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ORIGINAL PAPER

Nickel removal from electroplating waste water using stand-alone and electrically assisted ion exchange processes

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Abstract Wastewater discharged from metal-finishing processes usually contains nickel, a hazardous substance that is used extensively in the surface finishing industry. In the present study, an acidic solution containing nickel was treated using strong acid cation exchange resin. A continuous lab-scale cation exchange arrangement permitting the assessment of electric current as an enhancement mechanism was designed and utilized at different flow rates successfully. Applying the electrical potential enhanced the nickel removal by 12.7 % at flow rate 240 ml/h, and 2.5 % at flow rate 500 ml/h. Nickel recovery has been also investigated using hydrochloric acid as an eluent with and without electric current enhancement.

Keywords Industrial wastewater treatment · Nickel · Ion exchange · Electrically enhanced

Introduction

The release of heavy metals from industrial entities into the natural environment has led to serious pollution problems. Since these heavy metals are not biodegradable and can be biologically accumulated, their harmful effect on the environment lasts for long time. Among these different heavy metals, nickel is of high concern as it is extensively utilized in the modern industry. Direct exposition to nickel cause dermatitis, while some nickel compounds are carcinogenic and easily absorbed by skin (Vieria et al. 2010).

Wastewater containing nickel originates from the metal processing industries, steel foundries, motor vehicle, aircraft industries, printing and some chemical industries. Nickel plating is used for plating parts to provide a corrosion protection finish. This coating is significantly thinner than hard-chrome plates, and is applied only in minutes rather than hours or days as required for hard-chrome plating. The majority of nickel plating is done in an acidic medium, mostly in sulfate form, at pH value between 1.5 and 4.5, and moderate temperature between 40 and 65 °C. These conditions highly affect the selection of the treatment process to be used for the removal of nickel from waste water (Popuri et al. 2009). Traditional processes usually utilized for nickel removal from waste waters are adsorption (Vieria et al. 2010; Popuri et al. 2009; Kandah and Meunier 2007; Li and Champagne 2009; Aguilar-Gonzalez et al. 2010; Ewecharoen et al. 2008), bio-sorption (Ozturk 2007; Bhatnagar and Minocha 2010), precipitation (Forstner and Wittman 1979), electrochemical methods (Dermentzis 2010; Akbal and Camci 2011; Kabadasli et al. 2009; Pospisil et al. 2008; Njau et al. 2000), filtration (Katsou et al. 2010; Borbely and Nagy 2009; Karate and Marathe 2008; Channarong et al. 2010), electroflocculation-filtration hybrid system (Sun et al. 2009), liquid–liquid extraction (Gonzalez et al. 2010) and ion exchange (Rengaraj et al. 2001; Alyuz and Veli 2009; Halle et al. 1982). In fact, ion exchange is a well-known technology that we have utilized in several difficult separation tasks up to isotope separation (Ismail et al. 1997a, 1997b, 2002, 2001; Fujii et al. 1998; Nogami et al. 2001). Due to its high efficiency, low operating cost, recovery of metal value, selectivity, absence of sludge, ease of operation and reaching the required discharge specifications, ion

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exchange method is highly preferable for nickel ions separation (Alyuz and Veli 2009). Although there are several inorganic ion exchanger and/or adsorbents capable of separating nickel ions from aqueous waste solutions, synthetic organic resins are commonly preferred due to its high performance and low cost. Halle et al. successfully utilized the macroporous carboxylic cation exchanger Wofatit CA-20, in sodium form, for the removal of nickel ions from aqueous solutions (Halle et al. 1982). Alyuz and Veli preferred the strong sulfonic cation exchanger Dowex HCR S/S due to its high cation exchange capacity and managed to reduce the residual nickel and zinc in aqueous waste solutions below the discharge limits (Alyuz and Veli 2009). It was stated that more than 98 % removal efficiency was achieved under optimal conditions for nickel and zinc.

