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Electroadsorption of Ni^{2+} ions in an electrodialysis chamber containing granulated ion-exchange resin

N. A. LINKOV, J. J. SMIT

SASOL Centre for Separation Technology, Potchefstroom University for CHE, Potchefstroom 2520, South Africa

V. M. LINKOV*

Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

V. D. GREBENYUK

Institute of Colloid and Water Chemistry of Ukrainian Academy of Sciences, Kiev-225, Ukraine

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Electrochemical processes taking place in an electrodialysis chamber packed with the granulated ion-exchange resin, when a dilute solution of a heavy metal salt is flowing through it, have been studied. The influence of the quantity of electricity transferred through such a system on the value of surface electrical resistance of the electrodialysis chamber and the limiting current value was experimentally determined. A mechanism for current transfer in such a system is presented. It allows for some unusual relationships between process parameters: current-voltage curves, the limiting current, the specific surface resistance, the quantity of transferred electricity and the solution flow rate.

Keywords: *hybrid desalination method*, *electrodialysis*, *cation-exchange resin*, *heavy metal ions*, *electroadsorption*

1. Introduction

Limited water resources in many parts of the world require that more attention be paid to waste water recycling [1]. An analysis of water consumption in mid-latitude zones and in zones with moderate humidity shows that agriculture uses approximately the same quantity of water as is consumed by both industry and municipalities. The increasing percentage of total water resources utilized in the agricultural sector is largely due to the progressive development of artificial irrigation and the gradual implementation of water saving technologies in industry [2]. New water consumption schemes allow for the use of clean water for municipal and industrial needs and purified municipal and industrial waste waters for artificial irrigation. This approach can result not only in an increase in the amount of available water but also in a decrease in environmental pollution by biogenic elements such as nitrogen, phosphorus and potassium, the presence of which leads to intensive algae growth in natural reservoirs [3].

Two important factors which limit the wider application of the above concept are: pollution of the soil by heavy metals which are present in industrial waste waters and the high cost of underground irrigation. It has been shown that between 80 and 90% of heavy metal contamination is due to the disposal of waste waters from electroplating plants, immediate discharge from effluent-processing installations and washout from effluent dump sites [3]. These problems are well known and can only be solved by the direct extraction of heavy metals from industrial effluents and their further reuse [4–7].

A method describing the adsorption of individual heavy metals onto a polarized ion-exchange packing has recently been reported (electroadsorption) [8]. One of the advantages of this method is the considerably increased ion exchanger capacity which is achieved due to the superequivalent adsorption effect created by an electrical field [9]. The present paper describes some unusual electrochemical effects observed in an electroadsorption chamber and the influences which they have on the parameters of the heavy metal ion adsorption process.

2. Experimental details

Experiments were conducted with the apparatus schematically shown in Figure 1. The performance of the capillary electrodialysis chamber, filled with 5 g of acidic cation-exchange resin KU-2 (Russia) in a gel form was monitored with a specially designed galvano-potentiostat TACT GP-150 (7). The four-electrode measuring system consisted of two separate electrical circuits: one with two polarizing electrodes (cathode and anode) and another with two measuring electrodes (5). The electrode pairs were electrically separated from each other.

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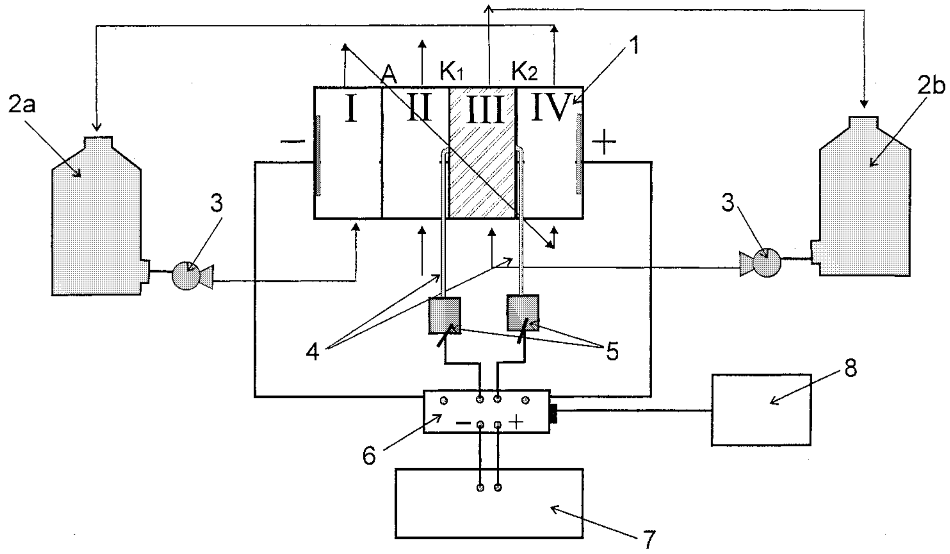

