Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11417

64 (2017) 233–236
February

The effectiveness of nickel recovery from spent electroplating baths by electrodialysis

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Received 8 April 2016; Accepted 28 August 2016

ABSTRACT

In this paper, the applicability of electrodialysis for nickel sulfate recovery from a spent nickel electroplating bath was discussed. The rate of $NiSO_4$ recovery and the electric current efficiency were determined along with boric acid and total organic carbon content reduction. High nickel sulfate recovery reaching 96% and the electric current efficiency of around 79% proved the effectiveness of electrodialysis in nickel sulfate recovery. The study has also demonstrated that total organic carbon and boric acid contents were reduced by 48% and 66%, respectively.

Keywords: Electrodialysis; Nickel recovery; Electroplating bath; Metal finishing

1. Introduction

The waste streams including heavy metals are produced by a variety of industries. One of the key processes that generate heavy metal rich wastewaters is electroplating. Another significant source of the above-mentioned wastes is metal etching, electroless deposition, and hydrometallurgy [1,2].

The well-known metal surface treatment process which allows for deposition of a thin nickel layer on metallic surfaces is nickel electroplating. The widely used nickel electroplating bath (Watt's bath) contains nickel sulfate, nickel chloride, boric acid, organic brightener and surfactant. Nickel electroplating, however, requires a number of water-consuming procedures, which generates large quantities of liquid wastes. Also, spent electroplating baths are produced periodically. Therefore, this technology generates substantial quantities of non-biodegradable effluents containing organic and heavy metals contaminants [1–3]. Heavy metals such as nickel are toxic, carcinogenic, as well as able to accumulate in living organism. High concentration of nickel can cause skin dermatitis, chronic asthma, nausea and damage to the nervous system. Moreover, the wastes containing Ni^{2+} ions have negative impact on the environment [3,4].

Nowadays, a wide range of methods that can be used for heavy metal recovery from industrial effluents are known. All of these methods have their drawbacks [3–7]. Chemical precipitation is the most frequently used for heavy metal removal from inorganic effluents; however, the major disadvantage of using this method is large quantities of heavy metal rich sludge and high costs of its disposal [8,9]. The ion exchange and adsorption processes have also their drawbacks, such as limited capacity of an adsorbent material and the requirement for frequent resin regeneration with concentrated acids or bases. In fact, the adsorption-based processes can only be applied for heavy metal removal from effluents with relatively low heavy metal content, due to limited capacity of the adsorbent [6,8,9]. Membrane separation processes can be an alternative to traditional wastewater treatment methods presented above

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Presented at the conference on Membranes and Membrane Processes in Environmental Protection (MEMPEP 2016), Zakopane, Poland, 15–19 June 2016

[10]. One of the membrane techniques that can be effectively used for the recovery of metal salts from electroplating wastes is electrodialysis (ED) [1,2,11]. ED allows for the transport of ions from one solution to another using an external electric field as the driving force. In the ED process two types of membranes are used: cation-exchange (CEM) and anion-exchange membranes (AEM). AEMs contain positively charged groups fixed to the polymer matrix, whilst CEMs contain negatively charged groups fixed to the polymer matrix. The ED process has a considerable amount of applications. This process has been mainly used for the production of pure water from sea and brackish waters, treatment of industrial sewage as well as resource recovery from various effluents [12,13].

Available literature [1,2,5,11,14] presents valuable results on electrodialytic removal of Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} ions from dilute aqueous solutions at the initial metal concentration of approximately several dozens of mg L^{-1}. These investigations have been mostly aiming at water recovery and the production of transition metals concentrate. Experimental results of electrodialytic recovery of nickel and water from nickel electroplating wastewater were reported in [1]. The nickel recovery efficiency by this method was 97.43%. Also in [2] nickel recovery by the ED method has been discussed. The results have shown that the nickel separation efficiency from electroplating wastewaters using the ED process increased from 47.3% to 96.8% [2]. Furthermore, the nickel electroplating baths contain brighteners, surfactant and boric acid, which can cause membrane fouling during the ED process. However, a decrease in pH or a temperature increase in a treated solution could eliminate the above-mentioned membrane fouling [15].

In this work, the possibility of nickel salt recovery from spent nickel electroplating bath in a laboratory-scale ED module has been investigated. The influence of chemical composition of spent electroplating baths on the effectiveness of ED in nickel sulfate recovery was discussed. Nickel sulfate recovery coefficient, electric current efficiency, as well as boric acid and total organic carbon retention coefficients were calculated and used as parameters to assess the ED process efficiency.

