Removal of Ni and Cu ions from aqueous solutions by means of a hybrid electrosorption/electrodialysis process

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Abstract

The hybrid adsorption/electrodialysis process was shown to be effective in the removal of Ni and Cu ions from aqueous solutions imitating electroplating effluents. Adsorption of the ions on the cation-exchange and amphoteric resins packed in the desalination compartment of the electrodialysis cell with (electrosorption) and without the influence of electrical current was studied. In the case of the ion-saturation operation carried out before the electrosorption process, no direct relationship between the type of resin and the ion-removal efficiency was found; the process performance was affected by over-equivalent adsorption resulting from electrochemical reactions taking place in the boundary layer between the resin and the solution. Under the influence of electrical current as high as sixfold higher metal ion extraction than in a conventional adsorption process was observed. The presence of ion-exchange resins in the desalination compartment also affected the performance of ion-exchange membranes used in the cell. The method was found more applicable to Cu containing solutions.

Introduction

Electrodialysis is widely used nowadays for desalination of diluted solutions (Schoeman, 1997; Belobaba and Pevnitskaya, 1992), among them effluents of the electroplating industry (Pevnitskaya, 1992, Takahashi et al., 1995, Purgy et al., 1995). If the final goal of effluent treatment is to obtain water with total salt concentration of 20 to 100 mg/ℓ, electrodialysis can be considered a suitable treatment method for a variety of electroplating processes. Higher ion recovery can be achieved by the introduction of packed ion-exchange resins into electrodialysis chambers resulting in adsorption and electrodialysis processes combined in one unit operation (Shimomura, 1994, Cheryan and Parekh, 1995). Usually resins with high selectivities are used for introduction into compartments of an electrodialysis installation, for example, a pyrolite A520E is recommended for nitrate removal and Amberlite for extraction of chrome and lead ions (Krumbholtz and Wein, 1990).

In a recently published paper (Grebenyuk et al., 1996) a novel process arrangement, where ion-exchange columns were situated next to an electrodialiser, was used for treatment of electroplating effluents in order to minimise metal losses and prevent environmental pollution. The method comprises three processes: sorption of heavy metals from the catching bath solution, regeneration of sorbent and electroprecipitation of heavy metals in the electrolyser.

The value of the static ion-exchange capacity of the sorbent is a natural limitation as far as the quantity of absorbed metal ions is concerned. For solutions of practical use the working capacity of the sorbent is limited by kinetic characteristics of the process such as the solution flow rate (Shubinok, 1992), diffusion coefficient of adsorbed substances, etc. When an electrical field is applied, the adsorption capacity of ion-exchange materials increases due to the electrosorption effect (Pevnitskaya, 1993). This results from an occurrence of electromigration flow and, most important, the generation of metal hydroxides and their accumulation both between the pellets of an ion-exchange resin and on the membrane surface, the latter process termed electrofiltration. In order to optimise the performance of hybride ion-exchange/electrodialysis processes and develop them to a stage of practical application it is of importance to study the effect of capacity of the ion-exchange packing on removal efficiency of heavy metal ions in the presence of an electrical field. In more detail, the objective of the study was to study electrosorption on saturated ion-exchangers with the purpose of determining the contribution of separate metal ions, that may be present in electroplating effluents, on the overall performance of the hybride effluent treatment process.

Experimental

A laboratory installation as shown schematically in Fig. 1 was used for the study of the electrodialysis-electrosorption hybrid process. The cell comprised four compartments: desalination, concentration and two electrode ones. The compartments were separated from each other by ion-exchange membranes. Cation-exchange membranes MK-40 and anion-exchange membranes MA-40 in the H^+- and OH^--forms respectively were used for the electrodialysis process. The membranes were supplied by the "Schekinoazot" company, Russia. The working membrane area was 10 cm^2 , the distance between membranes in the desalination compartment was 0.6 cm. Both the cathode and the anode in the cell were manufactured from platinum plates and wires. Solutions were circulated through the cells by means of peristaltic pumps. Pressures and flow rates in each compartment were independently monitored.