Fig. 1. Schematic of experimental installation: (1) electrodialysis cell (I, cathode chamber; II, concentration chamber; III, desalination chamber packed with granulated ion exchanger; IV, anode chamber); (2a) reservoir with 0.1 N Na_2SO_4 solution (constant flow rate of 200 ml min^{-1}); (2b) reservoir with 0.1 N Na_2SO_4 + $NiSO_4$; (3) peristaltic pumps; (4) capillaries; (5) Ag/AgCl electrodes; (6) electrical distributing unit; (7) galvano-potentiostat TACT GP-150; (8) 486 IBM PC.

The galvano-potentiostat delivered a maximum current of 150 mA. The current sweep rate varied from 0 to 150 mA min^{-1}. The maximum measured voltage was 3 V and the output resistance of the measured electrical circuit was 35 MΩ. Current–voltage measurements were carried out using 486 IBM PC connected to measuring electrodes through an electrical matching and distributing unit. The body of the cell with an effective area of 10 cm^2 was made from Perspex, the cathode was made from titanium and the anode from titanium covered with a layer of manganese dioxide. The distance between adjoining membranes was 0.6 cm. Two peristaltic pumps were used to circulate the solutions through the electrodialyser chambers. The feed solution, closely resembling electroplating rinse water, contained Ni ions in concentrations of 0.15, 0.3 and 0.4 g dm^{-3}. An 0.1 N Na_2SO_4 solution with pH 2 was introduced into the concentration chambers in a recirculation regime by means of a burette. Silver/silver chloride electrodes were connected via a salt bridge to Luggin capillaries [10] which were placed near the ion-exchange membranes at both sides of the desalination chamber. A correction for voltage drop across the feed solution, between the ends of the capillaries outside the chamber, was always taken into account. The temperature of the experiment was kept constant at 24 °C.

A preliminary study showed that the slopes of the sections of the current–voltage curves representing underlimiting current and, therefore, electrical resistance of the chamber, remained unchanged for current sweep rates higher than 10 mA min^{-1}. It was decided therefore to conduct all experiments at a current sweep rate of 20 mA min^{-1}.

3. Results and discussion

Electrochemical processes taking place in the electrodialysis chamber packed with the granulated cation exchanger, when a dilute solution of a heavy metal salt is flowing through it, can be described by a physical–chemical model shown in Fig. 2. When saturation of heavy metal ions occurs, hydrogen and hydroxyl ions are generated on the boundaries of the granules. Simultaneously, hydrogen ions are adsorbed by the cation exchanger, replacing heavy metal ions from it, and hydroxyl ions bind with heavy metal ions to form hydroxyl compounds which have low solubility. Collidal particles of metal hydroxides generated in such a way are polarized in the electrical field and receive an induced dipole moment. Due to the fact that the solution around the ion-exchange granules is dilute (the specific conductivity of the ion exchanger is much higher than that of the solution), the electrical field in the cation-exchange packing is nonhomogeneous. This results in a concentration of generated colloidal particles due to dipolarphoresis at

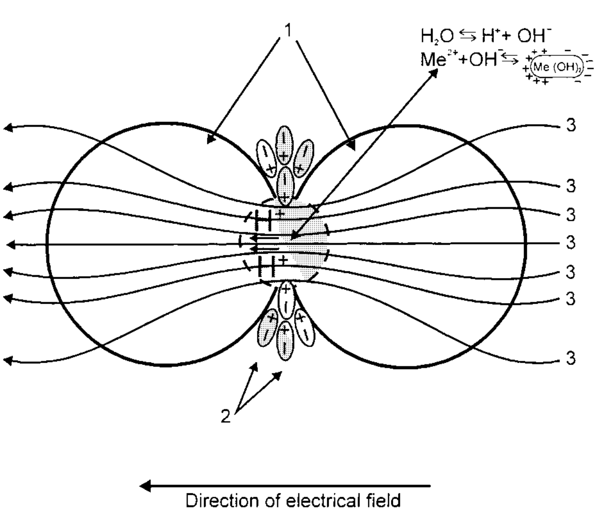

Fig. 2. Generation of nickel hydroxide precipitate around contact points of ion exchanger granules: (1) ion exchanger; (2) colloidal particles of hydroxide; (3) electrical field.

the contact points of the granules, where the intensity of the electrical field is the highest.