2. Materials and methods

The experiments were carried out using the EDR-Z/10-0.8 module (MemBrain, Czech Republic) with the effective membrane area of 64 cm^2. There were 10 pairs of membranes in the ED stack. The ion-exchange membranes (IEMs), used in this investigation, were AMC - CMC (IONSEP™, China). Their characteristics are given in Table 1. All the experiments were conducted periodically with the process solution recirculation. The investigated solutions compositions and volumes are provided in Tables 2 and 3. The studied spent nickel electroplating bath contained nickel sulfate ($NiSO_4$), boric acid (H_3BO_3), and organic compounds such as surfactants and brighteners of unknown chemical composition. Due to the unknown composition of the organic contaminants their content was determined only as total organic carbon (TOC).

The experiments were performed at a constant voltage, which corresponded to the initial electric current density of 300 $A\cdot m^{-2}$. Despite its high value, the electric current density applied was much below its limiting value, which was estimated to be in excess of 1000 $A\cdot m^{-2}$ (based on the conductivity of the examined solutions). During the experiments electric current, conductivity and pH of the diluate and concentrate solutions were continuously monitored. Initial pHs of the process solutions were equal to 1.0 while the final pH of the diluate reached nearly the value of 3.0. Each experiment was conducted until the diluate conductivity decreased down to the level of 5 mS cm^{-1}. Nickel (as nickel sulfate), carbon (as TOC) and boron (as boric acid) contents were determined using ICP-OES (Varian, Australia) in all the tested solutions.

Nickel sulfate recovery (R_{NiSO_4}), nickel sulfate electric current efficiency (CE_{NiSO_4}), boric acid retention coefficient ($SP_{H_3BO_3}$) as well as total organic carbon retention coefficient (SP_{TOC}) were calculated as follows:

$$R_{NiSO_4} = \frac{m_{NiSO_4}^{conc_t}}{m_{NiSO_4}^{dil_0}} \cdot 100\% \quad (1)$$

Table 1
Characteristics of IONSEP™ ion exchange membranes [16]

Type of membrane	CMC	AMC
Thickness, mm	0.42	0.42
Ion exchange capacity, mol kg^{-1}	2.4	2.2
Diffusion coefficient·10^{-3} mmol NaCl, $cm^2\cdot h\cdot mol\cdot dm^{-3}$	4.7	4.3
Ionic permselectivity, %	91	90
Surface electric resistant, $\Omega\cdot cm^2$	6–10	8–10

Table 2
Summary of the process solution composition

Experiment no.	Initial diluate			Initial concentrate	Electrode rinse solution
	$NiSO_4$, $g\cdot dm^{-3}$	H_3BO_3, $g\cdot dm^{-3}$	TOC, $g\cdot dm^{-3}$		
1	195.31	29.05	1.15	0.05 M H_2SO_4	0.05 M H_2SO_4
2	195.31	29.05	1.15		
3	216.76	26.39	0.635		
4	217.56	26.18	0.665		
5	214.45	28.12	0.658		
6	216.07	28.12	0.635		

Table 3
Volumes of the experimental solutions before and after ED

Experiment no.	Volume of the diluate, dm^3		Volume of the concentrate, dm^3		Volume of the electrode rinse solution, dm^3
	Before ED	After ED	Before ED	After ED	
1	0.7	0.270	0.250	0.88	0.150
2	0.7	0.400		0.76	
3	1	0.245		1.10	
4	1	0.250		1.10	
5	1	0.260		1.08	
6	1	0.260		1.10	

where $m^{dil_0}_{NiSO_4}$ is the initial mass (g) of nickel sulfate in the diluate solution before ED, and $m^{conc_t}_{NiSO_4}$ is the final mass (g) of nickel sulfate in the concentrate solution after ED.

$$CE_{NiSO_4} = \frac{F\cdot z\cdot \frac{C^{conc_t}_{NiSO_4}}{M_{NiSO_4}}\cdot V_{conc_t}}{n\cdot I\cdot \Delta t}\cdot 100\% \quad (2)$$

where F is the Faraday constant 96,485 C·mol^{-1}; z is a charge number of Ni^{2+}, V_{conc_t} is the volume of the concentrate solution after ED (dm^3), $C^{conc_t}_{NiSO_4}$ is a concentration of nickel sulfate in the concentrate solution after ED (g·dm^{-3}), M_{NiSO_4} is the molar mass of $NiSO_4$ (g·mol^{-1}), n is the number of membrane pairs, I is the electric current (A); Δt is a time interval (s).

$$SP_i = \left(1-\frac{M_i^{conc_t}}{m_i^{dil_0}}\right)\cdot 100\% \quad (3)$$

where $m_i^{dil_0}$ is the initial mass (g) of the i species in the diluate before ED and $m_i^{conc_t}$ is the final mass (g) of the i species in the concentrate after ED.