Electrochemical ion exchange (EIX) is an advanced ion exchange process, where the ion exchange is enhanced by applying an electrical potential (Henry and Van Lierde 1998; Turner et al. 1989; Bridger et al. 2007; Coletta et al. 1997; Adams and Hudson 1991; Cumming et al. 1997; Ahmed Basha et al. 2008). The EIX can be used in several applications, e.g. the removal of toxic, heavy metal ions, the recovery of precious metals, water deionization, and corrosive anion removal. EIX is unique as the exchange processes are controlled electrochemically. The use of regenerating chemicals is, therefore, highly minimized and it is possible to achieve large volume reduction factors. The presence of the ion exchange material not only reduces the cell potential required, but also increases the contact area with the waste stream, thus enhancing the performance of the cell. Also, reversal of the applied electrical potential could, in principle, cause the elution of the metal ion by replacement with protons (Coletta et al. 1997; Adams and Hudson 1991).

The aim of the work was to study the different parameters affecting the removal of nickel ion from synthetic solution by ion exchange process, construct an electrochemical ion-exchange column, carry out both loading and regeneration cycles and study the performance of column in case of applying electric current.

Materials and methods

Materials

The chemicals used in this work were all of analytical grade. Distilled water was used to prepare the solution and to wash the glassware in each experimental run. The ion exchange resins used were Purolite C150S and AG MP-50 strong acid cation exchange resins. Table 1 shows the resins' specifications.

Preliminary batch tests

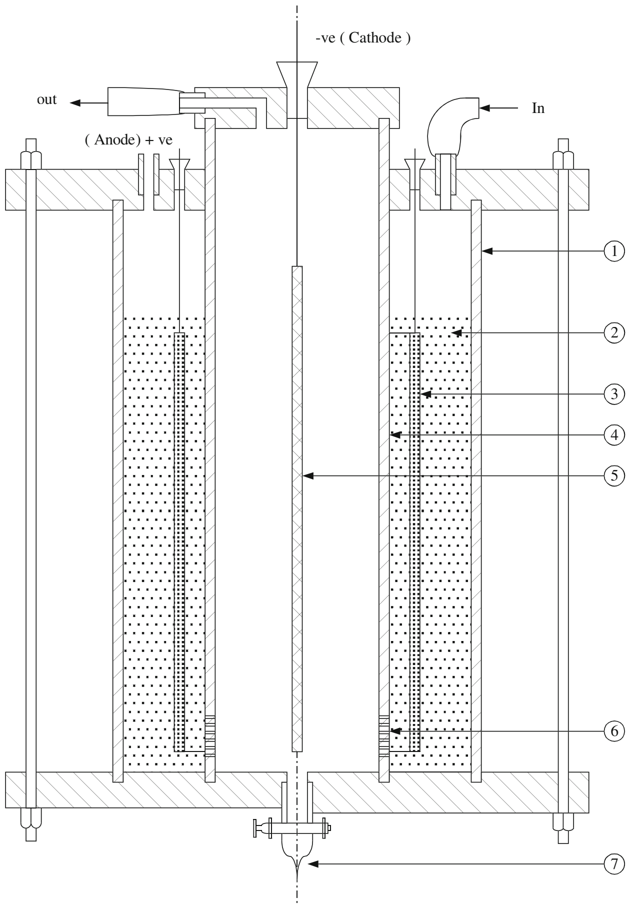
The following procedure was used to study the effect of several parameters on the uptake of nickel ions: a known weight of resin was added to a certain volume of solution having a known nickel concentration in a 50-ml bottle. Each sample was shaken for a certain time and then the test solution was filtered to separate the sorbent material from solution. The supernatant was analyzed and the residual concentration of the nickel ions in solution was determined.

Electrochemical ion exchange cell

A typical ion exchange column assembly was constructed as shown in Fig. 1. It consists of two cylindrical tubes: the outer has ID 80 mm diameter, and 500 mm length, while the inner tube has OD 32 mm diameter, and 650 mm length. There are two lead electrodes inside this column as shown in Fig. 1. The column was filled by 600 g of C-150S cation resin, which yields a bed height of 300 mm.

