Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Verbych, Svetlana , Hilal, Nidal , Sorokin, Genady and Leaper, Mark(2005) 'Ion Exchange Extraction of Heavy Metal Ions from Wastewater', Separation Science and Technology, 39: 9, 2031 — 2040

To link to this Article: DOI: 10.1081/SS-120039317

URL: http://dx.doi.org/10.1081/SS-120039317

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 9, pp. 2031–2040, 2004

Ion Exchange Extraction of Heavy Metal Ions from Wastewater

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ABSTRACT

In this study, ion-exchange resins of the cation exchanger universal (KU)-2 type with functional sulfate groups, a carboxyl-containing cation exchanger of a carboxyl containing cationite (KB) type, and polyampholyte amphoteric carboxyl containing ion exchanger (ANKB)-35 were studied for Ni^{2+} and Cu^{2+} ion extraction from water solutions. The high value of the ion-exchange capacity of the ionate KU-2 compared with the complex formation amphoteric ion-exchange resin ANKB appeared to be more suitable for use in wastewater treatment. The wet KU-2-20 resin has larger static ion-exchange capacity than other gel

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DOI: 10.1081/SS-120039317 0149-6395 (Print); 1520-5754 (Online)

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resins. This paper presents a technological circuit and installation for local treatment of rinsing water of nickel plating with subsequent metals utilization. It was found that the gradual accumulation of nickel occurs during multiple solution circulations with a low rate.

Key Words: Heavy metals; Ion exchange; Rinsing water; Electrochemical elimination; Water and metal reuse.

INTRODUCTION

Water and soils contamination with metals typically results from industrial processes, mining, military installation, and disposal of wastewater; it also may originate from the weathering of natural geological materials.[1−2] To avoid metal contamination to agricultural land and water resources, it is desirable to ensure that any wastewater discharged has been clariflocculated to minimize its metal content. The recovery of metals exiting processes also significantly reduces costs by allowing recycling. This is particularly significant in the electroplating industry, where large amounts of water are used for rising electroplated products.

The traditional method of galvanic wastewater purification, which is based on precipitation of metals, presents certain disadvantages, such as the necessity to maintain specific pH conditions, temperature, and ion concentration, it also encourages the formation of colloids, complexing agents, and metal anions. In addition, this method produces amounts of sludge several times greater than the initial amount of each metal;[2] combating this problem could involve the use of ion exchange, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis to reduce the concentration of metals.[3−6] Nevertheless, many of these approaches can be marginally cost effective or difficult to implement in developing countries. Therefore, there exists a need for a treatment strategy that is simple, robust, and compatible with local resources and constraints. The concentration of heavy metals by ion exchange is the most suitable in this respect and has been used previously for rinse-water purification [7−9] and has existing applications in water softening and nitrate removal in the potable water processes, as well as in refined technologies.[10,11] In addition, the use of ion exchange for control of waters with heavy metal pollution is also well known.[12] The ion-exchange resins are regenerated easily and returned to the cycle, with the result that from 60% to 100% regeneration of the initial ion-exchange capacity can be achieved. But, for the regeneration of universal ion-exchange resins, the consumption of acids and alkalis is three to four times higher than the required stoichiometric quantities. Because of that, application of the complex-forming ion exchangers is considered to be more cost effective.

After saturation of eluate with heavy metals, it can be regenerated by electrolysis, which is a cost effective and an ecological method for heavy metals removal from solutions.[13]

This study focuses on the new concept of water-treatment management to prevent sediment contamination and to protect the environment. The proposed approaches to develop closed-loop systems water consumption are based on the suppression of the heavy metals migration into wastewater by ion-exchange extraction of the particular heavy metal ions from the rinse water after the electroplating process. The purpose of this work is to investigate selectivity of universal cation-exchange resins and an aminocarboxyl ion exchanger for nickel and copper ions extraction and to determine the influence of diverse factors on the removal and the recovery of nickel from simulative rinse water after electroplating.