An acidic cation-exchange resin KU-2-8 in a gel form and an amphoteric macroporous ion-exchange resin ANKB-35 (both supplied by "Khimreactive" company, Russia) were prepared in the H^+- and Na^+-forms respectively according to the procedure described elsewhere (Polyansky et al., 1976). Separate experiments were carried out for each resin type and in both cases 5.0 g of the material was packed in the desalination compartment of the cell. Simulated electroplating effluents were prepared with

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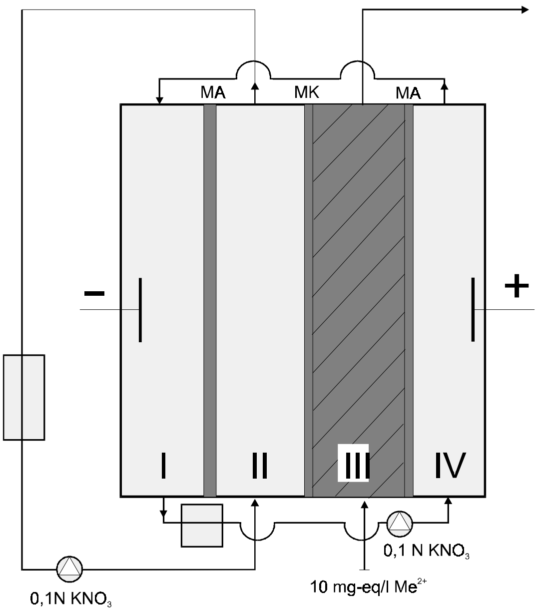

Figure 1

Schematic of experimental cell: I, IV - electrode compartments; II - concentration compartment; III - desalination compartment; MA - anion-exchange membrane; MK - cation-exchange membrane

a total salt concentration of 10 mg-eq/ℓ and a pH of 5. A 3:1 ratio of heavy metal cations (Ni^{2+} or Cu^{2+}) to other cations (Na^{+}) was maintained throughout the experiments.

In order to monitor the transmembrane transport of heavy metal ions into the concentration and electrode compartments, an 0.1 N KNO_3 solution was introduced into these compartments in a recirculation regime. The linear flow rate of the working solution through the desalination compartment was 0.1 cm/s.

The sorbents in the desalination compartment were saturated with heavy metal ions by circulating the working solution until the balance between the concentrations before and after the compartment was reached. After saturation, electrical current was applied to the cell without stopping the solution flow. The electrosorption without preliminary saturation of the ion exchangers was also studied. In this case electrical current was applied simultaneously with the initiation of the flow of working solution through unsaturated resins.

Samples were taken from septa at the inlet and the outlet of the desalination and concentration compartments in order to monitor pH and to analyse the content of Ni and Cu ions (Shwarzenbah and Flashka, 1970). On completion of each experiment the metals were eluted from ion exchangers using 20% sulphuric acid without disassembling the cell.

Results and discussion

The study started by establishing a material balance for heavy metals inside the cell (Q, mg-eq). The metal ions present in the following parts of the cell were accounted for: (i) concentration compartment, (ii) desalination compartment, (iii) cation-exchange membrane, (iv) anion-exchange membranes and (v) metal ions initially adsorbed on the ion-exchange packing. Components (i)-(iv) were determined by complexometric titration (Shwartsenbah and Flashka, 1970) and (v) from concentration - flow relationship at a constant flow rate. The change in Ni and Cu ion concentrations is represented using so-called “desalination degree” which was calculated according to the formula:

