis and applications of the chelating resins have been published extensively (1-11). The chelating sorbents are assumed to form chelate rings in the sorbent phase during the sorption of metal ions. The possibility of forming chelate rings in the sorbent phase is affected by different factors such as the nature of the chemically active groups capable of complexation, the physical nature of the polymeric matrix, steric factors, sorption conditions, etc.(12). On the other hand, the application of commercial ion-exchange resins to metal ion recovery from aqueous solutions is a concept which has received extensively study (13-15). The ion-exchange effectiveness of a strong acid resin can be offset by a lack of selectivity, specially when the metal ion of interest is in trace amounts (16). Selectivity can be enhanced with the weak acid cation-exchange resins wherein carboxylate groups are linked to either a styrenic or ethylenic backbone (17) but it leads to a decreased ability to exchange in the acidic pH region.

Consequently, in the current work 2-acrylamidoglycolic acid and a N,N'-dimethylacrylamide were copolymerized separately with 4-vinylpyridine to obtain chelating resins. The binding ability for environmentally relevant metal ions such as Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) ions by batch equilibrium procedure was

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assayed. The chelating properties were compared with the corresponding homopolymers, and the recovery of the resin was assayed in acidic media.

## Experimental Part

### *Materials*

All chemicals 4-vinylpyridine (4-VPy), 2-acrylamidoglycolic acid (2-AmGA), N,N'-dimethylacrylamide (DmAA), cadmium chloride, zinc chloride, lead(II) acetate trihydrate, mercury(II) nitrate, chromium(III) nitrate nonahydrate were analytical reagent-grade and obtained from either Aldrich, Fluka or Merck. All solutions and standards were prepared using deionized water (18 M $\Omega$  cm resistance).

### *Synthesis of the sorbents*

The reference homopolymers of DmAA (A), 4-VPy (B), 2-AmGA (C) and the copolymers poly(4-VPy-co-DmAA) (D) and poly(4-VPY-co-2 AmGA) (E) were obtained by using a method previously described (18).

4-VPy (0.2 mol) was polymerized in bulk with AIBN (1 mmol) and a mixture of isomeric divinylbenzenes (DVB) (12 mmol). 2-AmGA (0.2 mol) as well as DmAA (0.2 mol) were polymerized with ammonium persulfate (APS) (1 mmol) and N,N'-methylene-bis-acrylamide (MBA)\* (12 mmol). 4-VPy (0.1 mol) and 2-AmGA (0.1 mol) were copolymerized in presence of APS (1 mmol) and MBA (12 mmol). 4-VPy (0.1 mol) and DmAA (0.1 mol) were copolymerized in presence of AIBN (1 mmol) and DVB (12 mmol).

All the resins were washed repeatedly with water, and dried in vacuum until constant weight. The dried resins were ground and the 180-250  $\mu$ m particle size fraction was used throughout the experiments.

### *Sorption of metal ions on the resins*

A batch type equilibrium procedure was used to determine the metal ion uptake from aqueous solution by the resin. The pH of the aqueous solution varied from 0 up to 5 depending on the metal ion. The two phases were shaken in a mechanical shaker at room temperature (c.a. 20°C) for 1 h. After shaking, the phases were separated, and the supernatant solution was analyzed for Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) by using atomic absorption spectrophotometry. The amount of metal ion in the supernatant subtracted from the initial amount added gave the amount of metal ion adsorbed on the resin.

### *Desorption of metal ions*

Desorption assays were carried out with Cd(II)-, Hg(II)- and Cr(III)- loaded resins at maximum capacity. The ions were eluted by shaking 0.1 g of the loaded resin with 10 ml, of 1M, 2M, and 3M HNO<sub>3</sub> for 1 h. The resin was separated by filtration and the metal ions were analyzed in the supernatants as above.

### *Measurements*

Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) were analyzed by a Perkin Elmer 1100 atomic absorption spectrophotometer. pH measurements were carried out with a digital Exttech Microcomputer pH-meter. FT-IR spectra were recorded by a Magna Nicolet 550 spectrophotometer.

\* Systematic name: N-(acrylamidomethyl)acrylamide

## Results and Discussion

### *Synthesis of the sorbents*

All resins were synthesized by radical homopolymerization or copolymerization and were completely insoluble in water accordingly to the literature (18) (see Table 1).

