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MAGNETIC ADSORBENTS FOR ACTINIDE AND HEAVY METAL REMOVAL FROM WASTE WATER

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ABSTRACT

Magnetic adsorbents can be applied to the treatment of waste water in various physical forms. For example, barium ferrite ($\text{BaO} \cdot \text{Fe}_2\text{O}_3$) has been used successfully as powder, granules or pellets. Iron ferrite, or magnetite, a naturally occurring ore, can also be used in much the same manner. However, natural magnetite needs activation to have the same capacity as freshly prepared ferrite. Furthermore, ferrites have been used solely in a batch mode because of their finely divided nature. To permit utilization of activated magnetite in a column mode with good water flow-through properties, magnetic resins were prepared. In this work, the authors discovered a synergistic effect in using the magnetic resin in a column mode in conjunction with an external magnetic field for concentration of plutonium and americium from waste water. Thus ferrites in a column mode surrounded by a magnetic field greatly surpasses the metal removal capacity of ferrite used in a batch mode.

I. INTRODUCTION

Magnetic adsorbents have been used to separate a wide range of substances such as dissolved metal species, particulate matter, and

organic and biological materials; however, they have been used almost exclusively for metal waste treatment applications (1,2). For instance ferrites make excellent magnetic adsorbents for the separation of hazardous metals (cadmium, lead, mercury, etc.) and actinide elements (americium, plutonium and uranium) from waste water (3,4).

Ferrites are a class of mixed valence iron oxide compounds having the crystal structure of spinel, MgAl_2O_4 . Iron atoms in iron ferrite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), or magnetite, can be replaced by many other metal ions without seriously altering the spinel structure.

Ferrite treatment has a number of advantages over conventional flocculant precipitation techniques for trace metal ion removal from waste water. Ferrites are crystalline materials which can be more readily filtered and their ferromagnetic character allows for their separation from solution by magnetic means as well. The ferrite method is not affected by high salt concentrations, and most trace metal ions can be effectively removed in one step.

The adsorption mechanism of ferrite occurs through metal hydroxide species. In alkaline solution, most metal ions form insoluble species which may be complexed with additional

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hydroxide ions, depending upon the pH of the solution and the chemistry of the metal. Hydroxide ions are strongly adsorbed onto the surface of ferrite particles, so that metal ions can bond to the ferrite surface through the hydroxide ions to which they are bound. This mechanism is consistent with the phenomenon that alkali, alkaline earth and other metals, which do not form insoluble hydroxides, are not removed from solution by ferrites. Metals which form soluble hydroxide complexes at high pH, such as aluminum and zinc, also are not affected by ferrite.

It is known that ferrites can be applied to the treatment of waste water in various physical forms. Natural magnetite needs activation to have the same capacity as freshly prepared ferrite. The authors have found that magnetite ore can be effectively activated by various treatments to increase its surface area and adsorptive characteristics, and we have also discovered a synergistic effect in using supported ferrites in a column mode with an external magnetic field for concentration of plutonium and americium from waste water. In this work a magnetic absorbent was prepared by attaching activated magnetite to the outer surface of resin beads (to freely adsorb actinide ions) while the interstices between the beads promote good flow-through properties (5). We also compared the magnetic resin to similar resin beads (without magnetite) for actinide removal.

II. EXPERIMENTAL

A. Resin Preparation

The magnetic polyamine-epichlorohydrin (MPE) resin beads were synthesized with activated ferrite particles attached to the outer bead surfaces (6,7). This was done in a two step procedure. In the first step, 1.7 moles

(103 g) of aqueous ammonia solution (28%) were placed into a 1-L, 3-necked flask. The flask was equipped with a mechanical stirrer, a thermometer, and a dropping funnel (125-mL). One mole (92.5 g) of epichlorohydrin was placed into the dropping funnel and added dropwise to the stirred (500 rpm) aqueous ammonia solution. The epichlorohydrin was added over a 1-hour period with the rate of addition sufficient to maintain an exothermic reaction temperature of 90 °C. At the end of the 1-hour period, a clear, transparent polymer (ammonia-epichlorohydrin) was removed and cooled to ambient temperature (23 °C). Next, 95.0 g of the previously prepared ammonia-epichlorohydrin polymer, 58.0 g polyethylencimine (10% aqueous solution), and 9.0 g of the wet, activated ferrite (in this case, magnetite) were added to a 1-L, 3-necked flask that contained 150 mL of toluene and 4.5 g Aerosol™ GPG surfactant. The flask was equipped with a heating mantle, a thermometer, a mechanical stirrer, a Friedrichs™ condenser (350-mm), and a Dean & Stark™ water trap (20-mL).

The above mixture was next stirred for 5 minutes (1700 rpm) and then an additional 5 g of epichlorohydrin was added to the flask. The temperature was raised to 85 °C and the mixture allowed to stir (1000 rpm) while an azeotropic mixture of water and toluene were refluxed. Additional toluene (350 mL) was added as needed. The refluxing was continued for 4.5 hours and the water removed as necessary from the Dean and Stark trap. At the end of the heating period, the MPE resin product was cooled, filtered through Whatman No. 41 (20- to 25- μ m) filter paper, air dried, and sieved.

Non-magnetic, polyamine-epichlorohydrin resin was also synthesized by following the same procedure. In this case, no ferrites were used in the resin synthesis.