Table 1 Specifications of the cation exchange resin

Type	Purolite C150S (strong acid cation exchange resin)	AG MP-50
Structure	Macroporous resin of polystyrene crosslinked with divenylbenzene	Macroporous resin of polystyrene crosslinked with divenylbenzene
Active groups	R-SO_3 (sulphonic acid)	R-SO_3 (sulphonic acid)
Ionic form	Na^+ (Sodium)	H^+ (hydrogen form)
Particle size	0.42–1.2 mm	100–200 mesh
	$\leq$0.42 mm: 2 % max	75–150 µm
	$\geq$1.20 mm: 2 % max	
Effective size	0.55 mm	Large
pH range	0–14	0–14
Shipping weight	Approx. 800 g/l	Approx. 850 g/l
Supplier	PUROLITE	BIO-RAD



1- outer cylinder tube
2- Cation exchange resin
3- Lead-cylinder electrode (anode)
4- Inner cylinder tube
5- Lead-rod electrode (Cathode)
6- Teflon filter
7- Dreainage

Fig. 1 The electrochemical ion exchange setup

Instrumentation

All samples and chemicals used in the preparation of solutions were weighed using Sartorius analytical balance with a sensitivity of 10^{-4} g. The pH of solutions was measured using Philips pH meter, model PW 9422. The electric current was supplied by DC power supply and was controlled using digital multi meter, New General model 400. The solutions were fed to the column using dosing pump, MILO ROYAL model DC-1-93R. Nickel ion concentration was measured using atomic absorption spectrophotometer model GBC-902.

Experimental procedure

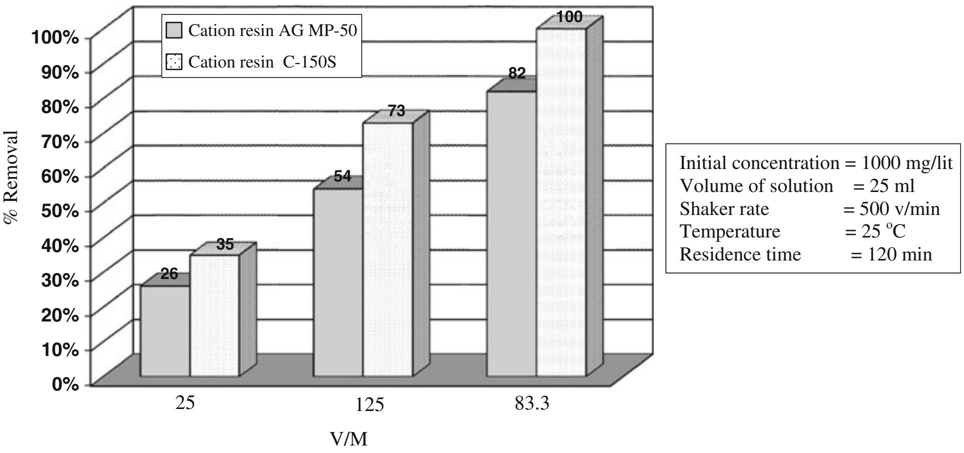
The feed solution was passed through the annulus between the outer tube and the inner tube from the top through the anodic electrode and cation exchange resin. After that the feed passed through a Teflon filter at the bottom of the inner tube and then it passed from the bottom to the top of the inner tube through the cathodic electrode. The solution effluent from the top of the cell was fractionated and selected fractions were tested. Electric current between the anode and the cathode is applied and controlled by a DC power supply and multi meter.

Results and discussion

Preliminary batch tests

Figure 2 shows the percentage removal of nickel ions by the two resins at different solution volume to resin mass ratios, V/M. It is clear that in all cases the uptake behavior of C-150S resin is better compared with AG MP-50. It was found that the uptake of nickel ions by C-150S is

Fig. 2 Effect V/M on the removal of nickel ions by the two resins



approximately 91 mg of nickel ions/g resin, while it is only 68 mg of nickel ions/g resin in case of AG MP-50. Therefore, C-150S resin was chosen to be used in continuous column operations.

Effect of flow rate on breakthrough curve

The most popular mode of operation of ion-exchange is the fixed bed mode. Therefore, it is essential to study this mode before implementing the proposed electrical enhancement process to compare the results and the performance criteria of the two schemes of operation. In this connection four break through runs were performed at different flow rates. If the breakthrough point is defined as the point at which the nickel concentration is 5 ppm, it is possible to measure the treated effluent volume for each run. Figure 3 shows the breakthrough curves obtained for different flow rates at the break point with concentration of 5 mg/l at each flow rate. It was found that the increase in flow rate decreases the volume of the treated solution at the break point, i.e. the capability of cation resin to remove the metal ion from the influent solution decreases as a result of the faster breakthrough, due to the decrease of residence time. Thus, the increase of flow rate decreases the contact time between solution and the cation resin in the column and hence residence time in the column. In other worlds, it increases the adsorption zone in the resin bed so the breakthrough of the nickel ions occurs earlier, i.e. increasing solution flow rate from 240 ml/h to 500 ml/h eventually reduces the efficiency from 80 to 60 %.