The initial and final mass of i species ($m_i^{dil_0}$, $m_i^{conc_t}$) in the diluate before ED and in the concentrate after ED were calculated using the formula:

$$m_i = C_i \cdot V_i \quad (4)$$

where C_i is a concentration of i species in the diluate or concentrate solution (g·dm^{-3}), V_i is the volume of the diluate or concentrate solution (dm^3).

3. Results and discussion

The main objective of this research was to investigate the effectiveness of nickel sulfate recovery from spent electroplating baths by the ED process. Six samples of spent electroplating baths with the initial nickel sulfate concentration in the range from 195.31 to 217.56 g·dm^{-3} (Table 2) were tested. During ED tests, the process progress was monitored by tracking changes in conductivity of the process solutions, as shown in Fig. 1. The diluate's conductivity decreased with time as a result of the nickel salt removal, whereas concentrate solution's conductivity increased. Once the tested solution become nickel-depleted a rapid decrease in the diluate conductivity below 5 mS cm^{-1} was observed.

Preparation of electroplating baths involves the use of organic compounds, with organic brighteners being most common [17]. The summary composition of the diluate solutions before the ED processes is presented in Table 2. It can be noted that samples number 1 and 2 contained two times more organic compounds expressed as TOC than subsequent samples. Table 4 shows the composition of the all process solutions upon the ED test completion. The efficiency of nickel sulfate recovery is presented in Table 5. It was observed that nickel sulfate is removed from the diluate very effectively by the proposed method with the recovery rate reaching 96.6% in the experiment No. 6. The diluate contained only a few percent of nickel sulfate present there initially and the concentrate contained more than 80% of the nickel salt contained in the initial diluate. Diluate and concentrate boric acid contents were similar in experiments No. 1 and No. 2 while for other experiments the boric acid diluate content exceeded the one in the concentrate only to a limited extent. As an electrically neutral molecule, boric acid molecules are not dragged by the electric field to the concentrate; however, due to its low molecular weight, it can freely diffuse across ion-exchange membranes. In contrast, concentrations of organic compounds in the concentrate, determined as TOC, were considerably lower than in the diluate, which

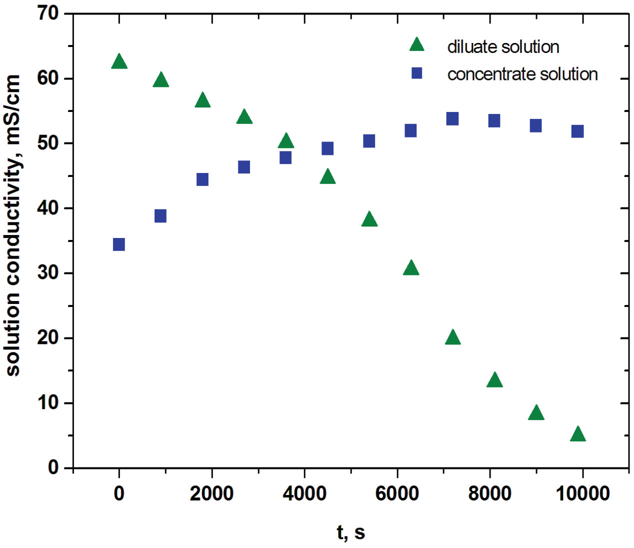

Fig. 1. An exemplary conductivity vs. time curves in an ED process (experiment no. 1).

