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*Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary*

COLUMN AND BATCH REGENERATION STUDIES FOR ZINC REMOVAL ON DIFFERENT ANIONIC EXCHANGE RESINS

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ABSTRACT. Five anion exchange resins were used to remove zinc chloride complexes from a synthetic acid pickling bath. The experiments were carried out for several cycles of adsorption-desorption in fixed bed column and batch mode. The results showed that the percent of zinc chloride sorption remained constant in the last three cycles (from six) in both cases. Comparing various resins, the following series was depicted based on the ionic exchange capacity: Purolite A600MB > Amberlite IRA410 > Purolite A103S > Purolite A400MBOH > Purolite NRW700. Also it was possible to concentrate the metal in smaller solution volume after regeneration, which will make its recovery much easier.

Keywords: *regeneration, fixed bed, batch mode, zinc chloride*

INTRODUCTION

The worldwide production and use of chemical compounds increased due to industrial proliferation and urbanization. The heavy metals are the most common pollutants found in effluents discharged from electroplating industries and cause serious environmental problems [1]. The most common method to treat these wastewaters is chemical precipitation followed by filtration or solid/liquid separation processes [2]. A method that could replace traditional solvent extraction systems can be the ion exchange process due to its ability to selectively and repeatedly adsorb and desorb metals [3].

In case of zinc, the principal sources of effluents are galvanizing processes. The main purpose of galvanizing is the protection of steel against corrosion, which can cause dangerous damage. During the pickling process

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the steel is dipped into a tank that contains acids. In the recent years, the sulfuric acid has been replaced by the hydrochloric acid due to its waste disposal cost which is smaller compared to sulfuric acid disposal [4]. The metals that contaminate the acid used in the pickling process are zinc and iron [5].

Selective separation of the chloride complexes of Zn^{2+} and Fe^{2+} is easy and based on their complexes stability since the iron does not form stable complexes at low acid concentrations [6].

The ionic state of zinc depends on concentration and acidity of the solutions. Thus the tetrachlorozincate $[ZnCl_4]^{-2}$ complex is formed in strong acid solution with HCl concentration in 1-6 mol/L range. With the decrease in acidity to 10^{-2} - 10^{-3} mol/L the amounts of aquacomplexes $[ZnCl_4(H_2O)_2]^{2-}$ and $[Zn(H_2O)_6]^{2+}$ increase. Therefore, anionic exchange resins can be used for $[ZnCl_4]^{-2}$ recovery [7]. In this context, the chloride complexes are retained in the resin bed by a reversible reaction. When the bed becomes saturated it must be regenerated. In this case, the volume of regenerate is much lower than the volume of the effluent and the metals are in a much higher concentration. Afterward, different methods such as precipitation, distillation or other recovery processes can be applied [5].

The main purpose of this study was to evaluate the ability of several anion exchangers to retain and desorb zinc chloride complexes in order to increase the zinc concentration in the regeneration step allowing its recovery by electrodeposition. Also in this study, the capacity of the Amberlite IRA410 resin was investigated for several cycles of sorption –desorption in fixed bed column and in batch mode.

RESULTS AND DISCUSSION

Fixed bed studies for resin usage

In our previous papers we concluded that besides other resin tested, Amberlite IRA410 resin was the best ionic exchanger for the removal of zinc ions as zinc chloride complexes [8]. The effect of different parameters were investigated in batch mode [8] and fixed bed column [9]. As sorption-desorption capacity for several cycles was not considered before, in this study, the results regarding this aspects were presented.

The experiments were carried out using a fixed bed containing 5 g of resin, 1.36 mL/min flow rate and 500 mg/L initial zinc concentration in a 24 mm diameter column. The synthetic solution (656 mL) was allowed to pass through the column in continuous down flow mode. The treated metal solution (20.5 mL) was collected at the outlet of the column every 15 min for 500 minutes and analysed [9]. The results obtained for zinc sorption by

Amberlite IRA410 for six cycles of sorption-desorption were presented in Figure 1. As it can be seen, the breakthrough curves did not follow the typical ‘S-shape’, which are regularly formed in ideal adsorption systems. The shape of the obtained breakthrough curves was due to the slow kinetics of zinc complex sorption on the resin, therefore an incomplete ‘S’ breakthrough shape was produced [9]. An increase of sorption-desorption cycles number does not lead to a substantial modification in ionic exchange capacity (Equation 2), values between 35.8 mg/g (first cycle) 35.5 mg/g (sixth cycle) were obtained. By comparing the six cycles curves it can be seen that the breakthrough behaviour remains unchanged with successive regeneration.