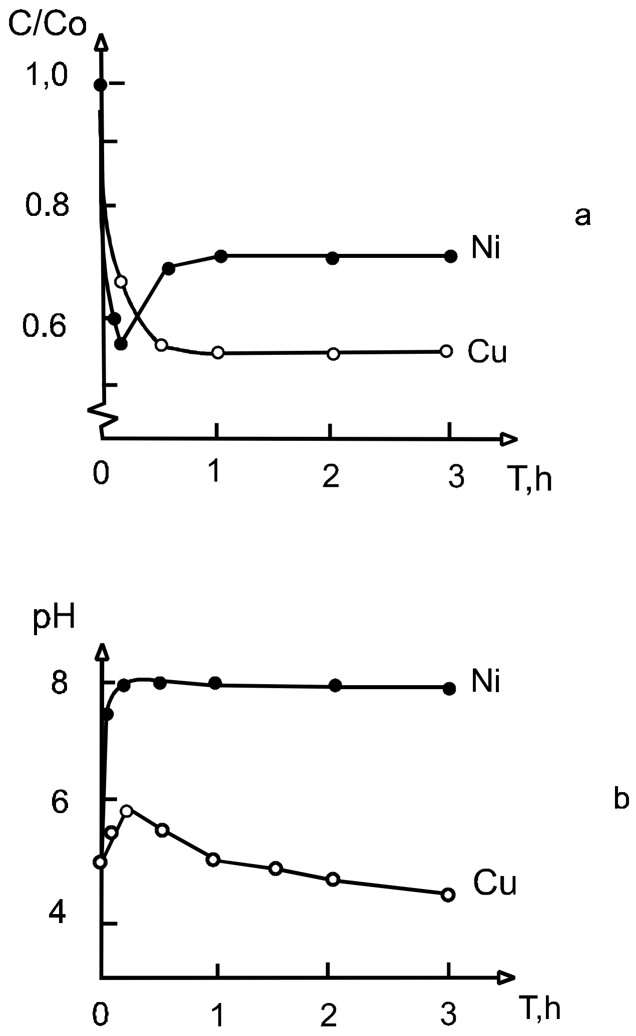

Figure 2

Electrodialysis of solutions without ion-exchange packing

$$F \quad = \quad (1 - C/C_0) \times 100\%$$

where:

F = desalination degree

C_0 = ion concentration in the inlet solution

C = ion concentration in the outlet solution.

Electrodialysis conducted using the cell without the ion-exchange packing allowed the determination of the quantity of the metal adsorbed on the membranes from both sides of the desalination compartment. At a current density of 10 mA/cm^2 and a constant linear flow rate a twofold decrease in concentration of both Cu and Ni ions was observed during the first 15 min of the experiment (Fig. 2). As this was taking place the pH of the Cu containing solution initially increased to 5.8 and then decreased to 4.5. During the next 40 min the desalination degree of Ni dropped from 47% to 34% and remained constant for at least 6 h. This was accompanied by a sharp increase in pH reaching 8 in just 7 min and remaining at this value until the end of the experiment.