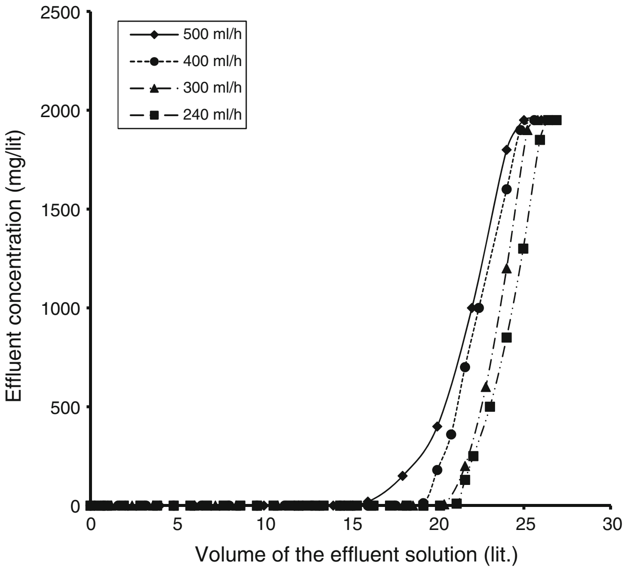


Fig. 3 Effect of flow rate on the breakthrough *curves*

Electrically Assisted Ion Exchange Process

The mechanism of the electrically assisted ion exchange process can be explained in its simplest form as follows (Cumming et al. 1997):

At the anode water is oxidized so that oxygen is formed with the release of protons:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

At the cathode hydrogen is evolved and hydroxyl ions are released by the reduction of water:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

The release of hydroxyl ions at the working electrode produces a local pH rise, which de protonates the active ion exchange groups, so that cations are adsorbed to maintain charge balance. If the electrode polarity is reversed, protons are produced in the solution then they exchange with the adsorbed cations, i.e. the adsorbed cations are released as the exchanger reverts to its hydrogen form. The application of potential between the counter electrode and the working electrode causes cations to migrate from the solution to the structure of the resin. Within the ion exchange matrix the cations will exchange with protons that will continue to carry the current. Hydroxyl ions flowing in the opposite direction will form water as they associate with the protons. Of course some of the current may also be carried by cations migrating through the ion exchange material, from ion exchange sites to nearby neighboring sites. It is possible that some cations will reach the working electrode without being exchanged due to mass transfer limitations within the ion exchange matrix. If this occurs then these cations would leak from the rear of the cell and contaminate the treated effluent and breakthrough is achieved.

Effect of current intensity on pH value of the effluent solution

By increasing the current intensity, the evolution of H^+ ions around the anode and the evolution of OH^- ions around the cathode increase. As the anode area is so large compared with the cathode area, the concentration of OH^- ions around the cathode is much increased compared with the acidity around the anode (Aguilar-Gonzalez et al. 2010). Therefore, the pH value of the effluent increases with the increase of current intensity, until turbidity appears due to the formation of $Ni(OH)_2$ at pH value above 6.5 according to Eq. (3).

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \tag{3}$$

Figure 4 shows the increase in the effluent pH with the increase in the current intensity. These results agree with