EXPERIMENTAL MATERIALS AND ANALYTICAL METHODS

Ion exchangers of different structure, porosity, and chemical properties were used with an aqueous nickel ion solution of concentration 30 mg eq/L. The solution under investigation was circulated with the velocity 0.65 cm/sec through the column containing swollen ion-exchange resin under fluidized-bed conditions. The materials used were strongly acidic resins with different binding degrees in H^+ form, macroporous resin (KU)-23 (30/100) containing 30% binding agent and 100% pore-forming substance, the weak acidic ion-exchanger KB-4 and polyampholyte (ANKB)-35 in the Na^+ form, produced in Ukraine. As well, these ion exchangers, KU-2-4 (Massachusetts, USA), KU-2-8 (Vladimir, Russia), KU-2-20 (Charkassi, Ukraine), were used and had a gel structure, being similar to a sulfacation exchanger of Dowex-50 type (USA), with the structure and properties of the ampholyte closely resembling those of Dowex-1-A, Chelex-100 (USA) and ANKB-10, ANKB-50 (Russia) resins. The method of preparation of all resins is described elsewhere.[14] The moisture content of the ion-exchange resins varied according to origin and is summarized in Table 1. To determine the moisture content, $4 \pm 2 \times 10^{-4}$ g of resin was dried at 90°C until it showed a constant weight. The concentration of metal ions was determined with complexometric titration. The degree of adsorption (F) was calculated as the ratio of the equivalent quantity of metal ions adsorbed by the ion exchanger during a fixed period of time to the equivalent quantity of functional groups, as defined in Eq. (1):

$$F = \frac{(C_0 - C) \cdot V}{E \cdot m} \tag{1}$$

Table 1. Physical–chemical characteristics of different types of ion exchange resins in Na^+ form.

Type of sorbent	Static exchange capacity of dry exchanger (mg eq/g)	Moisture content (%)		Static exchange capacity of wet exchanger (mg eq/g)
		Reference book[14,16]	Experimental data	
KU-2-4	5.31	62–70	62	2.04
KU-2-8	5.20	50–60	51	2.57
KU-2-20	4.77	30–40	28	3.44
KU-23	5.10	50–70	64	1.85
KB-4	10.00	55–65	61	3.91
ANKB-35	—	—	54	1.05

where C_0 is initial concentration of nickel ion in water solution, mg eq/L; C is current concentration of nickel ions, mg eq/L; V is solution volume, L; E is exchange capacity of the resin, mg eq/g; m is the mass of the wet resin, g.

The water sample used in this study had the same nickel ion concentration as rinse water after the nickel-plating process at the manufacturing plant.

EXPERIMENTAL EQUIPMENT DESIGN

Having obtained the properties of the test materials, an experimental rig was constructed to replicate conditions in the electroplating process, and this is shown in Fig. 1. According to plating standards, the parts are moved from the electroplating bath to a drag-out (catching) bath and then to the rinsing bath. The volume of drag-out losses and, hence, the heavy metal concentration in drag-out (catching) and flow-type rinsing baths depend on the composition and concentration of the electrolyte in the plating bath, and the geometrical configuration of the parts and their conveying speed on the coating line. Heavy-metal concentration increases to 1.2–1.7 g/l in the drag-out bath, and substantially exceeds the maximum permissible concentration in the rinsing bath during the shift. During this part of the process, 15–30 g of metal are lost for every 1 m^2 of plated parts and, consequently, valuable metal accumulates in the waste.