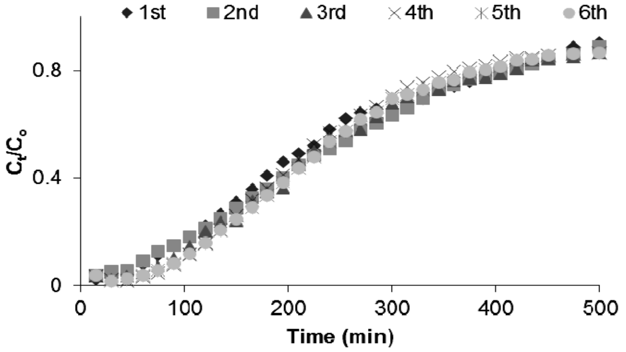

Figure 1. Breakthrough curves for Zn sorption during six sorption cycles in fixed bed column

Once the resin was saturated it is important to regenerate the resin in order to recover metal ions and also for the further use of the resin. The regeneration of the resin after the sorption cycles was made using double-distillate water.

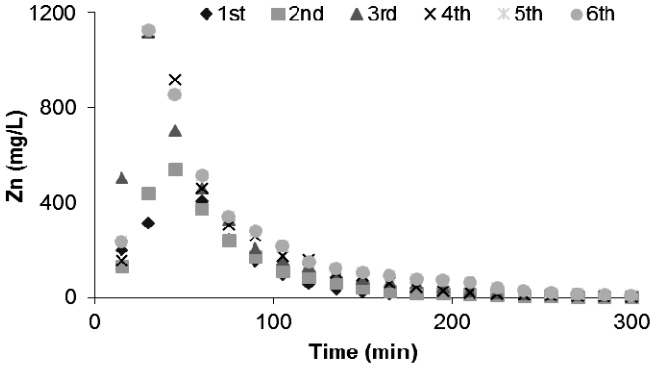

Figure 2. Zinc concentration during regeneration cycles in fixed bed column

The results obtained are presented in Figure 2. In the first minutes the concentration was very high, after that slowly decreased as the resin was regenerated.

Batch studies for resin usage

The batch studies were carried out for six sorption-desorption cycles using 100 mL solution (500 mg/L zinc initial concentration) contacted with 5 g of resin (Amberlite IRA410) for 300 minutes until the equilibrium was reached. The regeneration of the resin after the sorption cycles was made using double-distillate water.

The results (Figure 3) showed that the removal efficiency (Equation 3) decrease with the sorption-desorption cycles number and after the third cycle remained constant. The decline in efficiency was no more than 10% which showed that the resin had good potential to retain metal ions although it has been reused for several times [10].

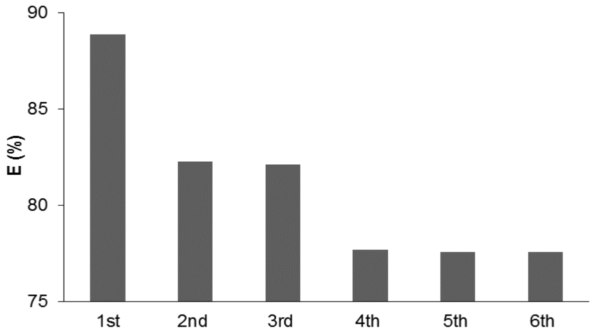

Figure 3. Removal efficiency after six sorption-desorption cycles in batch mode

Regeneration of different anionic exchange resins in batch mode

Regeneration of the resin is important in the economic development and implies the removal of metal loaded using an eluting agent without damaging the capacity of the adsorbent, making it reusable in several sorption-desorption cycles [11].

Five anion exchanger resins were tested in the same conditions for one sorption-desorption cycle using a higher volume of solution (400 mL) in this case in order to exhaust the resin. The results presented in Figure 4 showed that the maximum percent of sorption, about 48%, was obtained for Purolite A600MB and the minimum percent of sorption, about 42%, was obtained for Purolite A400NRW700. Comparing various resins, the following series was depicted based on their ionic exchange capacity: Purolite A600MB > Amberlite IRA410 > Purolite A103S > Purolite A400MBOH > Purolite NRW700.