**Table 1.** Start reagents and acronyms of the resins.

| Acronyms | Monomer 1 | Monomer 2 | Initiator | Crosslinker | Yield(%) |
|----------|-----------|-----------|-----------|-------------|----------|
| A        | DmAA      | -         | APS       | MBA         | 88       |
| B        | 4-VPy     | -         | AIBN      | DVB         | 91       |
| C        | 2-AmGA    | -         | APS       | MBA         | 95       |
| D        | 4-VPy     | DmAA      | AIBN      | DVB         | 80       |
| E        | 4-VPy     | 2-AmGA    | APS       | MBA         | 92       |

### *Sorption capacities for metal ions (batch method)*

It is well known that pH has two kinds of influence on metal uptake: an effect on the solubility and speciation of metal ion in aqueous solution, and on overall charge of the sorbents. Accordingly, the affinities of these resins for Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) were investigated by a batch operation at different pHs as outlined above. Unbuffered systems were used because it is known that buffers complex the metal ions causing a shift in equilibrium other than that produced by the acid. The meq of the metal ions taken up by the resins, as a function of the initial pH are reported in Table 2 for each resin under comparable initial conditions.

Examination of the uptake data by the resins shows that in the high acidic media (pH=0) only Cr(III) is highly retained by resin **D**. This is an unexpected result due to the low retention ability of resins **A** and **B** in the whole pH range studied. Moreover, it is known that Cr(III) has a great tendency to form complexes where the sixfold coordination is the most common and occurs only in one geometric form, the octahedral. The more stable complexes are those where chromium is bonded to nitrogen as in the pyridine moieties in **B**, **D** or **E**. The chromium uptake by these resins shows that DmAA contribute to enhance its retention at this lower pH, whereas the 2-AmGA become influent at pH 2. In consequence, DmAA, as well as 2-AmGA must contribute to the necessary flexibility, allowing the chains to acquire the best conformation needed by Cr(III). Resin **E** contains pyridine and carboxylic moieties as coordinating groups which would interact with the metal ion at the lower pH, but being favoured the collaboration of each other for the polymer-metal complexation at the higher pH, here it could be in the presence of a synergic effect. It was also observed for cadmium(II) by water-soluble poly(acrylic acid-co-acrylamide) (19). It is readily seen that Cd(II), Pb(II), and Zn(II) ions are retained on resin **C** at pH 3.0 due to the increment of the availability of carboxylate groups for complexation. Cadmium(II) and mercury(II) are significantly retained on resin **B** at pH 1.0 but on resins **D** and **E** the retention is lower, showing that there is no contribution of DmAA or 2-AmGA to enhance the uptake of these metal ions.

Resin **B** would show a selectivity toward Cd(II) from a mixture Cd(II)-Cr(III).

It is possible to discard the effect of the anion of the metal salt. However, the retention of the metal ions could not be significantly affected under these experimental conditions, particularly pH and concentration. It is due to that the respective free ions are predominant at the pH range.

**Table 2.** Metal ions uptake (meq/g) by the resins as a function of pH. Resin (0.1 g) in 10 mL aqueous solution (1g/L), 25°C for 1 h.

| Resin                      | pH values |      |      |      |      |      |
|----------------------------|-----------|------|------|------|------|------|
|                            | 0         | 1    | 2    | 3    | 4    | 5    |
| <b>Cd(II)</b>              |           |      |      |      |      |      |
| <b>A</b>                   | 0.02      | 0.14 | 0.04 | -    | 0.04 | -    |
| <b>B</b>                   | 0.16      | 1.14 | 0.37 | -    | -    | -    |
| <b>C</b>                   | -         | 0.00 | -    | 0.84 | -    | 0.18 |
| <b>D</b>                   | 0.05      | 0.18 | 0.21 | -    | 0.21 | -    |
| <b>E</b>                   | 0.07      | -    | 0.04 | -    | 0.12 | -    |
| <b>Cr(III)</b>             |           |      |      |      |      |      |
| <b>A</b>                   | 0.17      | 0.58 | 0.40 | -    | 0.40 | -    |
| <b>B</b>                   | -         | 0.00 | 0.46 | -    | 0.35 | -    |
| <b>C</b>                   | -         | 0.00 | -    | 1.70 | -    | 2.00 |
| <b>D</b>                   | 4.20      | -    | 1.60 | -    | 1.00 | -    |
| <b>E</b>                   | 0.17      | -    | 3.80 | -    | 1.60 | -    |
| <b>Hg(II)<sup>a)</sup></b> |           |      |      |      |      |      |
| <b>A</b>                   | 0.23      | 0.36 | 0.40 | -    | -    | -    |
| <b>B</b>                   | 0.18      | 0.94 | 0.62 | -    | -    | -    |
| <b>C</b>                   | -         | 0.00 | 0.07 | -    | -    | -    |
| <b>D</b>                   | 0.27      | 0.71 | 0.61 | -    | -    | -    |
| <b>E</b>                   | 0.05      | 0.25 | 0.50 | -    | -    | -    |
| <b>Pb(II)</b>              |           |      |      |      |      |      |
| <b>A</b>                   | 0.11      | 0.09 | 0.09 | -    | 0.14 | -    |
| <b>B</b>                   | 0.07      | 0.06 | 0.17 | 0.17 | -    | -    |
| <b>C</b>                   | -         | 0.03 | -    | 0.95 | -    | 0.95 |
| <b>D</b>                   | 0.09      | 0.14 | 0.14 | -    | 0.14 | -    |
| <b>E</b>                   | 0.06      | -    | 0.10 | -    | 0.31 | -    |
| <b>Zn(II)</b>              |           |      |      |      |      |      |
| <b>A</b>                   | 0.00      | -    | 0.09 | -    | 0.12 | -    |
| <b>B</b>                   | 0.03      | 0.49 | 0.28 | -    | -    | -    |
| <b>C</b>                   | -         | 0.00 | -    | 0.98 | -    | -    |
| <b>D</b>                   | 0.00      | 0.15 | 0.21 | -    | 0.15 | -    |
| <b>E</b>                   | 0.03      | -    | 0.03 | -    | 0.09 | -    |