B. Column Preparation

The upper portion of a glass, chromatographic column (19-mm i.d. x 25-cm) was packed with a small plug of glass wool and a 10-cm plug of fine, No. 431 stainless steel wool and placed (with the bottom portion of the stainless steel wool) between the pole faces of an electromagnet. The bottom and top of the column was fitted with a stop-cock and rubber stopper with exit tube, respectively. Tygon tubing was attached to both ends of the column.

Next, the magnetic polyamine-epichlorohydrin (MPE) resin was activated by stirring the MPE resin with a solution of barium hydroxide (2.6 mmol per gram of magnetite) for 10 minutes at ambient temperature. The excess barium hydroxide solution was then decanted and sodium hydroxide solution (pH 12.0) was added to the wet MPE resin. This MPE slurry was then pumped (up-flow at 10 mL per minute via a peristaltic pump) into the glass column while a field strength of 0.3 Tesla (3,000 Gauss) was applied to the electromagnet. The experimental set-up is shown in Figure 1.

Figure 1. Column System

III. RESULTS AND DISCUSSION

Ferrites have been used effectively for actinide removal, but in a batch mode. For example, two grams of magnetite (when used alone) were required to treat one liter of waste water and lower plutonium concentration from 10^{-4} to 10^{-8} g/L (1). Typically, 650 grams of magnetite were required to lower plutonium from 10^{-4} to 10^{-8} g/L in 325 liters of water. However, as shown below, only 20 grams of

the magnetic resin were needed to achieve similar results.

Twenty grams of MPE resin (<0.125- to 0.063-mm) were evaluated for plutonium and americium removal from water at pH 12.0 (column mode). Representative breakthrough curves are shown in Figures 2 and 3. A total of 341 L of actinide solution (1.28×10^{-4} g/L plutonium-239 and 3.57×10^{-7} g/L americium-241) were processed through the MPE

Figure 2. Plutonium Removal Via MPE Resin

Figure 3. Americium Removal Via MPE Resin

resin bed (up-flow) at 3.5 mL/min/cm². The results show that 325 L of actinide solution were lowered to 2.77×10^{-8} g/L plutonium and 7.17×10^{-10} g/L americium before the plutonium activity in the effluent started to increase. This translates to 4.16×10^{-2} grams of plutonium and 1.16×10^{-4} grams of americium which were sorbed from 325 liters of water. This represents treating 8,550 liters of contaminated water with one liter of MPE resin.

For comparative purposes, the polyamine-epichlorohydrin (PE) resin (no magnetite) was compared to MPE resin for removal from water at pH 12.0 (column mode). The breakthrough curves are shown in Figure 4. Fourteen liters of actinide solution (1.16×10^{-4} g/L plutonium) were pumped (up-flow) through 20 grams of the PE and MPE resins (0.125- to 0.063-mm) at 3.5 mL/min/cm². The column effluent was then filtered through Whatman No. 41 (20 to 25- μ m) filter paper to ensure complete removal of the PE resin particles.

Figure 4. Plutonium Removal Via MPE and PE Resin in a Magnetic Field

The results show that there is no significant adsorption of plutonium on the PE resin in the presence of a magnetic field.

A similar experiment was performed using MPE resin (0.125- to 0.063- μ m) and a plutonium feed of 1.16×10^{-4} g/L. The effluent fractions were filtered through Whatman 42 filter paper prior to alpha counting. The results (Figure 5) show the effect of the magnetic field being shut off after approximately four liters of feed were passed.

Figure 5. Magnetic Effect on Plutonium Removal Via MPE Resin

The above results show that improved water decontamination can be accomplished using the magnetic resin in the presence of a magnetic

field, as compared with water decontamination methods employing ordinary ion exchange resins or ferrites taken separately. The results also show the effect of the external magnetic field on enhanced actinide breakthrough capacities.

IV. CONCLUSIONS

An apparent synergistic effect between polymers containing ferrites and a magnetic field yields enhanced capacity for actinide removal from water as compared to the batch mode. The magnetic polymer materials can be used to remove heavy metals and actinides from a wide variety of aqueous waste solutions; this is based on well known metal adsorptive properties of various ferrites (2). The magnetic polymers may be regenerated and reused thus providing a recovery material for heavy metals and actinides, but more studies are required to optimize the process.

REFERENCES

1. T. E. Boyd and R. L. Kochen, Ferrite Treatment of Actinide Waste Solutions: Continuous Processing of Rocky Flats Process Waste, U.S. DOE Rept. RFP-3476, Rockwell International, Rocky Flats Plant, Golden, CO, March 18, 1983.
2. T. E. Boyd, M. J. Cusick and J. D. Navratil, "Ferrite Use in Separations Science and Technology," in *Recent Developments in Separation Science*, Vol. VIII, CRC Press, 1986.
3. R. L. Kochen, Actinide Removal From Aqueous Solution With Activated Magnetite, U.S. DOE Rept. RFP-4100, Rockwell International, Rocky Flats Plant, Golden, CO, August 10, 1987.
4. J. D. Navratil, Removal of Impurities from Metal Feed Solutions and Purification of Same Using Ferrites and Activated Magnetite, Australian Patent Application PJ0198, August 8, 1988.
5. R. L. Kochen and J. D. Navratil, Removal of Radioactive Materials and Heavy Metals From Water Using Magnetic Resin, U.S. Patent Application S-75,566, January 21, 1992.
6. C. A. Feldt and G. T. Kekish, Weakly Basic Anion Exchange Resins, U. S. Patent 3,092,617, 1963.
7. N. V. Blesing, et al., Some Ion-Exchange Processes For Partial Demineralization, in *Ion Exchange in the Process Industries*, Society for Chemical Industry, London, 1979.

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