Table 4
Composition of the process solutions after ED

Experiment no.	Diluate solution			Concentrate solution		
	$NiSO_4$, g·dm^{-3}	H_3BO_3, g·dm^{-3}	TOC, g·dm^{-3}	$NiSO_4$, g·dm^{-3}	H_3BO_3, g·dm^{-3}	TOC, g·dm^{-3}
1	2.40	13.68	0.532	132.01	13.51	0.454
2	2.93	13.97	0.540	144.71	13.64	0.396
3	5.93	22.69	0.714	184.84	16.10	0.283
4	3.76	21.60	0.701	187.64	16.17	0.273
5	5.05	21.94	0.745	187.11	16.81	0.281
6	4.66	21.70	0.726	189.78	16.03	0.286

Table 5
Results of the R_{NiSO4}, CE_{NiSO4}, $SP_{H_3BO_3}$, and SP_{TOC} coefficients

Experiment no.	R_{NiSO4},%	$SP_{H_3BO_3}$, %	SP_{TOC}, %	CE_{NiSO4}, %
1	85.0	53.5	50.6	68.4
2	80.4	53.0	62.7	68.0
3	93.8	32.9	53.4	75.6
4	94.9	32.1	52.7	72.9
5	94.2	35.4	54.4	75.3
6	96.6	37.3	52.2	79.4

suggest that the majority of the organic matter in the spent electrolytic baths was in an electrically neutral form as boric acid. However, its diffusion into the concentrate was somehow limited by the membranes, probably due to high molecular weight.

During the ED tests, a considerable decrease in the diluate volume and related increase in the concentrate volume due to electroosmosis was observed. Therefore, a mass-balance of the results obtained during the tests was performed. Table 5 summarises the results for nickel sulfate recovery, boric acid and organic carbon retention coefficients, and nickel sulfate electric current efficiency. The lowest nickel sulfate recovery ($R_{\mathrm{NiSO_4}}$) and the highest H_3BO_3 retention were observed at the highest initial diluate TOC content (Exp. 1 and 2). Such a behavior can be attributed to the presence of organic compounds in the diluate, which causes membrane fouling, thus it hampers the ion transport and accelerates the rate of neutral boric acid transport [1]. In addition, charged nickel-organic species migrate much slower across IEMs than free metal ions or their hydrated forms, which seems to be supported by the decreased current efficiencies observed at high TOC concentrations (Table 5). Linstrandt et al. stated that a wide range of organic compounds (e.g., surfactants) present in effluents cause IEMs fouling and affect nickel sulfate transport [18]. Regardless of the initial diluate TOC content, approximately 50% of TOC was retained in the diluate (Table 5), thus a two-fold reduction in the content of organic compounds, typical for nickel electroplating baths, was observed.

As shown in Table 5, the $NiSO_4$ electric current efficiency was not correlated with the feed nickel sulfate concentration, boric acid content and TOC content. It was found that the CE_{NiSO4} was in range of 68.4%–79.4%. The remaining percentage of the electric current was utilized either for the transport of excess sulfuric acid (experiments were conducted at the pH of approximately 1) or for the transport of charged organic species.

4. Conclusions

In this work, the possibility of nickel sulfate recovery from a spent nickel electroplating bath by the ED method was investigated. The results of experiments on ED of spent nickel electroplating baths have demonstrated the nickel sulfate recovery rate of up to 96.6% at the electric current efficiency as high as 79.4%. It is in agreement with previous research on the effectiveness of nickel removal by the ED process. Benvenuti et al. [1] investigated nickel recovery from electroplating wastewaters with low nickel concentration (1.29 $g \cdot dm^{-3}$), and reported the percent nickel removal of 97.43%. There is a direct evidence that the presence of some of the organic compounds, specific for nickel electroplating baths, has an influence on the effectiveness of nickel salt recovery. The amounts of these compounds can be, however, reduced by a factor of 2 by using ED.

Acknowledgement

This work was financially supported by the Polish National Centre for Research and Development, and National Fund for Environmental Protection and Water Management Project no. GEKON2/O5/267906/10/2015.

Symbols

$CE_{\mathrm{NiSO_4}}$ — Nickel sulfate electric current efficiency, %
C_i — Concentration of *i* species in diluate or concentrate solution, $g \cdot dm^{-3}$
F — Faraday constant, 96,485 $C, \cdot mol^{-1}$
I — Electric current, A
$M_{\mathrm{NiSO_4}}$ — Molar mass of $NiSO_4$, $g \cdot mol^{-1}$
$m_i^{\mathrm{dil_0}}$ — Initial mass of *i* species in diluate before ED, g
$m_i^{\mathrm{conc}_t}$ — Final mass of *i* species in concentrate after ED, g
n — Number of the membrane pairs
$R_{\mathrm{NiSO_4}}$ — Nickel sulfate recovery, %
SP_i — Retention coefficient, %
Δt — Time interval, s
V_{conc_t} — Volume of the concentrate solution after ED, dm^3
z — Charge number of Ni^{2+}

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