Portugaliae Electrochimica Acta 24 (2006) 367-376

PORTUGALIAE ELECTROCHIMICA ACTA

A Modified Electrodialytic Cell to Recover Heavy Metals from Wastewater

N.S. Abo-Ghander, S.U. Rahman,* S.M.J. Zaidi

Electrochemical Research Group, Chemical Engineering Department
King Fahd University of Petroleum & Minerals, Dhahran-31261, Saudi Arabia

Received 17 October 2005; accepted 13 December 2005

Abstract

A modified electrodialytic cell integrates electrodialysis and reduction of metal ions. The cell is able to recover metallic copper from wastewater containing 1000 ppm cupric ions and bring the concentration down to about 1 ppm. The kinetic data of decreasing copper ion concentration fit well in first order kinetics and allow calculation of the over all reaction rate constant. Effect of several parameters, namely, width of wastewater compartment, applied potential and concentration of anolyte and catholyte solution; on the over all reaction rate constant and specific energy consumption were studied. The best combination of parameters results in an overall rate constant of 7.84×10^{-4} sec^{-1} and specific energy consumption of 48.18 kW-h/kg copper.

Keywords: electrodialysis, electrolysis, copper ions, wastewater, water treatment.

Introduction

Wastewater containing heavy metal ions is generated in large quantities from the mining, ore processing, microelectronics, metal finishing and photographic industries. The concentration of these ions varies between 50 to 1000 ppm while the discharge concentration limit typically ranges from 0.1 to 1 ppm [1]. Electrolytic and electrodialytic methods are excellent options for removing heavy metals ions [2, 3, 4]. The electrolytic processes are mainly mass transfer controlled and cell configuration that increases the mass transfer at cathode improves the performance of the cell. For example, the performance was improved by using rotary drum [5], fluidized bed [6], flow through a porous electrode [7], gas-sparging cell [8], rotating cylinder electrode [9], bipolar trickle cell [10], rotating disc [11], tumbling barrel [12, 13, 14, 15].

Despite of the improved mass transfer, the electrolysis method becomes expensive when the concentration of the wastewater becomes small due to

* Corresponding author. E-mail address: srahman@kfupm.edu.sa

increased ohmic resistance. At this condition, the dominant reaction becomes the hydrolysis which manifests itself as low current efficiency for metal deposition. One way of solving this problem is to add some salt to increase the electrolyte conductivity. However, this will result into increase in the total dissolved solids in wastewater.