<sup>a)</sup> Due to the precipitation of the corresponding Hg(II) oxide, sorption up to pH 2 was tested

At pH 2.0 resin **E** retains significantly Cr(III) and Hg(II) among all the metal ions studied.

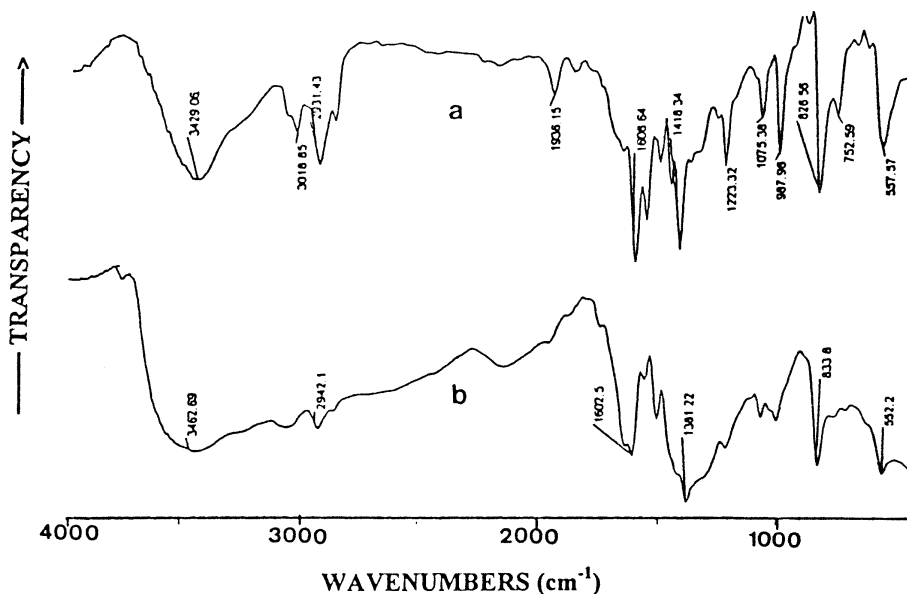
The maximum retention capacity (MLC) was determined for those resins with higher retention values as a function of pH. These results are summarized in Table 3. It is noteworthy the high values of MCL of the resins **B** and **D** for mercury(II) at pH 1.0, but it decreases strongly at pH 2.0. On the other hand, for the resin **D**, the MCL for chromium(III) is 5.7 meq/g at pH 0.0. In all the cases the MCL values are significantly higher than those corresponding to the sorption pH which correspond to those obtained after one contact. In contrast, the MCL values were obtained after three successive contacts with the corresponding fresh solution.

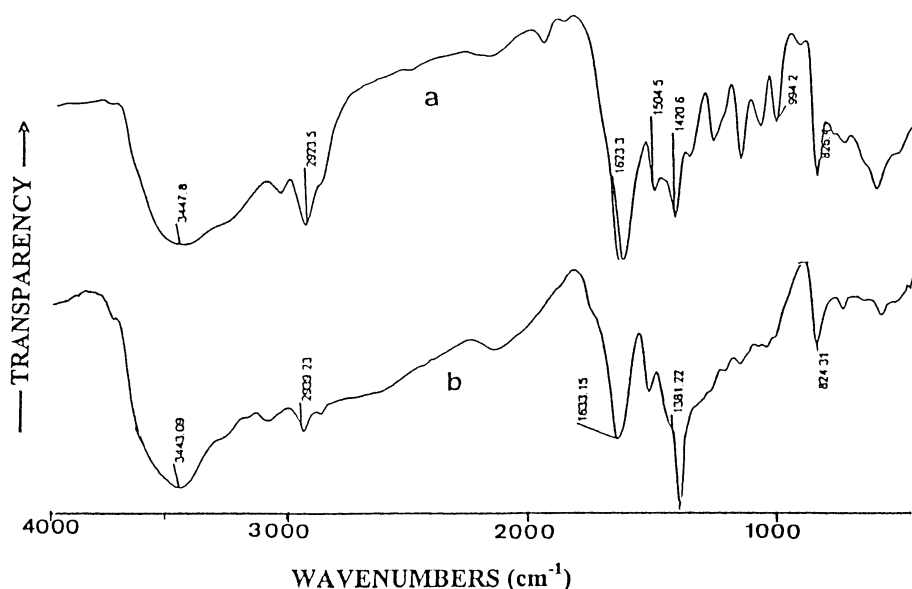
**Table 3.** Maximum capacity of load(MCL)[meq/g of the resin] at different pH.