In this study, the ion-exchange column is placed directly on the coating line, as shown in Fig. 1. Solution from a drag-out bath (2) continuously moves via a pump (7) through a column with cation-exchange resin (4) at a fluidizing velocity of 0.65 m/s. After absorbent saturation of the first column with metal ions is achieved, the flow of solution from a drag-out bath is switched into

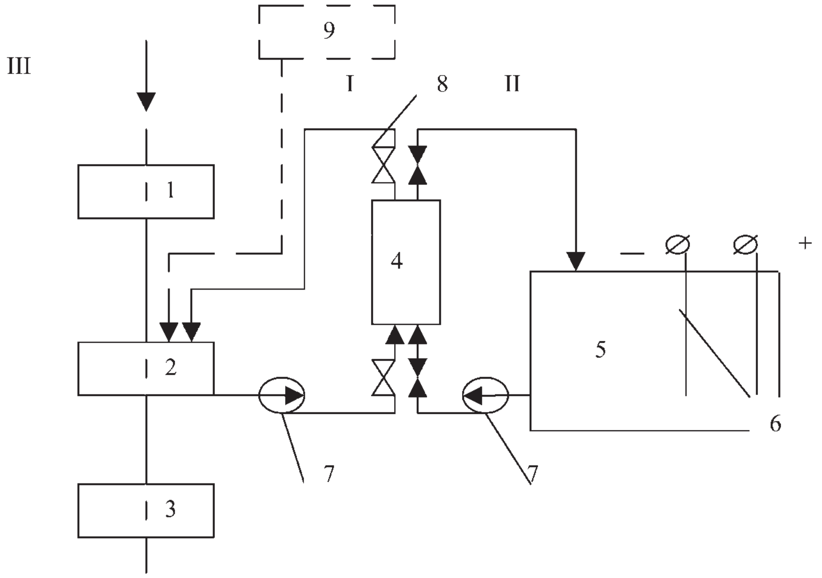

Figure 1. Scheme of installation. (1) Plating bath; (2) drag-out bath; (3) bath for continuous rinsing; (4) sorption column; (5) electrolyzer; (6) cathode; (7) pump; (8) valve; (9) softening block; (I) solution flow of the drag-out bath; (II) recovered solution flow; (III) movement of work pieces along the line.

the second column. The column of spent material is connected to the regeneration path by another pump. The quantity of the ion-exchange resin for the column is selected in such a way that imposes a maximum on the concentration of heavy-metal ions in the drag-out bath for the duration of the experiment.

The regenerated solution circulates through the electrolyzer (5) and the ion exchange column (4), which displaces heavy-metal ions, as shown in Fig. 1. Under these conditions, the heavy metals ion concentration reaches 3–4 g/l, which deposits metal on to the cathode of the electrolyzer. The extracted nickel can be used as an anode in the electroplating bath, depending on the quality and thickness of the deposit.

RESULTS AND DISCUSSION

Industrially produced ion-exchange resins have a gel or a macropore structure. The functional groups of gel ion exchangers are distributed over the resin grain. The concentration of the cross-linking agent—divinyl benzene (DVB)—is in the range of 2–20%. The functional groups of macropore resins are accessed more in the exchange process because of their large pore size within the particles.[15] Unfortunately, the capacity of porous resins is lower than capacity of gel resins because of the lesser number of functional groups in the ion exchanger grain. The volumetric fraction of pores is about 10–30% of polymer frame volume, reducing exchange capacity.[15] It was detected that the highest extraction rate of nickel is achieved by using resin KU-2-8, since its exchange capacity is more than that of resin KU-2-4, despite the fact that the binding degree of this one is half, as shown in Fig. 1. The nickel extraction rate is high for the resin KU-2-4 for the first 15 min of the process. This could be explained by the easy access of sulfonic functional groups for ion exchanging. It is natural that a high degree of swelling, as well as a cross-linking agent concentration, leads to the polymer chain extension that makes the functional groups of resin efficiently involved in the exchange process.

The wet KU-2-20 resin has a larger static ion-exchange capacity than the other gel resins. A high degree of cross-linking (20% DVB) of this exchanger does not lead to a high rate of nickel sorption, and, therefore, only 45% of sorption capacity has been used for extraction. An increase in DVB concentration in the ion-exchange resins KU-2-type decreases the moisture content and also decreases the steric hindrances in the grain, as shown in Table 1. This impedes the movement of metal ions toward the functional groups, making the counterions mobility decrease with increasing cross-linking. The ion-exchange rate of gel-type resins is limited by the diffusion of the metal ions.