Earlier research had shown the weak effect of electrical

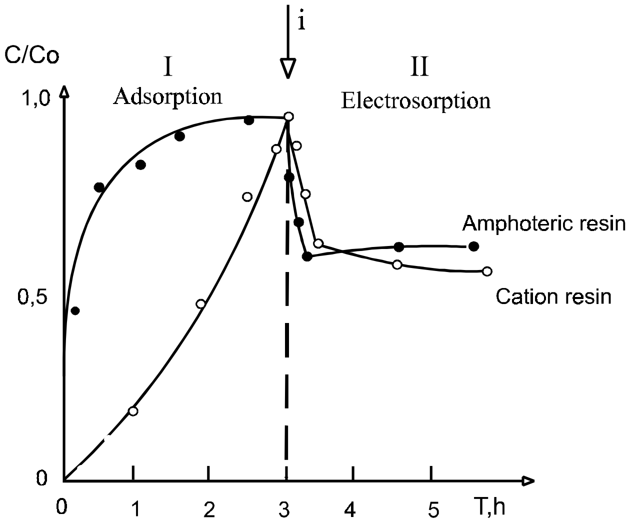

Figure 3

Concentration ratio of Ni ions in desalination compartment with different resins

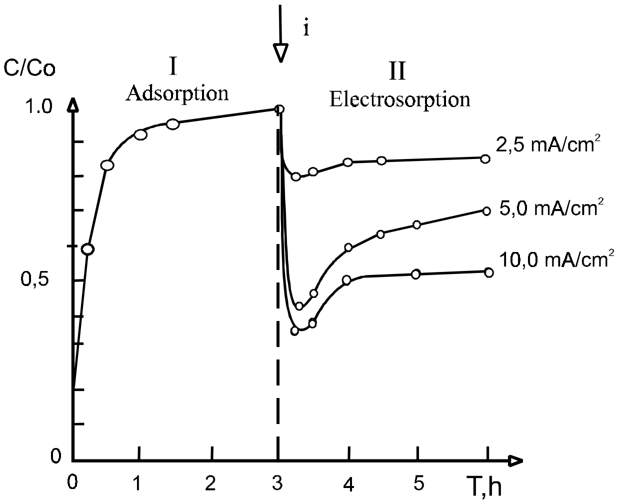

Figure 4

Concentration ratio of Cu ions in desalination compartment with amphoteric resin

current on the electrosorption process conducted in the underlimiting current regime (Belobaba and Pevnitskaya, 1992; Pevnitskaya, 1992). Taking this into account, in the present study all experiments were performed at currents higher than limiting values, by means of which the generation of H^+- and OH^--ions in the boundary layer between the ion exchanger and the solution was facilitated; naturally this process was accompanied by increased formation of insoluble hydroxides. Desalination of the Cu solution due to the ion transport through the membrane was unaffected by this event. When Ni solution was introduced to the desalination compartment, complication of ion transport occurred due to the presence of precipitated Ni hydroxide resulting in a decrease in the desalination degree.

Electrosorption of Ni ions on the saturated ion-exchange packing is represented in Fig. 3. During the first 10 min of the experiment without electrical current 45% of Ni was adsorbed onto the amphoteric resin and another 25 to 30% - during the next hour. The capacity of the amphoteric resin was exhausted after 2.5 h. In the case of the cation-exchange resin due to its high capacity (2.5 mg-eq/g of wet resin) more than half of all metal ions transported through the compartment during a 3 h experimental run were adsorbed.

When electrical current with a density of 10 mA/cm² was applied to the cell an electrosorption effect occurred. In this case the kinetics of extraction of Ni ions from the solution was affected by the following simultaneous processes: electrofiltration, electromigration and transport of metal ions through the cation-exchange membrane. A desalination degree of 35 to 45% was observed with only slight dependence on the nature of the ion-exchange packing. However, in the case of the amphoteric resin the value of over-equivalent adsorption, resulting from both electrofiltration and electromigration, was twofold higher. A high pH value of 7.5 and precipitation of Ni hydroxide in the desalination compartment were attributed to the presence of sodium hydroxide washed from the pores of the Na^+ form resin at the initial stage of the experiment. The use of the cation-exchange resin in the H^+ form resulted in the acidification of the solution in the desalination compartment (pH 4.5). In this case the ion transport occurred mainly through the ion-exchange membrane.

Conventional adsorption of Cu ions on the amphoteric resin took place in the way similar to that described above for Ni and the resin capacity was exhausted after 2.5 h (Fig. 4). As far as application of electrical current is concerned, for both Ni and Cu, it initially resulted in a sharp decrease in the concentration of the metal ions in the desalination chamber. After just a few minutes the opposite trend occurred and after 0.5 to 1 h an equilibrium was reached. This was due to electromigration of the ions deeper into the porous structure of the ion-exchange resin.

The desalination degree for Cu ions was found to be directly proportional to the current density (Fig. 4). The quantity of Cu extracted from the working solution in the desalination compartment under the influence of electrical field was calculated according to the equations:

$$Q_{el} = Q_d - Q_{sor} - Q_m$$
$$Q_{total} = Q_d - Q_c$$

where the quantities (mg-eq) extracted in different cell compartments and under different conditions are represented:

Q_{el} = by electrosorption in the desalination compartment
Q_d = total in the desalination compartment
Q_{sor} = initially adsorbed on the ion-exchange packing
Q_m = in the ion-exchange membrane
Q_{total} = total in the cell
Q_c = in the concentration compartment

It is clear from Fig. 5 that with an increase in the current density the amount of metal ions transported through the membrane increases from 20 to 65% of the total amount of the ions extracted in the cell. Another serious effect of a current density increase is the decrease in the relative metal quantity extracted due to electrosorption (40% to 18%). It may be suggested that a slight decrease in the quantity of the metal adsorbed by the ion-exchange packing results from its partial desorption from the resin under the influence of electrical current.

