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Acid–Salt Separation by Selective Adsorption with Ion-Exchange Resins

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ABSTRACT

A separation technique based on the selective adsorption characteristics for an acid–salt mixture on an anion-exchange resin was used to separate acid and salt from solution. Its application can lead to the recovery and reuse of the waste acid solution in such metallurgical process as steel pickling and mineral extraction. Experimental studies were carried out in this work. Concentrated nitric acid and cuprous nitrate were treated with the strong anion-exchange resin Dowex 1. In column experiments the concentrated acid solution used was about 3 N and the cuprous nitrate concentration about 15 to 25 g/L. After the treatment, about one-fifth to one-third of the treated waste solution can be recovered and reused.

INTRODUCTION

The application of preferential adsorption of acid over salt of an acid–salt mixture on an anion-exchange resin is an effective method for salt and acid separation. The process known as "acid retardation" (1) can be utilized in a large number of industries. In water treatment or water purification by ion exchange, the used regenerant operating in an acid cycle can be treated to recover the pure acid for reuse. In the mining industry the concentrated acid solution used to extract precious metals from ores can also be processed by the acid retardation technique to recover and recycle the acids as solvents. In metallurgical processes the pickling and surface finishing operation results in large quantities of concentrated acids which are contaminated with irons and other metallic elements. Acid retardation is an ideal method of treating these types of waste products by separating acids and the contaminated metallic ions. In the last two decades there has been renewed interest in this novel separation technique. In the industry, Eco-Tec (2) fabricated a device known as an APU (acid purification unit) for the recovery of concentrated acids from contaminated solutions in the metal finishing process. Lancy et al. (3) designed and operated a moving bed for recovering aluminum from phosphoric acid. A US patent by Burke and Moore (4) also proposed use of the acid retardation method for recovering HCl from the waste regenerant solution in an ion-exchange process. The most recent extensive studies on the acid retardation technique come from Germany. In two successive papers, Gotzelmann et al. (5, 6) studied the application of this method on various acid systems, including sulfuric, nitric, hydrochloric, phosphoric, and hydrofluoric acid. The metallic ions considered included iron, copper, nickel, cobalt, and zinc. In this study we will report on the experimental work of separation of cuprous nitrate from nitric acid solution.

OBJECTIVE

The separation of a acid–salt mixture is made possible by the different degrees of preference of sorption on an anion exchanger. Since the mixtures to be treated are very concentrated (most of the applications are directed toward the separation of salt and acid in concentrated solution), the strong base resin Dowex 1 was used throughout the study. The primary aim of this study is to investigate the extent of separation between acid and salt in the mixture. The other important factor to be examined is the amount of resin required per unit volume of solution treated per cycle. Equally important is to find out what fraction of the treated solution, which consists mostly of acid with a small amount of metallic elements, can be recycled and reused. The amount of elutant, which is water, used in the elution was also studied to examine the effect of dilution on the product concentration and the elution efficiency.

EXPERIMENTAL

Column Experiments

A cylindrical glass tube with an inside diameter of 1.5 cm was used for the column experiments. Before preparing the resin bed for the acid retardation study, Dowex 1 resins (8% crosslinking, 20–50 mesh) were converted to the NO_3 form. The column was prepared by filling it with distilled water. The resins were slowly added to the column and allowed to settle down by gravity. Since the flow rate applied was extremely slow, flow by gravity was employed. The flow rate was adjusted by a stopcock attached to the glass tube at the outlet of the column. The flow rate was adjusted to 1 mL/min in all runs, corresponding to about 0.14 gpm/ft^2. For a particular run, the bed was packed to the desired height. Prior to the introduction of feed solution, the bed was thoroughly washed and rinsed with distilled water. A feed solution of known acid and salt concentrations was then introduced. The volume of feed solution treated was 1 bed void volume to about 0.4 of bed volume. Distilled water with a volume equivalent to about half the bed volume was used for the elution. The effluent was collected after the entrained solution in the column was displaced from the bed. The samples were collected in 3 mL intervals. These samples were then taken for analysis by appropriate volumetric methods.