The highest value of exchange capacity and the moisture content corresponds to the weak acidic carboxyl-containing cation exchanger KB-4 (Table 1). However, the efficiency of nickel extraction by this resin is low. It was assumed that during the first 15 min, H^+ ions transport would compete with the exchange of Ni^{2+} ions from solution. As a result of this process, hydrolysis of functional groups would occur. This hydrolysis was accompanied by the replacement of Na^+ ions by H^+ ions and by the release of OH^- ions into the solution, causing the pH of the solution to change from 4.5 to 6.5. The formation of low-dissociated –COOH groups in the ion exchanger led to a decrease in extraction rate.

With the conversion of the ion exchanger from the Na^+ into the Ni^{2+} form, the formation of hydrocomplexes of bivalent cations in the pores of a macroporous exchanger KU-23 (30/100) also was observed. The kinetic of sorption in this case was accompanied by a decrease in pH value.

There are additional coordinating binds in the polyampholyte ANKB-35, which led to the formation of strong complexes of transition metals, which also depended on the degree of protonization of the nitrogen in the amino groups. It has been observed that on increasing the acidity of the solution, the concentration of complex-forming ionogenic groups decreases and their electrodonor properties and the swelling degree change significantly.[16] A decrease in the swelling degree and the concentration of complex-forming groups leads to a decrease in stability of ion-exchange complexes. It was found experimentally that Ni^{2+} and Cu^{2+} ions adsorption decreased with a reduction in the pH. The extraction degree of Cu^{2+} ions did not exceed 0.1 at pH 1.3 and Ni^{2+} ions sorption did not occur at all from acidic solutions at pH < 2, as shown in Fig. 2. However, at high pH values, complex formation was limited by the generation of basic salts of the metals and poorly soluble precipitates of hydroxides.[17] However, Fig. 3 shows that the adsorption degree of ampholite ANKB-35 is less than resins KU-2-8 and KU-2-4, and the adsorbent filling with Ni^{2+} ions is limited by the low-exchange capacity of ampholyte ANKB-35 in comparison with resins noted above (Fig. 3). Thus, the extraction of heavy metal ions from water solutions can be carried out efficiently by using the ion-exchange resin KU-2-8.

It also was found that during multiple solution circulation with a low rate, the gradual accumulation of nickel ions occurs (Fig. 4, curve I). At a flow rate more than 10 l/hr, independent of sorption–regeneration cycle, nickel ion concentration in the drag-out bath does not exceed the indicated quantity (curves II, 1–7), while in the flow-type rinsing bath, it will always be lower than the maximum permissible concentration.

During Ni^{2+} sorption from tap water, Ca^{2+} ions also are adsorbed by the cation-exchanger. Insoluble calcium sulfates are formed, blocking the functional group of the exchanger with sodium sulfate during subsequent regeneration. This brings about a gradual loss of the capacity of the sorbent

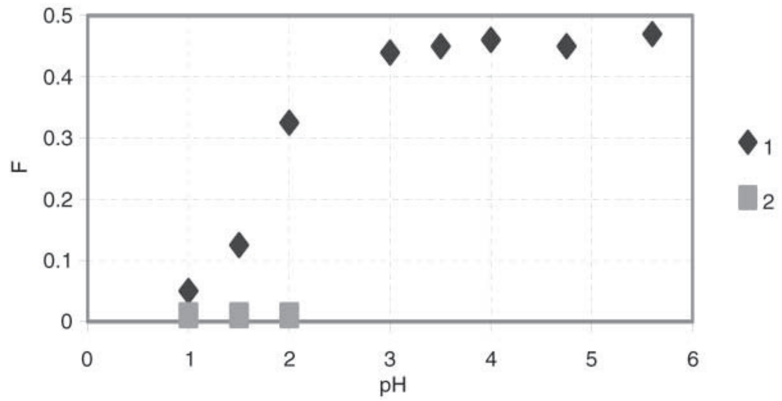

Figure 2. Influence of solution pH on adsorption degree (*F*) of Cu^{2+} (1) and Ni^{2+} (2) ions by exchanger ANKB-35.

