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Selectivity of Amidoxime Polymers for the Sorption of Gallate

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TECHNICAL NOTE

Selectivity of Amidoxime Polymers for the Sorption of Gallate

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ABSTRACT

The sorption of gallium from alkaline solution using amidoxime resins or polyampholytes was studied. Gallium is extracted by amidoxime resins, even from Bayer leachates, but amidoxime polyampholytes are limited to dilute alkali hydroxide solution up to 5 M. The elution of gallium runs well with acetylacetone.

Key Words. Ion exchange; Amidoxime resins; Amidoxime polyampholytes; Bayer leachates; Sorption of gallate and aluminate

INTRODUCTION

An important unsolved problem has been the recovery of gallium from the strongly alkaline leachates of the Bayer process. In addition liquid–liquid extraction (1), chelating resins containing amidoxime anchor groups have shown promising results (2). Duolite ES 346 (Rohm & Haas) is a resin of this type. While gallium can be well sorbed, the resin has no ability to extract aluminum from such solutions. Polyelectrolytes containing amidoxime and hydroxamic acid groups are another type of agent. They result from the modification of polyacrylonitrile by hydroxylamine

(3). The sorption and elution behaviors of amidoxime polymers were studied to continue earlier work.

EXPERIMENTAL

Amidoxime Resin

The chelating resin Duolite ES 346 (Rohm & Haas) was used. The resin was swollen for 1 day in water, and then it was treated successively with 1 M HCl and 1 M NaOH. The treatment with HCl and NaOH was repeated twice. The ion-exchange experiments were conducted in columns containing 20 or 5 mL resin in a fixed bed. The flow rate during loading and elution was 1 mL/min.

Amidoxime Polyampholyte

GoPur 3000 is an acrylamidoxime–acrylhydroxamic acid copolymer which can be used as a flocculant to separate metals from wastewater. It is soluble in acidic and alkaline solutions. For batch experiments, a solution of the polymer (w = 1%) in 0.1 M NaOH was reacted with calcium chloride until precipitation was complete. One liter of this precipitate corresponds to 3.9 g dry weight. For batch experiments, 100 mL of the moist product were used at a time.

Metal Solutions

For the preparation of test solutions, $Al(NO_3)_3 \cdot 9H_2O$ and $Ga(NO_3)_3 \cdot 9H_2O$ were dissolved in separate NaOH solutions of the desired concentration. The metal concentrations were standardized to 1 mmol/L.

Metal Determination

Aluminum and gallium were determined by AAS (1100 B, Perkin-Elmer). In the case of high hydroxide concentrations, the solutions were diluted before analysis.

RESULTS AND DISCUSSION

Figure 1 shows the sorption of gallate and aluminate (equal concentrations) by Duolite ES 346 from a strongly alkaline solution (c_{NaOH} = 1 M). Whereas gallate is well bound, aluminate is not sorbed by the resin. Loading of the resin by passing sodium hydroxide solution (42%) causes a pink discoloration. Because Bayer leachates contain a large excess of aluminate over gallate, the sorption was studied at a concentration ratio