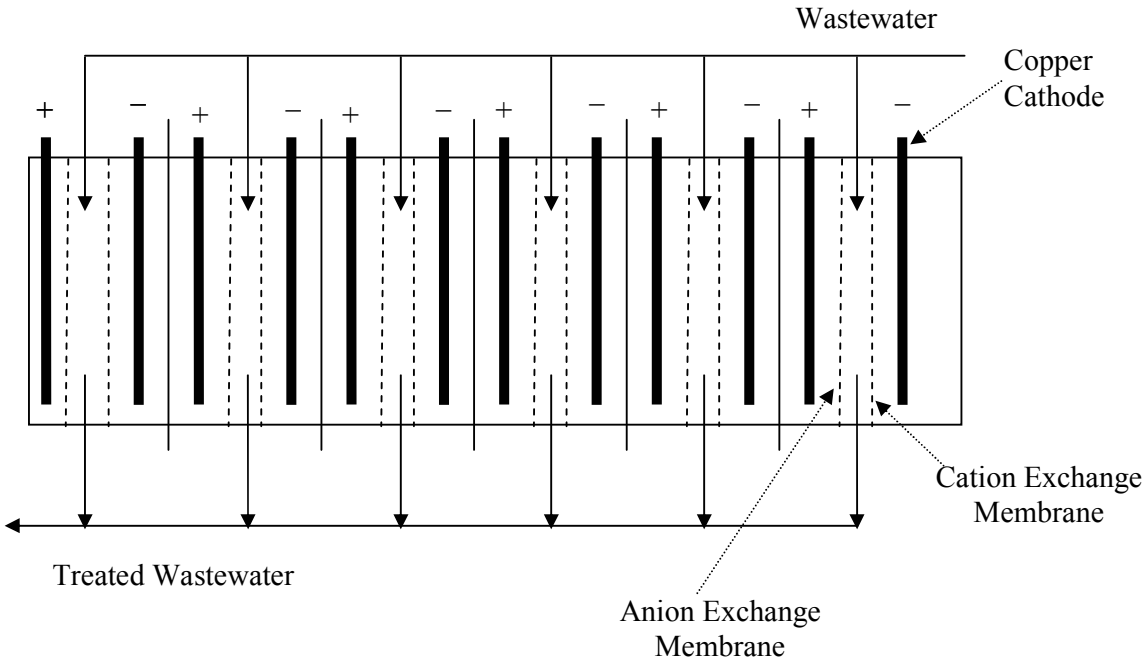

Figure 1. Removal of metal ions using modified electrodialysis cells.

The electrodialysis uses a number of anion and cation exchange membranes held between two electrodes. This technique is capable of treating low concentration wastewater but produces a concentrated stream that needs further treatment. It has been used to treat seawater [16], metal ion recovery in metal finishing and metallurgical industry [17, 18, 19] and treating industrial wastewater [20, 21, 22]. It is attractive to integrate electrolytic and electrodialytic cells to remove metal ions and recover them in useful metallic form and to avoid treating the concentrated stream produced by electrodialysis. In addition the integrated system will be able to treat dilute wastewater streams, which are difficult to treat by electrolysis alone. One way of integration is to electrolytically treat the concentrated stream exiting from the electrodialytic cell. This requires that the wastewater is pumped back and forth and demands an elaborate control system.
In this work we are proposing a modified electrodialysis cell that integrates the electrolytic deposition of metal with electrodialytic separation of metal ions from the wastewater. Unlike an electrodialytic cell, which has a battery of cation and anion exchange membranes between two inert electrodes, the modified process

contains a number of cells, each of them comprises of a pair of membranes and a pair of electrodes as shown in Fig. 1. Upon application of a potential, the ions diffuse through respective ion exchange membranes akin to the electrodialysis cell. However, the cations that diffuse through the cation exchange membrane reduce to metal at cathode:

$$M^{n+}(aq) + ne^- \rightarrow M(s) \quad (1)$$

Depending upon the applied potential, hydrogen evolution reaction also takes place at cathode:

$$2H_2O + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \quad (2)$$

Hydrogen gas can be collected as a byproduct. The anions (Cl^-, and/or SO_4^{-2}) diffuse through the anion exchange membrane and reach the anode. At the anode, oxygen evolution reaction takes place:

$$2H_2O \rightarrow 4e^- + 4H^+(aq) + O_2(g) \quad (3)$$

Consequently, concentration of anions and protons increases in the anolyte solution. Therefore the cell can be used for concentrating mineral acids.
In this article, it is demonstrated that a single modified electrodialytic cell, working in batch mode, is able to reduce the concentration of copper ions from 1000 ppm to about 1 ppm. In addition effect of various parameters on the performance and energy expenditure in the modified cell has been studied.

Experimental

Materials

The anion exchange membrane (CM-1) and cation membranes (CM-2) were procured from Tokuyama, South Korea [23]. Copper sulfate ($CuSO_4.5\ H_2O$) with a purity of 98.5% and sulfuric acid were procured from Fluka. Lead oxide electrodes were obtained from the commercial car battery. Deionized water was used to prepare all solutions.

Experimental procedure

A three compartment cell (10.5 cm high and 10.0 deep) was constructed using perplex sheets and flanges. The width of the anolyte and the catholyte compartments were held constant at 6.5 cm and 11.4 cm, respectively, while the width of wastewater was either 5.0 cm or 7.1 cm. The anion exchange membrane (CM-1) and cation exchange membrane (CM-2) were tightly held between the flanges. A pad of copper mesh, which worked as cathode, was placed next to the cation exchange membrane. A sheet of lead oxide worked as anode and was placed next to the anion exchange membrane. The electrodes were connected to a D.C. power source and two digital multimeters that measure the applied potential and cell current.
Synthetic wastewater was prepared by dissolving copper sulfate in deionized water to obtain a concentration of about 1000 ppm. All experiments were conducted in potentiostatic mode and current was recorded at predetermined

intervals. Two hundred microliter samples were drawn from the wastewater compartment at different intervals. The concentration was measured by using atomic absorption (Model 3100, Perkin Elmer).