Analytical Methods

$CuNO_3$ was analyzed by EDTA titration with murexide as indicator. The hydrogen concentration was determined with the aid of a cation-exchange bed. A sample of the mixture of HNO_3 and $CuNO_3$ was introduced to a cation bed with resins in the H^+ form. The effluent sample was analyzed for its total H^+ content by standard acid–base titration. The HNO_3 concentration in the mixture was calculated from the known $CuNO_3$ concentration and from the total H^+ content of the effluent sample from the cation bed.

Experimental Conditions for Column Runs

Table 1 is a summary of the experimental conditions used for column runs. In practical application, the acid content of waste acid solution from a process industry ranges from 100 to 500 g/L while the metal ion content can be between 10 and 50 g/L. The treated effluent solution concentration of both the acid and salt can be expressed in normality, molarity, or grams

TABLE 1
Summary of Operating Conditions for Column Runs. Column Inside Diameter, 1.5 cm; Flow Rate, 1 mL/min

Run	Acid (concn)	Salt (concn)	Bed height (cm)	Solution volume (mL)	Water volume (mL)
1	HNO_3 (3 N)	Cu^{2+} (15 g/L)	50	36	45
2	HNO_3 (3 N)	Cu^{2+} (20 g/L)	50	36	45
3	HNO_3 (3 N)	Cu^{2+} (25 g/L)	50	36	45
4	HNO_3 (3 N)	Cu^{2+} (20 g/L)	75	54	66

per liter. It is usually more convenient to use the relative concentration with respect to feed concentration as a means of evaluating the quality of separation between acid and salt. The amount of waste acid solution to be treated per cycle is usually set at about 1 bed void volume. The use of at least 1 bed void volume is to ensure that the feed solution will have a minimum of 1 residence time in the column. Since the acid retardation process uses only water as the eluting agent, no extra chemical cost is imposed on the process. Obviously, the amount of water used per cycle will affect the separation of acid and salt as well as the concentration of the recovered acid. In general, a smaller volume of water used means less dilution of the recovered acid concentration. However, a smaller volume of water used may result in a poor quality of separation of salt and acid. Regardless of how much solution is treated and how much water is used for elution, a mass balance can always be applied to check the experimental results. The mass balance can be carried out by the graphical method of obtaining the area under the elution curve for each column run. The total effluent acid and salt content must match the amount of acid and salt charged to the column per cycle to satisfy the mass balance.

RESULTS AND DISCUSSION

General Features of Acid Retardation Process

In the column experiments, mixtures of salt and acid representing the waste acid solutions from pickling, mineral extraction, or ion-exchange regeneration processes are treated. The primary aim of applying the acid retardation technique is to be able to separate the waste acid solution into several products. One of these products is relatively low in salt (metal) content, and thus can be recycled to the process as makeup acid. If the metallic ion content of the acid waste solution can be reduced by one-third to one-tenth, it is quite suitable for reuse as makeup acid in the pickling or mineral extraction process. The high salt and low acid content portion of the product can be further treated by processes such as electrolysis to recover valuable metal. The low acid content portion of the solution can then be treated with minimum cost by neutralization before its disposal.

Approach to Cyclic Steady State

By using an ion-exchange resin as adsorbent in a packed column, the acid retardation operation is essentially a cyclic process. It is similar to the operation of a conventional fixed-bed ion-exchange process. In a normal fixed-bed ion exchange, the first cycle is started with the bed free of ions to be removed. Unless an unlimited volume of regenerant is used, complete regeneration of the bed is not possible. Thus the bed composition will fluctuate in conditions far from complete saturation and complete regeneration until a cyclic steady-state is reached. From then on, both breakthrough concentration history and regeneration characteristics will be repeated from cycle to cycle.

In the acid retardation process, if a very large quantity of water is used for elution, the result of the first cycle will be essentially the same as those of cyclic steady-state. This is due to the fact that each cycle starts with a bed that is free of any acid or salt species in the resin. On the other hand, if less than 1 bed void volume of water is used for elution, several cycles may be required before cyclic steady-state is attained because the starting bed condition varies from cycle to cycle. An experimental run on the nitric acid–cuprous nitrate system regarding the approach to cyclic steady-state is shown in Fig. 1.