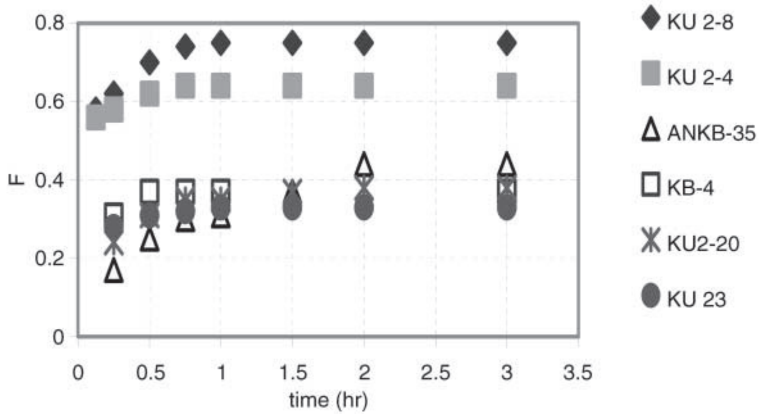

Figure 3. Kinetics of Ni^{2+} ions adsorption by ion-exchange resins.

with each sorption–desorption cycle. This can be avoided by using a softened water unit containing a softening block. For effective functioning of the unit, the block must operate for about 2 days a week. However, the block's cation-exchange capacity gradually falls due to organic compounds and chelates of iron and aluminium hydroxides present in tap water. This can be remedied by washing the resin with 3.5 N of sulfuric acid every 2 months. (or after 7 sorption–regeneration cycles). After that, the resin should be washed by

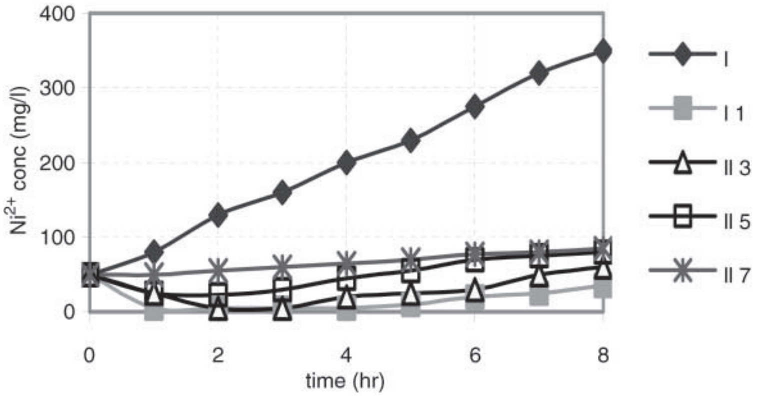

Figure 4. Kinetics of change in nickel ions concentration in the drag-out bath on numbers of solution circulation: 2 rps/hr (l) and 12 rps/hr (II). Number of curves–number of cycles of sorption with cation-exchanger recovery.

water and converted into a sodium form by salt to reuse in the softened water unit. Thus, in this way, the adsorption technology greatly reduces the presence of nickel ions in the wastewater and yields pure extracted metal that can be used as an anode in the electroplating process.

CONCLUSION

This paper presents our study of a variety of ion-exchange resins available for an ion-exchange system for removing metal cations from wastewater by using a fluidized bed adsorber and regenerator. The most suitable type of these resins was found to be KU-28. A system with two solution circulations per hr is the most effective method for reducing the concentration.

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