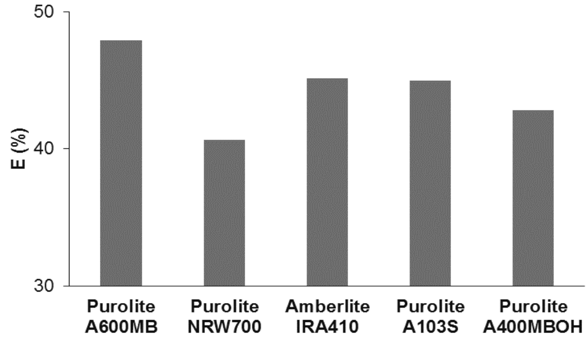

Figure 4. Removal efficiency for zinc sorption on different anionic exchange resins

The regeneration of the resins after the sorption cycle was made using double-distillate water and the obtained results are presented in Figure 5.

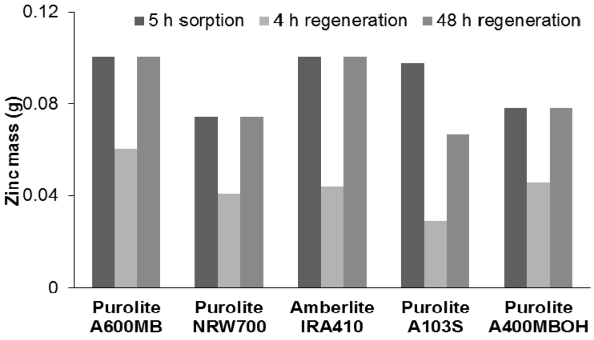

Figure 5. Zinc mass after sorption and regeneration studies

In order to identify if the resin was completely regenerated, zinc mass was calculated after sorption and regeneration. The zinc mass sorbed by the resin in 5 h was calculated taking into account the volume and the concentration of the solution used (400 mL, 500 mg/L), calculated by difference between the initial zinc concentration and the final zinc concentration. The zinc mass after regeneration was calculated, by taking into consideration the volume used for regeneration and the determined zinc concentration.

The maximum zinc mass desorbed after 4 h was obtained for Purolite A600MB and the minimum zinc mass for Purolite A103S. With a further increase in time, all the resins were completely regenerated with exception of Purolite A103S. Comparing various resins the following series was depicted based on recovered zinc mass after 4 h: Purolite A600MB > Purolite A400MBOH > Amberlite IRA410 > Purolite NRW700 > Purolite A103S.

Effect of the initial zinc and iron concentration

Taking into consideration that from the Purolite A600MB resin the highest quantity of zinc was recovered after 4 h regeneration and that usually iron is also presented in pickling baths, further sorption-desorption experiments with multicomponent solutions (zinc and iron) were also considered.

The experiments were carried out using 5 g of Purolite A600MB which was contacted with 400 mL solution containing zinc (500-900 mg/L) for 300 min at 500 rpm. In each case 1000 mg/L iron were also added. The obtained results are presented in Figure 6 (due to the fact that iron concentration remained unchanged, in order to preserve image clarity only one iron curve was presented).

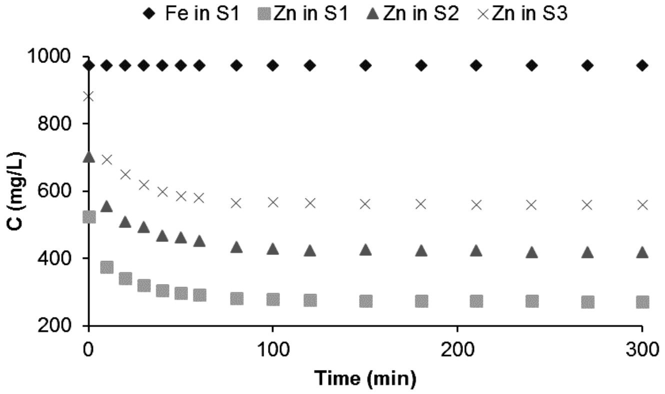

Figure 6. Effect of zinc initial concentration on zinc sorption by Purolite A600MB in presence of iron (S1=1000 mg/L Fe+500 mg/L Zn; S2=700 mg/L Zn +1000 mg/L Fe; S3=900 mg/L Zn+1000 mg/L Fe)

In this range of concentration, zinc sorption was rapid in the first 10 min, after that, the sorption rate slowly decreases as the process reaches equilibrium. The initial iron concentration remained constant during the experiments, due to the fact that in hydrochloric acid medium iron will not form complexes. The zinc ionic exchange capacity (Equation 1) at 500 mg/L was 5.02 mg/g (48% efficiency) and 6.48 mg/g (37% efficiency) at 900 mg/L.