In spite of the fact that the desalination degree was quite high (40%) at a current density of 2.5 mA/cm², the relative quantity of the metal electrosorbed in the desalination compartment was

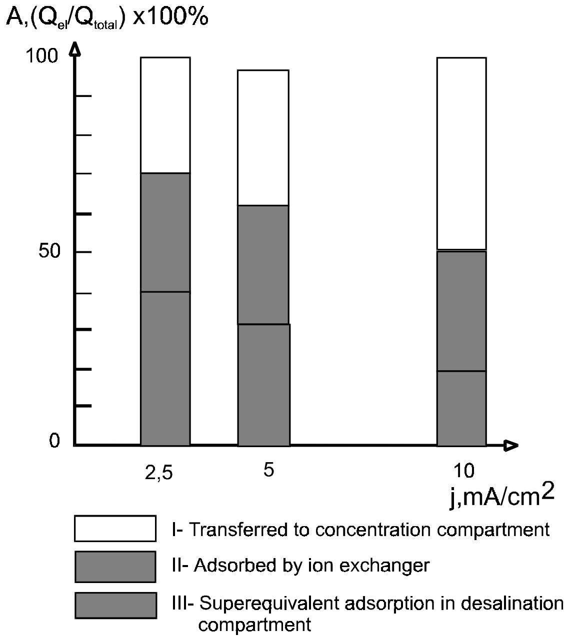

Figure 5
Influence of electrical current density on desalination degree of Ni ions

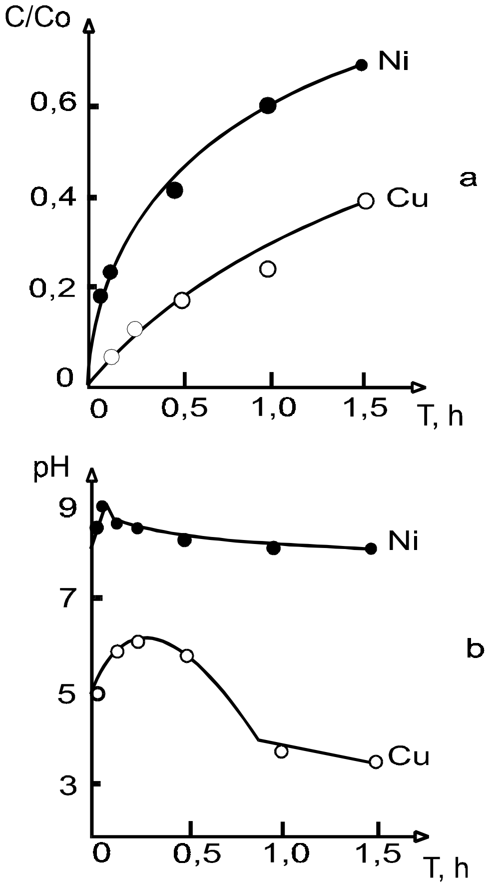

Figure 6
Electrosorption of Ni and Cu ions using amphoteric resin

virtually unchanged for all current densities and varied in the range from 7 to 10% (Fig. 4 and 5). Hence an increase in the current density to just under the conditions of the overlimiting current led mainly to an increase in the transmembrane ion transport.

When electrosorption of Cu- and Ni-containing solutions was carried out without the preliminary adsorption operation the concentration curves of the desalination compartment had different shapes (Fig. 6). When electric current was applied simultaneously with the solution flow through the desalination compartment, high desalination degrees occurred during the first 10 min (95% for Cu and 80% for Ni). A smooth decrease in the desalination degrees was observed over longer periods of time resulting in stable 65% for Cu and 40% for Ni after 1.5 h of the experiment. These steady-state desalination degrees were somewhat higher than those obtained by either pure electrodialysis or adsorption (Figs. 2, 3 and 4).

It is noteworthy that in the case of Ni-containing solutions the tendency for a decrease in the rate of the solution flow through the desalination compartment was observed during the whole experiment and after 1.5 h it was impossible to maintain it at 10 mℓ/min with unchanged pressure.