The nonconductive precipitate prevents mixing of the solution and this leads to its depletion near the granule contact points and, consequently, to an increase in the electrical resistance of the whole system. It was therefore of special interest to investigate the influence of the quantity of electricity transferred through such a system, in the presence of nickel ions, on the surface electrical resistance of the chamber and the limiting current [11–14].

The typical shapes of the current-voltage curves for the desalination chamber filled with cation exchanger are shown in Fig. 3(a) and (b). The curves in Fig. 3(a) have an unusual shape with a maxima at the initial stage of polarization. Such a shape was reproduced during the first 5–10 successive measurements. In subsequent experiments, the descending part of the curves disappeared and was replaced by an ascending part. The current-voltage curves shown in Fig. 3(b) are typical of these later experiments.

As this phenomenon has not yet been described in the literature, an attempt is now made to explain it, using the electrochemical model for the progressive accumulation of nickel hydroxide in the contact points of the ion exchanger granules.

The gradual build up of the precipitate in the desalination chamber was responsible for the first ascending part of the current–voltage curves. When the limiting current was reached (maximum voltage values on the curves, see Fig. 3(a) and (b), the local electroneutrality at the points of contact of adjoining cation-exchange granules was disrupted, electrically charged areas were created and the convective flow of electroosmosis occurred [15, 16]. During the first several experiments, this flow was able to dislodge particles of nickel hydroxide due to the small amount of precipitate generated and the rather week adhesive interaction between the particles and the granule surfaces. This led to ‘deshielding’ of the granule surfaces with a subsequent decrease in electrical resistance in the near-contact areas, and was accompanied by a decrease in voltage which resulted in an unusual replacement of an ascending part of the current-voltage curve by a descending part, with the maximum point corresponding to a limiting current