The following experiments were made in order to determine the ability of this anionic exchange resin to be regenerated for further uses and to increase the zinc concentration in the regeneration step allowing its recovery by electrodeposition.

Desorption experiments for all the concentrations were carried out using different volumes of double-distilled water (20-80 mL). The obtained results were presented in Figure 7. The zinc mass increased with increasing the volume of the double-distillate water used. A volume of 80 mL double-distillate water ensured the complete regeneration of the resin. The concentration of zinc in 80 mL was between 1.3-1.8 g/L in the studied range of concentration. Afterwards zinc electrodeposition could be applied in order to obtain pure zinc deposits.

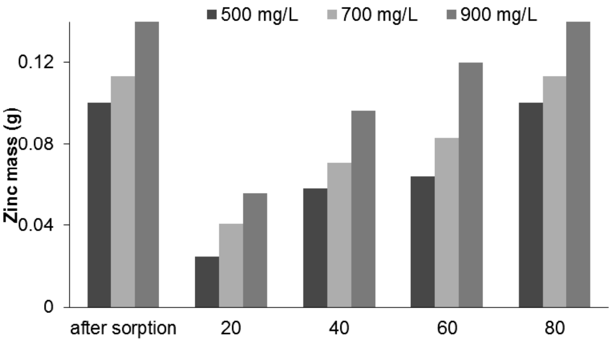

Figure 7. Desorption experiments using different volumes of water

CONCLUSIONS

Sorption-desorption experiments were carried out in fixed bed column and in batch mode for six cycles in order to investigate the capacity of the considered resins to retain zinc complexes. After several sorption-desorption cycles the decline in efficiency was maximum 10%, which indicated that the resins had good potential to remove zinc from a synthetic acid pickling bath. Purolite A600MB resin presents the best regeneration ability of those studied. Therefore it was possible to concentrate the metal in a smaller volume and afterwards zinc electrodeposition could be applied in order to obtain pure zinc deposits.

EXPERIMENTAL SECTION

Five strong base anionic exchange resins, Purolite A600MB Amberlite IRA410, Purolite A400MBOH, Purolite NRW700 and a weak base anionic exchange resin, Purolite A103S were considered in order to investigate their capacity to remove zinc chloride complexes. Before usage, the resins were soaked in double-distilled water for 24 hours.

Initial solutions were prepared by dissolving $ZnCl_2$ and $FeCl_2$ salt in hydrochloric acid 1 M.

The sorption experiments were realized in a fixed bed column where zinc solution of known concentration (500 mg/L) was allowed to pass through the column using a peristaltic pump for 500 min and in batch mode where 5 g of resin were contacted with 100 and 400 mL of zinc (500 mg/L) for 300 min under 500 rpm magnetic stirring. The treated solution collected at the outlet of the column and the samples of 1 mL taken from the solution at previously established time intervals (batch mode) were analyzed in order to determine the exact concentration of zinc using an atomic absorption spectrophotometer Avanta PM GBC (Australia).

The regeneration experiments were realized as follows: (a) in case of the fixed bed, the regeneration solution (distilled water) was allowed to pass through the column at 1.36 mL/min flow rate for 300 min; every 15 min, one sample was collected at the outlet of the column and analyzed; (b) in batch mode, by contacting the exhausted resin (5 g) with volumes between 20 and 80 mL double-distilled water for 48 hours without stirring; at the end of the experiment zinc concentration was determined.

Ionic exchange process and sorption-desorption cycles were followed using ionic exchange capacity (Equation 1, 2) and removal efficiency (Equation 3) [8, 9].

$$q_e = \frac{(C_0 - C_e)}{m} \cdot \frac{V}{1000} \text{(batch) (1)} \quad q_t = \frac{(C_0 - C_e)}{m} \cdot \frac{V}{1000} + q_{t-1} \text{(fixed bed)} \qquad (2)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad (3)$$

where, C_0, C_e are the initial and equilibrium zinc ion concentrations (mg/L); q_e is the ionic exchange capacity (mg/g) [8], q_t, q_{t-1} are the amount of zinc ions sorbed at times t and (t-1), respectively (mg/g); V is the volume of zinc ion solution (mL); m is the mass of resin (g) [9].

ACKNOWLEDGMENTS

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