During the electrosorption study of the Cu-containing solution a steady growth in potential across the cell was detected. After 1.5 h gas formation in the cell became obvious. On completion of the experiment a layer of finely divided black particles was located on the surface of ion-exchanger pellets. Earlier this effect was attributed to the formation of bipolar microelectrodes (Pevnitskaya, 1992).

Joint action of electrical current and the alkaline solution present in the case of the amphoteric ion exchanger resulted in more radical precipitation of Ni hydroxide in the desalination compartment in comparison with electrodialysis without the ion-exchange packing at the same current density. pH value exceeded 9 during the first 10 min and remained higher than 8 throughout the experiment (Fig. 6). Rapidly growing precipitate filled the volume of the precipitation chamber resulting in complications in both the ion-exchange process and the transmembrane transport. An analysis of the concentration compartment solution carried out on completion of the experiment showed 30-fold less metal ions present than in the similar experiment with Cu containing solutions (0.15 mg-eq against 5.1 mg-eq). Lower electrosorption efficiency of Ni solutions is a direct result of the above events.

A fluctuation of pH of the Cu containing solutions in the desalination compartment indicated the potential of Cu hydroxide formation. During the first 0.5 h of the experiment a higher than 6 pH was recorded pointing to a possibility of local pH values reaching the limit required for the formation of Cu hydroxide (Zapolsky and Obraztsov, 1989). At the same time the consecutive drop in pH to 3.5 suggested that complete retention of Cu hydroxide in the desalination compartment took place unlike in the case of Ni hydroxide. This was due to a lower dissociation constant of Ni hydroxide ($pK_{Cu(OH)2}$ = 6.47, $pK_{Ni(OH)2}$ = 4.6) (Rabinovich and Havin, 1991). The longer experimental time resulted in the compact layer of precipitate deposited on the membrane surface starting to obstruct the transmembrane transport of Cu ions, leading to an increased potential drop across the cell.

The nature of the ion-exchange packing had a significant influence on the extraction of ions during the electrosorption process. For instance in the case of the cation-exchanger with a capacity of 2.5 mg-eq/g a steady 100% ion removal was observed

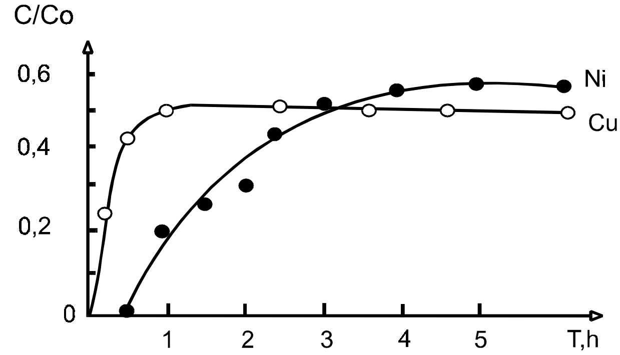

Figure 7
Electrosorption of Ni and Cu ions using cation-exchange resin

during the first 30 min of the experiment with a steady decrease to 55% after 4 h (Fig. 7). A higher desalination degree in the case of the Cu-containing solution was due to higher stability of Cu ion complexes formed with functional groups of the resin.

Conclusions

- Due to its higher adsorption capacity the cation-exchanger KU-2-8 exhibits a greater removal efficiency for heavy metal ions in the conventional adsorption process than that of the amphoteric ion-exchanger ANKB.
- In the electrosorption process the efficiency of the cation-exchanger is also superior to that of the amphoteric resin because of insoluble species formation in the latter case accompanied by an increase in electrical resistance of the desalination compartment.
- Although the desalination degree in the electrosorption process with preliminary adsorption is independent of the type of ion-exchange packing, the over-equivalent adsorption in the desalination compartment is twofold higher in the case of the amphoteric resin.
- A sixfold higher metal quantity was adsorbed on the amphoteric ion exchanger under the influence of electrical current than what is expected from the adsorption capacity of this resin.
- The removal efficiency of Cu ions by electrosorption with preliminary adsorption on the amphoteric resin grew threefold with a fourfold increase in the current density accompanied by a twofold decrease in the over-equivalent adsorption.
- Electrosorption process is more effective for desalination of solutions containg Cu than Ni ions.

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