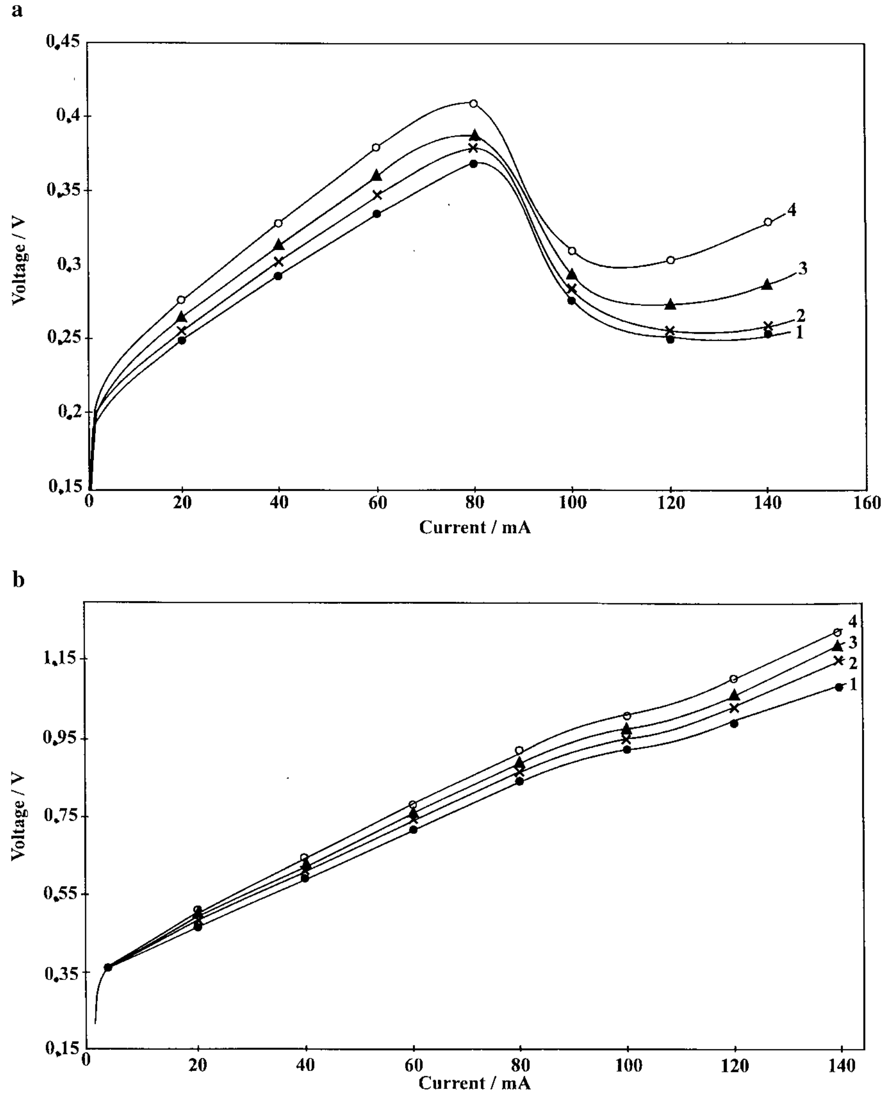

Fig. 3. Current–voltage curves (a) in the initial (first 5–10 experiments, numbers next to curves) stage of precipitate generation and (b) in the later stages (after first 10 experiments) of precipitate generation.

Table 1. Coefficients a and b of Equation 2 and specific resistance (ρ_s, Ω cm^{-2}) at Ni^{2+} concentration of 150 mg dm^{-3}

Experiment	*Underlimiting current*			*Overlimiting current*		
	a	*b*	ρ_s/Ω cm^{-2}	*a*	*b*	ρ_s/Ω cm^{-2}
1	1.7	0.155	40.28	−5.4	0.735	19.5
3	2.6	0.203	58.73	−4.6	0.689	22.9
5	3.5	0.251	76.83	−3.6	0.623	26.3
7	4.1	0.282	88.00	−2.3	0.536	30.6
9	4.7	0.301	97.16	−1.5	0.498	34.8
11	5.1	0.313	103.17	−0.8	0.462	38.2
13	5.4	0.320	107.33	−0.1	0.438	42.8
15	5.6	0.328	110.67	0.7	0.381	45.1
17	5.7	0.337	113.17	1.4	0.320	46.0
19	5.8	0.346	115.67	1.9	0.276	46.6

value (Fig. 3(a)). During a step-by-step recording of a series of current–voltage curves, progressive structuring and thickening of the precipitate took place, leading to strengthening of the interaction of the precipitate with the surfaces of the ion exchanger granules. Simultaneously, the resistance of the system increased, the maxima of the curves in Fig. 3(a) became smoother and, eventually, the shapes of the current–voltage curves approached those shown in Fig. 3(b). The latter curves have a more usual appearance, with the parts responsible for the overlimiting current ascending with a smaller slope then those of the parts responsible for the underlimiting current.

The initial ascending parts of the current–voltage curves responsible for the underlimiting current and the points where limiting current occurred were studied. The current–voltage curves obtained during the experiments were subjected to linear approximation; their sections were represented by the linear equation (this approximation was valid for currents greater than 5 mA):

$$U = a + bI \qquad (1)$$

where I is current, U is voltage, and a and b are linear coefficients.

Using this approximation, the resistance (R/Ω) and, consequently, the specific surface resistance (ρ/Ω cm^{-2}) of the electroadsorption system, for both underlimiting and overlimiting current conditions, could be evaluated, according to the following equation:

$$R_{1,2} = a_{1,2}/I + b_{1,2} \qquad (2)$$

where R_1, a_1, b_1 correspond to the underlimiting current condition and R_2, a_2, b_2 correspond to the overlimiting current condition (Table 1).

In electroadsorption systems where precipitate generation in the boundary layer between the ion exchanger and the solution does not occur, the thickness of the diffusion layer in the laminar flow is inversely proportional to the cube root of the solution flow rate [9]. Consequently, the electrical resistance of the system decreases and the limiting current increases with increase in flow rate. However, when the generation of precipitate occurs, variation in the flow rate does not affect the hydrodynamic conditions in the granule contact areas. This may result in the surface resistance of the chamber and the value of the limiting current being independent of the solution flow rate, whereas the precipitate quantity, which is proportional to the quantity of transferred electricity, has a significant effect on the electrical resistance of the system, as shown in Fig. 4.

The relationship between the specific surface resistance and the quantity of transferred electricity,