| pH values      |     |     |     |
|----------------|-----|-----|-----|
| Resin          | 0   | 1   | 2   |
| <b>Cd(II)</b>  |     |     |     |
| <b>B</b>       | -   | 3.2 | -   |
| <b>Cr(III)</b> |     |     |     |
| <b>D</b>       | 5.7 | -   | -   |
| <b>E</b>       | -   | -   | 3.4 |
| <b>Hg(II)</b>  |     |     |     |
| <b>B</b>       | -   | 6.8 | 2.3 |
| <b>D</b>       | -   | 4.3 | 1.2 |
| <b>E</b>       | -   | -   | 0.5 |

*FT-IR spectroscopy*

The FT-IR spectra of resin **B** unloaded (Figure 1a) and loaded with mercury(II) (Figure 1b) show the C-H heteroaromatic stretching vibrations of the pyridinic groups above  $3000\text{ cm}^{-1}$ . Moreover, the ring-stretching absorption bands that occur in the region between  $1600\text{ -}1300\text{ cm}^{-1}$ , which involves stretching and contraction of all the bonds in the ring and interaction between these stretching modes, are increased when complexation occurs. On the other hand, the corresponding FT-IR spectra of resin **D** (Figure 2a and 2b) show the C-H stretching absorption band as above but when complexation occurs the C=O stretching absorption (amide I band) in  $1623.3\text{ cm}^{-1}$  is decreased indicating involvement of the amide group in coordinating with Hg(II).

**Figure 1.** FT-IR spectra of resin **B**, unloaded (a) and loaded with Hg(II) (b)



**Figure 2.** FT-IR spectra of resin **D**, unloaded (a) and loaded with Hg(II) (b).

#### Elution assays

In order to recover the resins, nitric acid solutions at different concentrations were added to cadmium(II), chromium(III) or mercury(II) - loaded resins being mercury(II) almost quantitatively eluted at higher concentrations of the acid, whereas cadmium(II) is not eluted significantly as it is seen in table 4. This can be advantageous if a mixture of Cd(II)-Hg(II) must be separated, where Hg(II) can be selectively eluted after retention of both metal ions. On the other hand, it is also shown in table 4 that chromium(III) is partially eluted in acidic media.

**Table 4.** Elution (%) of the metal ions by HNO<sub>3</sub>. Amount of the loaded resin 100 mg, contact time 1 h.

| Eluents        |    |                     |                     |                     |
|----------------|----|---------------------|---------------------|---------------------|
| Resin          | pH | 1M HNO <sub>3</sub> | 2M HNO <sub>3</sub> | 3M HNO <sub>3</sub> |
| <b>Cd(II)</b>  |    |                     |                     |                     |
| <b>B</b>       | 1  | 0                   | 0                   | 4                   |
| <b>Cr(III)</b> |    |                     |                     |                     |
| <b>D</b>       | 0  | 28                  | 72                  | 78                  |
| <b>E</b>       | 2  | 10                  | 47                  | 50                  |
| <b>Hg(II)</b>  |    |                     |                     |                     |
| <b>B</b>       | 1  | 27                  | 83                  | 98                  |
|                | 2  | 45                  | 88                  | 93                  |
| <b>D</b>       | 1  | 72                  | 74                  | 89                  |
|                | 2  | 43                  | 98                  | 87                  |
| <b>E</b>       | 2  | 38                  | 46                  | 82                  |

## Conclusions

The resins containing 4-VPy and DmAA (**D**) or 2-AmGA (**E**) showed a strong capability to bind chromium(III) at pH 0 and 2 respectively. Resin **D** shows a remarkable selectivity for chromium(III) toward cadmium(II), lead(II), and zinc(II) at pH 0, where a synergetic behavior is suggested. The maximum capacity of resins **B** and **D** for mercury(II) is strongly supported by FTIR spectra, where 4-VPy moieties participate in the formation of a stable complex in **B**, but another complex with a lower stability is observed with resin **D** because of the influence of the DmAA moieties. At higher pH values, resin **C** shows a higher retention for the metal ions studied due to the increment of the carboxylate groups which participate in the complex formation. Nitric acid has been probed to be a suitable eluent for mercury(II) and in some extent for chromium(III), from the corresponding loaded resins.

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