Results of Column Runs

All the experimental column results reported in this study pertain to one operation cycle. That is, the results are for the first cycle of operation. In this first cycle of operation a specific volume of feed solution was introduced, followed by a specific volume of water for elution. In all runs

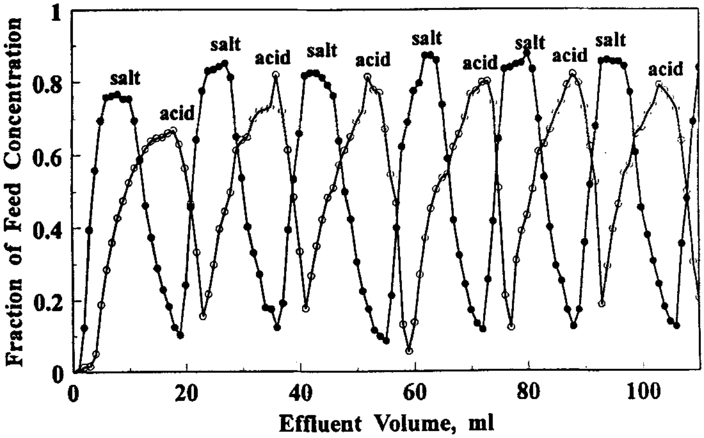

FIG. 1 Approach to cyclic steady state.

the feed volume was set at 1 bed void volume, while the volume of water used for elution was slightly higher than 1 bed void volume. For one cycle runs, extra water was used to ensure that all the salt and acid charged were completely eluted out in preparation for another column run. By doing this a mass balance can be performed based on the total salt and acid charged to the column and from graphical integration of the areas under the effluent curves for both salt and acid. In practice, at least 1 bed void volume of feed and 1 bed void volume of water for elution are recommended. The use of more than 1 bed void volume of water dilutes the products but gives better separation between acid and salt. Rough estimation of areas under the effluent curves for all column runs showed the mass balance error was within 3 to 5%. This level of discrepancy is satisfactory, considering the errors introduced in collecting samples and in the analysis.

The feed solutions prepared for the experimental work have a nitric acid concentration of 3 N (about 200 g/L HNO_3) with a Cu^{2+} concentration ranging from 15 to 30 g/L. A column height of 50 cm was used to study the separation of HNO_3 and $CuNO_3$ for feed concentrations of 15, 20, and 25 g/L Cu^{2+}. In all column runs the flow rate was set at 1 mL/min. In Runs 1, 2, and 3, 36 mL of solution was loaded to the column followed by using 45 mL of water for elution. Figures 2, 3, and 4 show the results for these three runs using a bed height of 50 cm. These results indicated as much as 15 mL of acid solution can be recovered with the Cu^{2+} concentration reduced to 1–2 g/L from about 15–25 g/L in the feed.

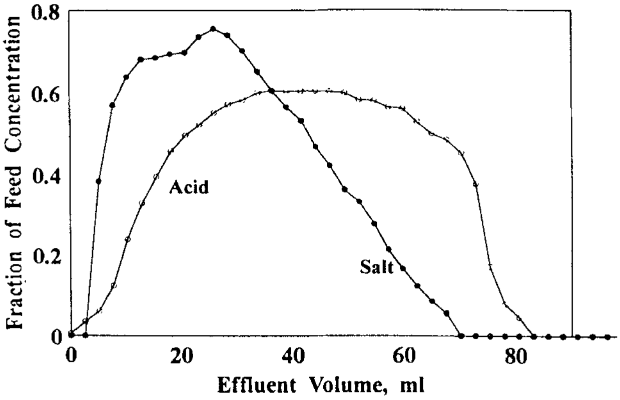

FIG. 2 Results of Run 1.

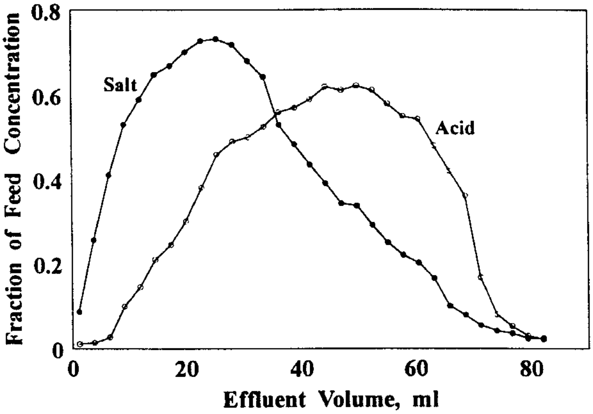

FIG. 3 Results of Run 2.