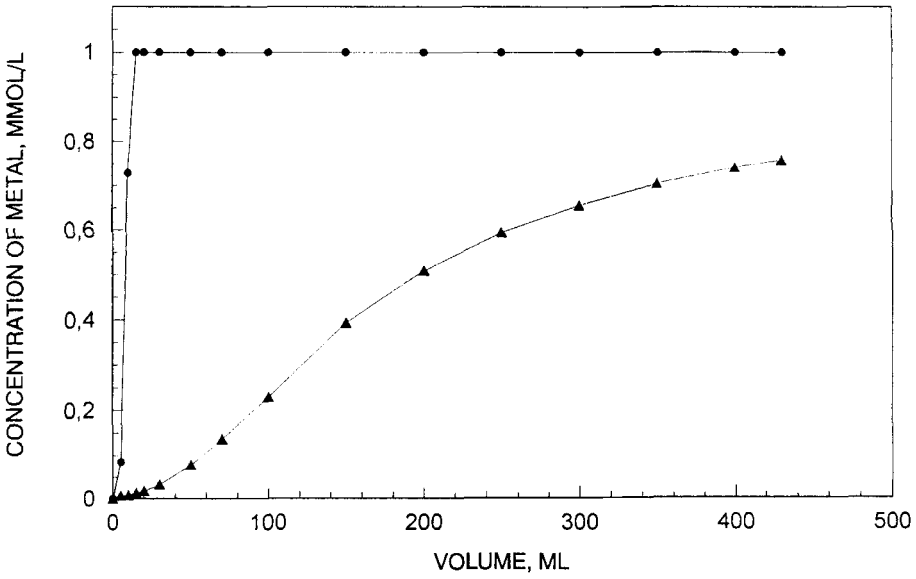

FIG. 1 Sorption of gallate and aluminate from alkaline solution: 20 mL resin, $c_{OH^-} = 1$ M, $c_{Ga} = c_{Al} = 1$ mmol/L, (▲) gallate, (●) aluminate.

of Al:Ga = 100:1. This results are given in Fig. 2. It can be seen that after passing 22.5 bed volumes, only about 1% of the aluminum but 52.4% of the gallium are sorbed, and loading is not yet finished. This shows that the resin is also suitable for extracting gallate from the original Bayer leachates.

During the elution of gallium from resin, acidic solutions must be avoided because of the limited stability of the amidoxime group under these conditions (2). A good eluent is acetylacetone (Fig. 3). The eluate contains only traces of aluminum and can be easily reworked. The gallium is extracted from the eluate with chloroform and remains behind as the acetylacetonate complex after the solvent is stripped.

The resin can be repeatedly used for practical applications. If a solution of aluminate and gallate ($c_{Al} = c_{Ga} = 1$ mmol/L) in 1 M NaOH passes the resin, it is loaded by 46.3% with gallate after 86 bed volumes. By elution with 0.1 M acetylacetone (400 mL), 75% of the gallium is recovered. The resin is again available for the exchange process. The loading runs as are described before, but gallium breaks through somewhat earlier.

The selectivity of the amidoxime group for the sorption of gallium prompted us to extend our studies to a macromolecular polyelectrolyte

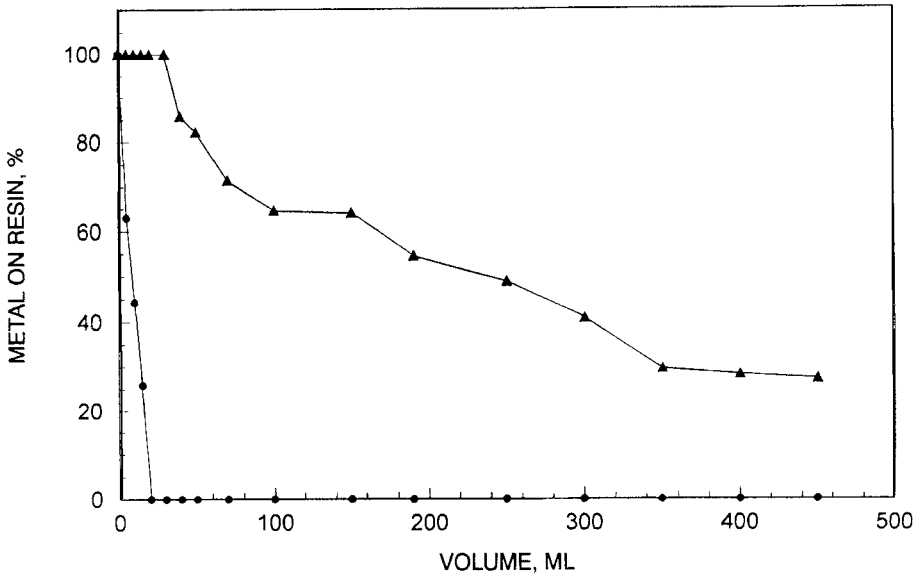

FIG. 2 Sorption of gallate and aluminate from alkaline solution: 20 mL resin, c_{Ga} = 1 mmol/L, ω_{OH^-} = 42%, $c_{Al}:c_{Ga}$ = 100:1, (▲) gallate, (●) aluminate.