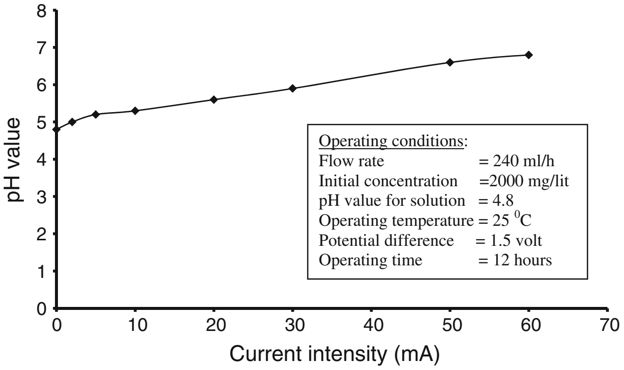


Fig. 4 Effect of current intensity on the effluent pH without resin

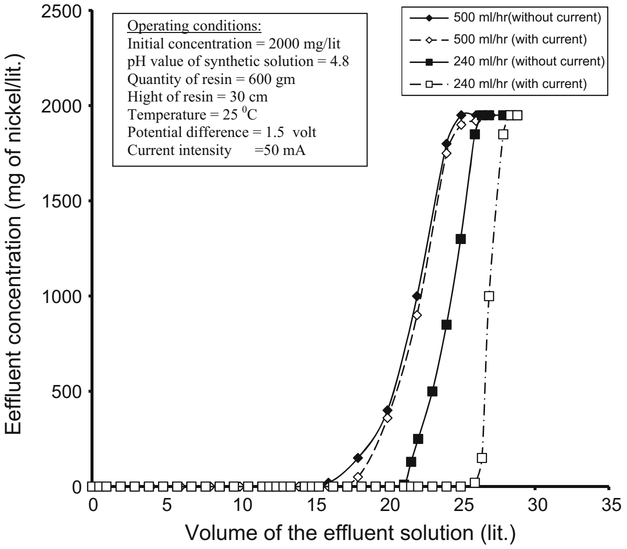


Fig. 5 Effect of current intensity on the breakthrough *curves* at *different flow rates*

the results reported by C. Ahmed Basha et al. who studied the total dissolved solids removal by electrochemical ion exchange (EIX) process where, the pH of the effluent increased from an initial value of 7 to a maximum of 10.5 with due course of operation (Ahmed Basha et al., 2008). Such results were highly needed to determine the maximum working current, which was found to be 50 mA.

Effect of 50 mA current intensity with influent flow rate variation

Figure 5 shows the breakthrough curves obtained at 240 and 500 ml/h flow rates in the absence and in the presence of 50 mA current intensity. Either in the case of normal ion exchange breakthrough, in absence of electric current, or in the case of electrically enhanced ion exchange breakthrough, the increase of flow rate decreased the effluent volume treated at break point. In both flow rate cases, the volume of the treated solution at the break point was increased upon applying the electric current as compared with the case of normal ion exchange process. At the low flow rate 240 ml/h, the volume of treated solution, with 5 mg/l, increases from 21 to 26 l, while the effect is relatively small in the case of high flow rate 500 ml/h, where the volume of treated solution with 5 mg/l increases from 16 to 18 l. The amount of nickel ions removed was measured at the two flow rates in the case of applying current and in the absence of electric current and are shown in Fig. 6. The amount of nickel removed from the solution and sorbet by the resin at a flow rate of 240 ml/h was increased by 12.7 % upon applying the electric current, while the increase of this amount at a flow rate of 50 ml/h due to electric current was only 2 %. This can be attributed to the mobility of ions in case of high flow rate; also the electric current increases the ion velocity and this in turn improves the mass transport and nickel removal.

Regeneration of cation resin and recovery of nickel ions

For any ion exchange process, regeneration is ultimately needed. The regeneration was carried out using hydrochloric acid. Reversing of polarity of the applied current and the utilization of different concentrations of hydrochloric acid were studied. Figure 7 shows the elution curve of nickel ions from the column by 2 M hydrochloric acid solution in the presence and absence of reversed electrical current. It is noticeable that there is no much improvement due to electrical current compared with the case of nickel loading, i.e. the enhancement of electrical current is limited in case of high velocity as a result of lower residence time. The amount of hydrochloric acid used to elute nickel ions from the full-load resin bed was measured in the case of applying current and in the absence of electric current. The highest effluent concentration by regeneration with reversed potential is 11,000 mg/l, but no more than 9800 mg/l was achieved in the absence of current. Most of the nickel will be eluted by the second and third liters of 2 M hydrochloric acid, where more than 85 % of eluted nickel is contained within 40 % of the effluent. These two liters can be collected in storage tank for reuse, and the dilute quantity can be recycled to elute nickel ions or collected in a receiver tank to re-concentrate the nickel ions, i.e. about 40 % of the 2 M hydrochloric acid can be

