STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVI, 1-2, 2001

THE RECOVERY OF THE ZINC AND NICKEL IONS BY IONIC EXCHANGE FROM ELECTROPLATING WASTEWATERS

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ABSTRACT. This paper presents the possibility of recovering the ions of heavy metals (such as zinc or nickel that usually appear in acid galvanic wastewaters) after they were retained on a chelate resin of the Purolite S 930 type. By eluting them with a regenerative solution based on different mineral acid, the metals may be selective recovered from the resin.

Introduction

The traditional technology used in the course of time by the majority of electroplating enterprises, meant to prevent the pollution of effluents, consists in the precipitation and dilution of the noxious solutions down to concentrations, which would not affect the quality of the environment. However, due to a dramatic exhaustion of the water resources, modern waste water treatments have been promoted recently, with a view to aligning our country up with the environment, the saving of water and raw material resources.

Made the various ways of purifying galvanic wastewaters, mention could be mach of [1]: precipitation, reverse osmosis, electrodialysis, evaporation, electrolysis and ionic exchange.

From the point of view of the effectiveness in removing the heavy metals out of galvanic wastewaters, ionic exchange is the most attractive method. This becomes attractive especially due to the purification of wastewaters, with the possibility to recover the valuable components (heavy metal ions) retained during the exhaustion stage. The ionic exchange method is simple and economical (economy of water, raw materials and reagents) and this explains why it is preferred to the other water purification methods. This method has been applied lately in our country, too, as a result of the appearance on the market of new types of exchangers, produced by PUROLITE/VIROLITE Company (USA); due to their higher quality, these exchangers have replaced the domestically produced ones.

The paper presents a comparative study on the possibility of recovering, out of the galvanic rinse waters, the ions of zinc and nickel respectively, after they had been retained on the Purolite S930 chelate exchanger.

Since the efficiency of the resin regeneration process depends on a multitude of factors [1-3], the paper focuses on certain aspects regarding the resin operation during regeneration stage, under certain operating conditions, with a view to increasing the efficiency of valuable component recovery. The purpose was thus to determine the influence of the following factors on the regeneration of the Purolite S930 type of resin: flow rate, concentration, temperature and type of regeneration agent.

Experimental Part

The experimental installation and the influence of the certain factors on the loading of the resin with zinc and respectively, nickel ions for the recuperative purification of galvanic wastewaters were minutely described in some prior studies [4-5]. Using synthetic waters, the characteristics of the rinse wastewaters were simulated. These characteristics correspond to the acid sulphate type of electroplating baths. The experiment, under dynamic operating conditions, using a chelate exchanger resin (Purolite S930 type), whose main characteristics were presented in technical bulletin [6].

In order to study the influence of certain factors on the process of regeneration with a view to recovering the zinc and respectively, the nickel ions, the loading of the resin with metallic ions was performed each time under the same conditions; the flow rate of the processed solution at passage down through the column was F_v = 5 mL/min, the initial concentration of solution c_0 = 0.5 g/L Me(II); pH of zinc solution pH_{Zn} = 5.5, pH of nickel solution pH_{Ni} = 5.6; the experiment was made at room temperature (t = 18 °C); the quantity of dry resin used was a = 2.83 ± 0.02 g. The analyse of the metallic ions was performed complexonometrically [4-5].

The regeneration was performed in equicurrent, by eluting the zinc and respectively, nickel ions from the exhausted resin with mineral acid solutions (HCl, H_2SO_4), under certain experimental conditions.

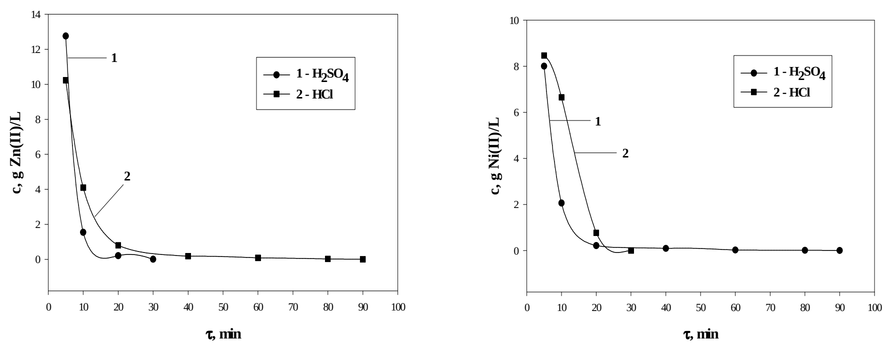
The operating flow rate ranged between 2-5 mL/min. Corresponding to the flow rate of 2 mL/min, the average speed rate of the regeneration solution through the column was of $0.18 \cdot 10^{-3}$ m/s. The temperature range under study was between 18-30 °C. The concentration of the regenerative solutions ranged between 2-5 % H_2SO_4 and 10% HCl respectively. Their representative concentrations were selected, taking into account the maximum allow able concentration of acids for which the resin structure would not be affected due to oxidising effects [1].