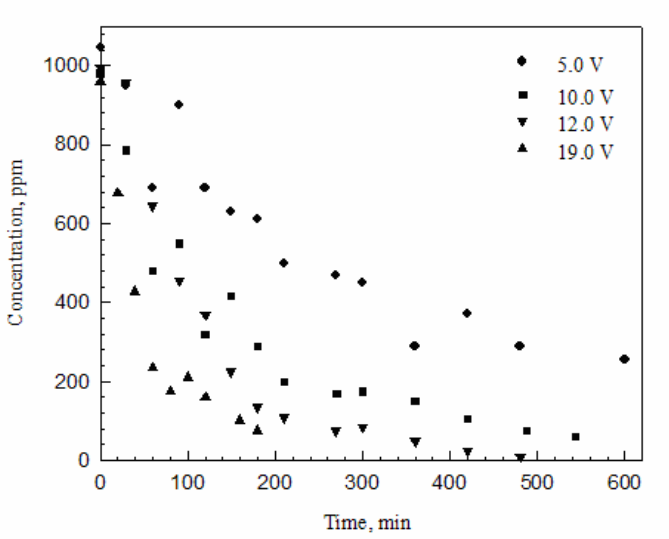

Figure 2. Concentration of copper ions in wastewater versus time plots for 7.1 cm wide wastewater compartment with anolyte and catholyte solution of 0.5 M H_2SO_4.

Results and discussions

Concentration of copper ion in the wastewater compartment is plotted against time in Fig. 2 at different applied potentials when anolyte and catholyte compartments had 0.5 M H_2SO_4 solution initially. The width of wastewater compartment was 7.1 cm in these experiments. The starting copper ion concentration was about 1000 ppm. The concentration decreased very fast in the beginning and became slow later in all experiments. Eventually, the concentration becomes very low (≈10 ppm). The concentration of the catholyte solution was measured at different interval and found to be negligible. Also the mass of the cathode increased during the course of each experiment. It is inferred from these observations that copper ions diffused through the cation exchange membrane and reduced at the cathode. The time taken to bring the concentration down to few ppm from 1000 ppm took about 500 minutes which is relatively high due to the un-optimized cell design.

The decay of concentration with time suggests that the overall process is governed by first order kinetics represented by:

$$\ln C(t) = \ln C_o - kt \qquad (4)$$

where k is a lumped overall rate constant and C_o is the initial concentration of cations in the wastewater. The ions move towards electrodes due to two reasons; namely, applied electric field (ion migration) and Fickian diffusion in electrolytes and membranes. Therefore the overall rate constant depends upon the hydrodynamics, applied potential, intrinsic kinetic parameters (exchange current density and charge transfer coefficient). The value of the overall rate constant is

obtained by regressing experimental concentration data into equation (4) as shown in Fig. 3.

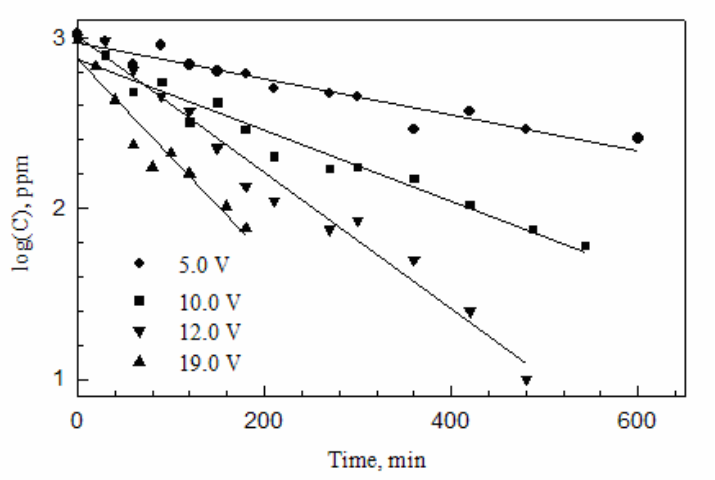

Figure 3. Semi-logarithmic plots of concentration of copper ions with time for 7.1 cm wide wastewater compartment with anolyte and catholyte solution of 0.5 M H_2SO_4.

A number of design and operating parameters affect the performance of the modified cell, e.g., membrane materials, temperature, conductivity of the synthetic wastewater, electrode materials, applied potential, conductivity of the anolyte and catholyte solutions, and distance between membranes. In this work, the effect of applied potential, concentration of the sulfuric acid in anolyte and catholyte compartments, and distance between membranes have been studied.