At this level of Cu^{2+} concentration the recovered acid solution can be recycled to the process acid bath as makeup to pure fresh acid. Another experiment with the bed height increased to 75 cm was also performed to see the effect on the improvement of separation between HNO_3 and $CuNO_3$. For this run the volume of feed solution treated was increased from 36 to 54 mL. The volume of water used for elution was also increased to 66 mL. Results of this experiment are shown in Fig. 5. In this run about 25 mL of acid solution, with the Cu^{2+} concentration reduced to 2 g/L,

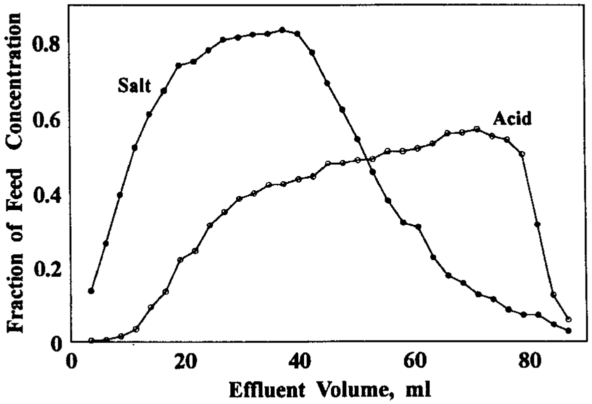

FIG. 4 Results of Run 3.

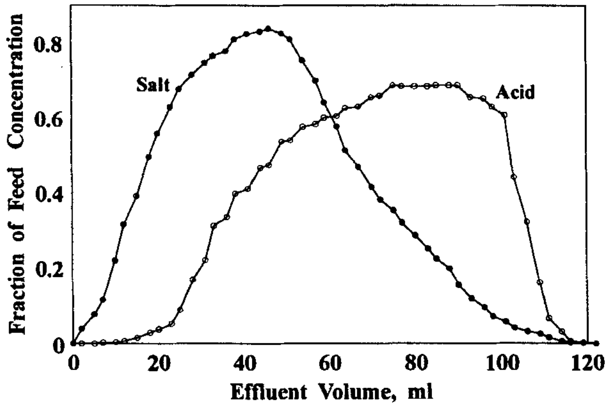

FIG. 5 Results of Run 4.

can be recovered. In addition, about 10 mL of solution which contains essentially only $CuNO_3$ can be separated. The acid concentration of these 10 mL of solution is less than 3 g/L. The separation of acid and cuprous nitrate can be further improved when beds higher than 75 cm are used.

SUMMARY AND CONCLUSIONS

Column results indicated that the acid retardation technique can be used to remove contaminating metallic salt from waste acid solution provided a sufficiently large bed height is used. For the systems studied in this work, in which the acid concentration was about 150 to 200 g/L and metallic ions concentration was about 15 to 30 g/L, about one-fifth to one-third of treated waste solution can be recovered and reuse. All the column experimental results suggested that a column bed height no less than 75 cm should be employed for effective removal of salt from acid. The bed height should be even larger if the flow rate applied is greater than 1 mL/min. A smaller volume of water used for elution, although it will minimize the dilution of the product solution, nevertheless causes poorer separation of the acid and salt. One bed void volume of acid solution together with slightly higher than 1 bed void volume of water should be used for most acid retardation processes.

ACKNOWLEDGMENT

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REFERENCES

1. M. J. Hatch and J. A. Dillon, *Ind. Eng. Chem., Process Des. Dev.*, *2*(4), 253 (1962).
2. *Eco-Tec APU Unit Technical Brochure*, Eco-Tec Limited, Pickering, Ontario, Canada, 1984.
3. L. E. Lancy, F. A. Steward, and J. H. Weet, *US EPA Technical Report EPA-670/2-75-015*, 1975.
4. D. J. Burke and R. B. Moore, "Separating Acid from Salt by Adsorption with Recycling," US Patent 4,528,101 (1985).
5. W. Gotzelmann, L. Hartinger, and M. Gulbas, *Metalloberflaeche*, *41*, 208 (1987).
6. W. Gotzelmann, L. Hartinger, and M. Gulbas, *Ibid.*, *41*, 315 (1987).

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