Results and Discussions

The Influence of the Regenerative Agent

Figure 1 – a, b presents the elution curves of Zn(II) and respectively, Ni(II) ions retained on the chelate resin when the following regeneration agents are used: 5% H_2SO_4, 10% HCl. Due to the mineral acids, the resin is brought under the H^+ form; the sulphuric acid is preferred to the hydrochloric acid, because, by using the former, we obtain a zinc or nickel sulphate as eluted substance. These

solutions after adjusted the composition, might be recycled eventually in the electroplating bath of the sulphate type. As can be see in Figure 1 – a, b, the elution of the Zn(II) ions takes place faster in the presence of the H_2SO_4 solution, while the Ni(II) ions are more easily eluted when using the HCl solution. The average concentration of the eluted substance at the end of the regeneration process of the resin with mineral acids is of 4.54 g Zn(II)/L and 1.2 g Ni(II)/L, respectively – when using a 5% H_2SO_4 solution - and of 1.51 g Zn(II)/L and 3.59 g Ni(II)/L, respectively – when using a 10% HCl solution. Higher concentrations of the metallic ions from the eluted solution may be obtained through an incomplete regeneration of the resin, i.e. by stopping the process at certain time intervals, corresponding to the appearance of traces of metal in the effluent (eluted solution). The results obtained indicate the possibility of performing a selective elution in case the nickel and zinc ions are mixed in the solution, by successively using H_2SO_4 and HCl solutions of various concentrations, so that the ions might be extracted in turn, thus obtaining high purity eluted substance in effluents.



a b

Fig. 1. Time - dependent variation of the concentration of Zn(II) - a, respectively, Ni(II) - b, ions from the eluted solution during the regeneration process of the S 930 type of resin, with various regeneration agents: 1 – 5% H_2SO_4; 2-10% HCl. a = 2.83 ± 0.02 g dry resin; F_v = 2 mL/min; t = 18 °C.

The discussions will focus on the regeneration of the resin when using H_2SO_4 solution, because in this case the resulting eluted solution contains $ZnSO_4$ and respectively, $NiSO_4$, both of which are main components of the electroplating baths of the sulphate type.

The Flow Rate of the Regenerative Solution

Figure 2 - a, b presents the time – dependent variation of the concentration of the metallic ions from the eluted solutions for different flow rate of the regenerative solution.

The higher the flow rate, the lower the regeneration time span. However, this induces an increase in the volume of the eluted solution and thus a decrease in the concentration of the metallic ions.

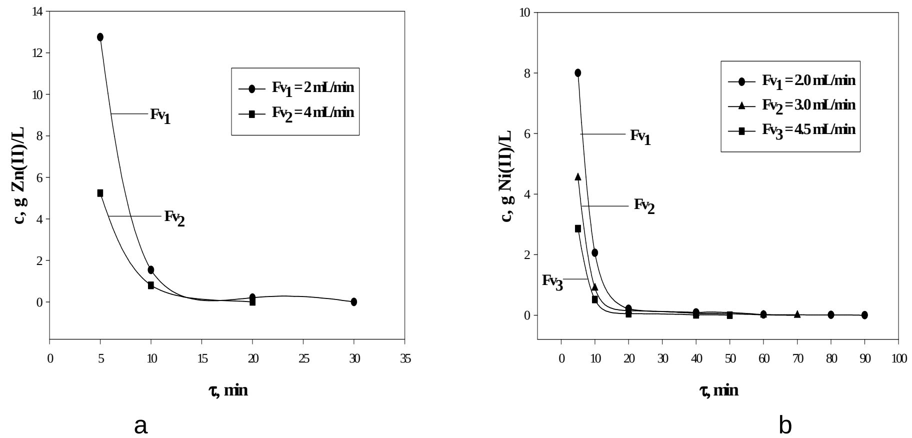


Fig. 2. Time-dependent variation of the concentration of Zn(II) – a , respectively Ni(II) – b, ions from the eluted substance during the regeneration process of the S 930 type of resin. a = 2.83 ± 0.02 g dry resin; t = 18 °C; c_{H2SO4} = 5%.

The Concentration of Regenerative Solution

The use of higher concentration of regenerative solutions favours the displacement of the ionic exchange equilibrium to the left. Hence, appears the possibility to obtain, in a shorter period, eluted solutions with a higher concentration of metallic ions; for low concentrations, the regeneration process is slowed down and the concentration of the eluted solutions becomes lawyer.

The Temperature of the Regenerative Solution

As it has already been shown [4-6], the direct ionic exchange reaction is endothermic, while the reverse reaction is exothermic. In conformity with what has been stated, the temperature increase will favour only the direct reaction and the equilibrium will be displaced far off, to the right. However, the experimental data pointed to a slightly beneficial influence of temperature on the regeneration process (the reverse reaction), which is better evinced in the initial moments of the process. This could be the result of the intensification of the mass transfer and of the difference between the solvation energies of the ions in the solution and those of the ions in the resin. Another explanation may be found while taking into account the beneficial influence of temperature on the reaction rate, especially if the system under study is far from the state of equilibrium as a result of the hydrodynamic operating conditions. It can be noticed that, towards the end of the regeneration process, the influence of temperature becomes less and less significant.

Conclusions

- On the basis of the kinetic curves, it can be stated that the Zn(II) ions are more easily eluted with sulphuric acid, whole the Ni(II) ions are more easily eluted with hydrochloric acid, which might enable one to perform a selective separation of the two from the mixture;
- The use of high flow rate of the regenerative solution leads to a shortening of the regeneration time, but also to a decrease in the concentration of the metallic ions from the eluted solution;
- A highly concentrated eluted solutions may be obtained when the concentration of the regenerative solution increases; in this case the regeneration time reduces dramatically;
- The influence of temperature on the regeneration process is made manifest at the beginning of the process, when due to the intensification of the mass transfer under the impact of heat, a slightly higher concentration of the eluted solutions is obtained; at the same time, the regeneration time span is reduced when higher temperatures are used for the regenerative agent;

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