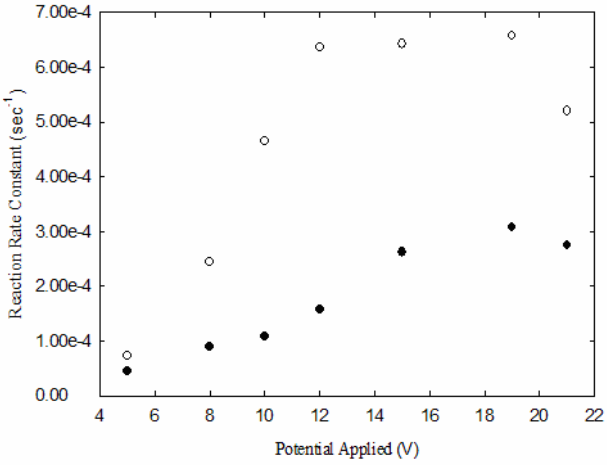

Figure 4. Effect of potential on the over all rate constant using 0.5 M H_2SO_4 as anolyte and catholyte solutions and wastewater compartment width of 7.1 cm (•) and 5.0 cm (○).

Fig. 4 exhibits the effect of the applied potential on the overall rate constant when the initial concentration of the anolyte and catholyte solution was 0.5 M

H_2SO_4. The rate constant increases as the applied potential is increased before it starts decreasing after passing through a maximum value. The initial increase in the rate constant is due to improved kinetics of cation reduction reaction. When the width of the wastewater compartment was 5.0 cm, the rate constant had a maximum value at a potential of 12.0 V. At this potential difference, the rate of cation reduction reaction is very fast and the overall reaction becomes diffusion controlled. Any further increment in potential did not improve the kinetics. Beyond 18.0 V, the overall rate constant decreased. The electrodeposition at this potential was associated with evolution of bubbles that is inferred as hydrolysis of water as side reaction. At high potential differences, both reactions (1) and (2) occur at the cathode resulting into a lowered rate of reaction (1).

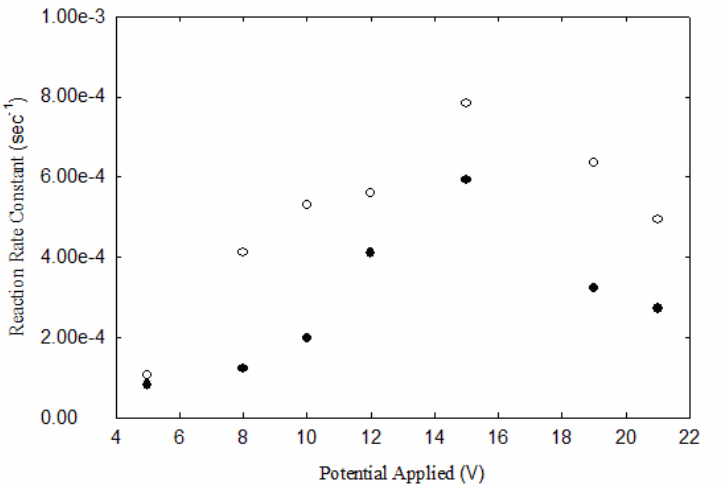

Figure 5. Effect of potential on the over all rate constant using 0.25 M H_2SO_4 as anolyte and catholyte solutions and wastewater compartment width of 7.1 cm (•) and 5.0 cm (○).

When the width of the wastewater compartment was increased to 7.1 cm, the overall rate constant had similar dependence on applied potential. However, the maximum value of the rate constant was observed at 18.0 V. The value of the rate constant was much lower at any given value of applied potential. The main reason of the decreased performance with wider wastewater compartment was increased ohmic losses. This suggests that the efficient design of the cell should have small spacing between membranes. In the same fashion, length of the anolyte and catholyte compartments should also be small. Fig. 5 shows plots of rate constant when the concentration of anolyte and catholyte compartments was 0.25 M H_2SO_4. These plots corroborate well with the observation and inferences from Fig. 4.