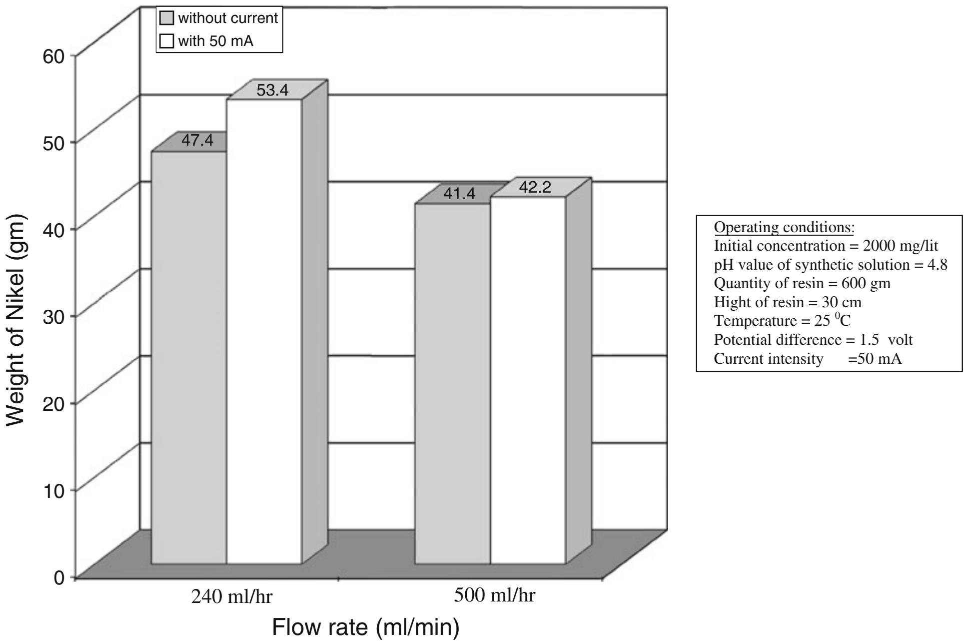


Fig. 6 Effect of current intensity on the amount of nickel ions removed at *different flow rates*

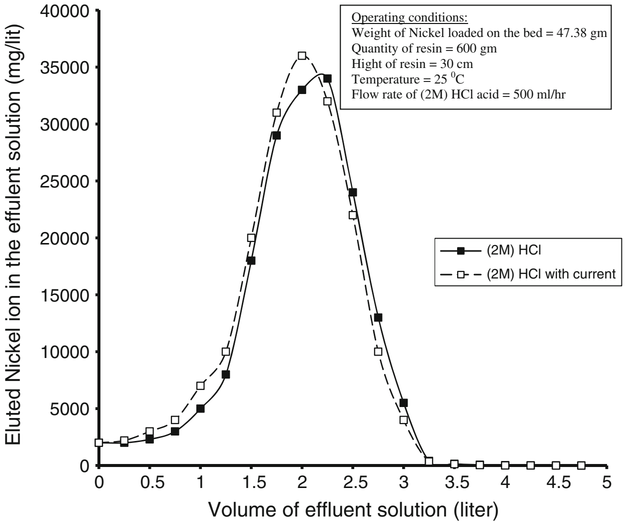


Fig. 7 Effect of current intensity on elution *curves* of nickel ions by 2 M HCl

reused to initiate regeneration in the second regeneration cycle followed by a fresh 2 M hydrochloric acid. This of course requires implementation of a monitoring system. Based on percentage removal data the regeneration cycle could be terminated using about 3.2 l of 2 M hydrochloric acid, and discarding the first portion of the elute nickel, thus permitting favorable conditions for recycle.

Conclusion

A synthetic solution resembling metal-finishing processes wastewater contaminated with nickel ions was treated using strong acid cation exchange resins. A continuous lab-scale cation exchange arrangement permitting the assessment of electric current as an enhancement mechanism was designed and utilized at different flow rates successfully. Applying the electrical potential enhanced the nickel removal by 12.7 % at flow rate 240 ml/h, and 2.5 % at flow rate 500 ml/h. Nickel recovery has been also investigated using hydrochloric acid as an eluent with and without electric current enhancement.

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