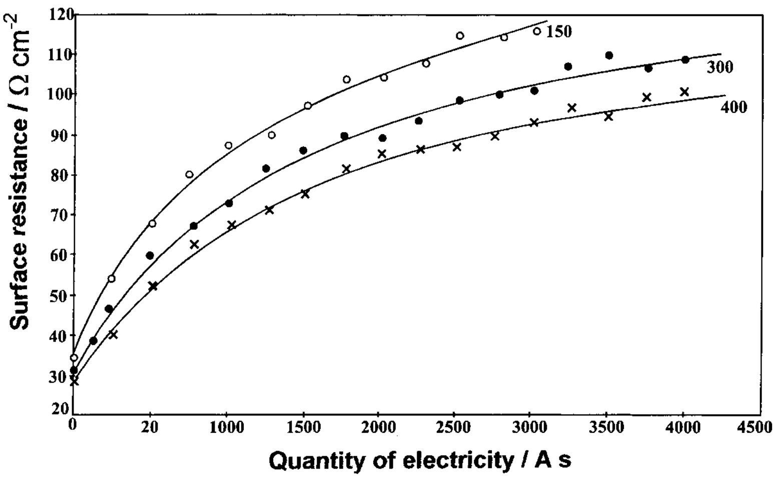

Fig. 4. Relationship between specific surface resistance and quantity of transferred electricity for underlimiting current condition (I = 60 mA, Ni^{2+} concentrations given in mg dm^{-3}).

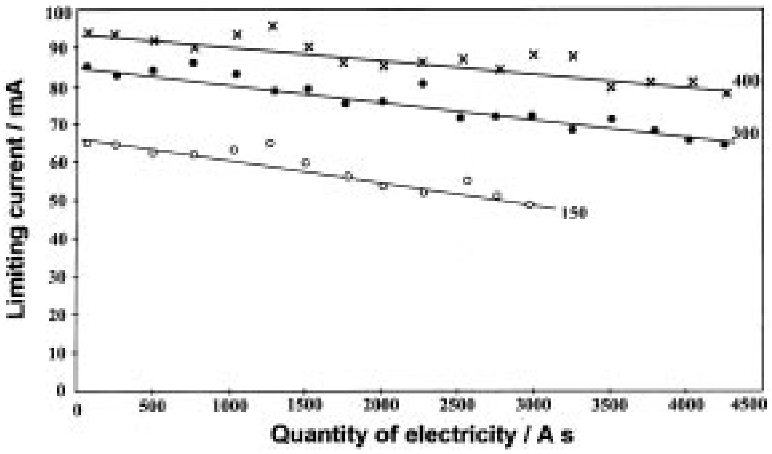

Fig. 5. Relationship between limiting current and quantity of transferred electricity (Ni^{2+} concentrations given in mg dm^{-3}).

shown in Fig. 4, can be approximated by a curve with the following equation:

$$\rho_s = c + dQ^n \tag{3}$$

where ρ is the specific surface resistance and Q is the quantity of transferred electricity. For concentrations of the inlet nickel solution of 150, 300 and 400 mg dm^{-3} ($I = 60$ mA) the coefficients c, d and n of Equation 3 have the following values: $c = 14.832$, 11.796 and 8.651; $d = 0.673$, 0.635 and 0.618; and $n = 0.618$, 0.598 and 0.586.

The values of the limiting current densities (i_{lim}) can be calculated using Equation 4, as proposed in the literature [17]:

$$i_{\text{lim}} = DSCF/\delta(t' - t) \tag{4}$$

where C is the concentration of the solution surrounding the ion exchanger, D the ionic diffusion coefficient, F the Faraday constant, S the chamber surface area, t' and t are transfer numbers of the counterion in the ion exchanger and in the solution, respectively, and δ the diffusion layer thickness.

The limiting current (i_{lim}) can also be determined from the experimentally obtained current–voltage curves:

$$i_{\text{lim}} = (a_2 - a_1)/(b_1 - b_2) \tag{5}$$

where $a_{1,2}$, $b_{1,2}$ are the coefficients form Equation 2.

Taking the above mechanisms of current transfer in an electroadsorption system containing granulated cation exchanger into account, it is shown how the limiting current depends on the solution flow rate through the system. The limiting current decreases only slightly with increase in the quantity of electricity transferred, as shown in Fig. 5. This decrease can be approximated by the following linear equation:

$$i_{\text{lim}} = e - fQ \tag{6}$$

where $e = 67.129$, 84.972 and 93.429 and $f = 0.0065$, 0.0042 and 0.0036 for inlet solutions with concentrations of 150, 300 and 400 mg dm^{-3}, respectively.

The significant scatter of experimental points in Fig. 5 can be explained by the spontaneous detachment of precipitate particles, resulting in some oscillation of the electrical current in the electroadsorption system.

4. Conclusions

The mechanism of current transfer in an electroadsorption system comprising a bed of granulated cation exchanger and a solution containing heavy metal ions flowing through it is presented. This mechanism allows some unusual relationships between the parameters of the system, such as: current–voltage curves, the limiting current, the specific surface resistance, the quantity of transferred electricity and the solution flow rate, to be explained.

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