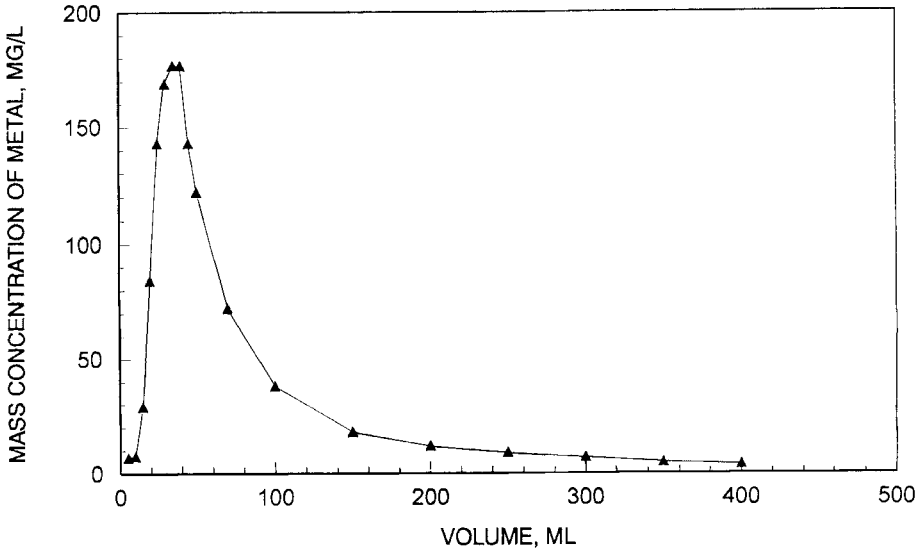

FIG. 3 Elution of gallium with acetylacetone from amidoxime resin, c_{eluent} = 0.1 M.

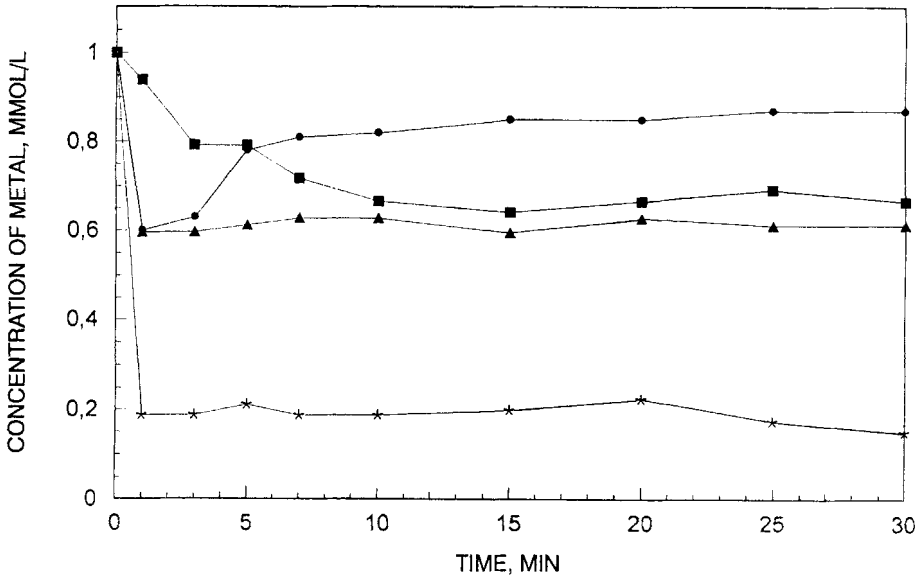

FIG. 4 Sorption of gallate and aluminate from alkaline solutions with amide oxime polyampholyte GoPur 3000, $c_{Ga} = c_{Al} = 1$ mmol/L, (*) gallate (1 M NaOH), (▲) gallate (5 M NaOH), (■) gallate (42% NaOH), (●) aluminate (5 M NaOH).

having amidoxime and hydroxamic acid groups. This polymer is known to form complexes with different metal ions. Because it is soluble in sodium hydroxide solution, it was transferred into the insoluble calcium compound and then checked for the sorption of gallium following the batch method. Figure 4 shows that gallium is well extracted from alkaline solution, but the extraction rate decreases with increasing hydroxide concentration. The high basic strength of Bayer leachates prevents the extraction of gallium by the polymer as well as the separation of gallium and aluminum.

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