The compositions of anolyte and catholyte are very important parameters for the performance of the modified electrodialysis cell. As the reaction progresses, OH- and H+ ions are generated in catholyte and anolyte, respectively. Consequently, the concentration of acid drops in the catholyte while it increases in the anolyte. However, the rate at which copper ions diffuse and eventually the overall

reaction is a function of initial concentration of acid in the catholyte and the anolyte, their relative volumes, diffusivity of the ions, etc. In the present experiments, it is observed that the overall reaction rate constants are higher when 0.25 M H_2SO_4 was used as catholyte and anolyte. It should be noted that the performance can be improved by using a basic solution (e.g., NaOH or KOH solution) in the catholyte in stead of an acid.

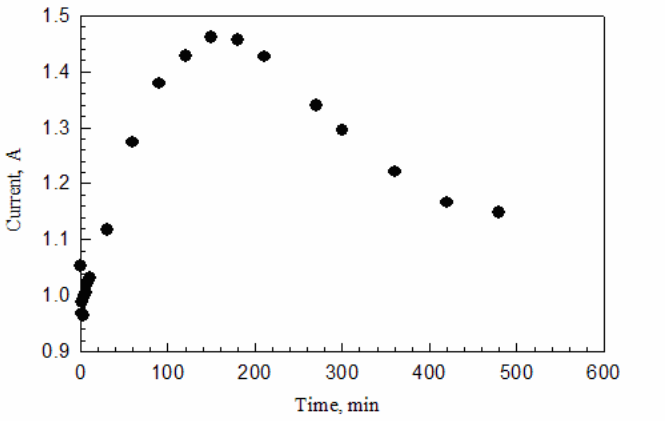

Figure 6. Variation of cell current with time for a cell with 7.1 cm wide wastewater compartment using 0.5 M H_2SO_4 as anolyte and catholyte solutions at 12.0 V of applied potential.

Specific energy consumption, defined as energy consumption per unit mass of recovered copper, is an important parameter. It is calculated using following equation:

$$E = \frac{\int_0^{t_c} VI\,dt}{\upsilon_w \times (C_o - C(t_c))} \tag{5}$$

Here V is the applied potential which is held constant in each experiment. The upper integration limit is t_c, which is the time when the wastewater concentration becomes almost constant (i.e. $\frac{dC}{dt} \approx 0$). The volume of the wastewater in the cell is υ_w. The cell current, I, changed and recorded through out an experiment. Fig. 6 shows a typical plot representing change of cell current with respect to time. The data were regressed into third order polynomial that has been used in eq. (5).

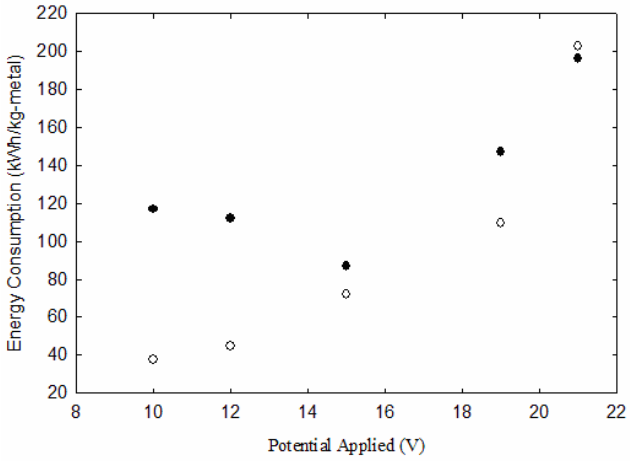

Figure 7. Effect of applied potential on the energy consumption using 0.5 M H_2SO_4 as anolyte and catholyte solutions and in 7.1 cm (•) and 5.0 cm (○) wide wastewater compartments.

Fig. 7 shows the effect of the applied potential on specific energy when anolyte and catholyte concentration was 0.5 M H_2SO_4 for different widths of wastewater compartment. In general, the energy consumption increases sharply at high applied potential. This is due to increasing dominance of cathodic hydrogen evolution. In the lower range of applied potential, the energy consumption decreases when the length of wastewater compartment was 7.1 cm. Apparently, the rate of copper ion reduction reaction is under kinetic control in this range of potentials. However, when the length of wastewater compartment was 5.0 cm, the initial decrease in the specific energy consumption was not observed. Similar observation and inferences can be drawn from Fig. 8 where the specific energy consumption was plotted against applied potential for anolyte and catholyte of 0.25 M H_2SO_4.

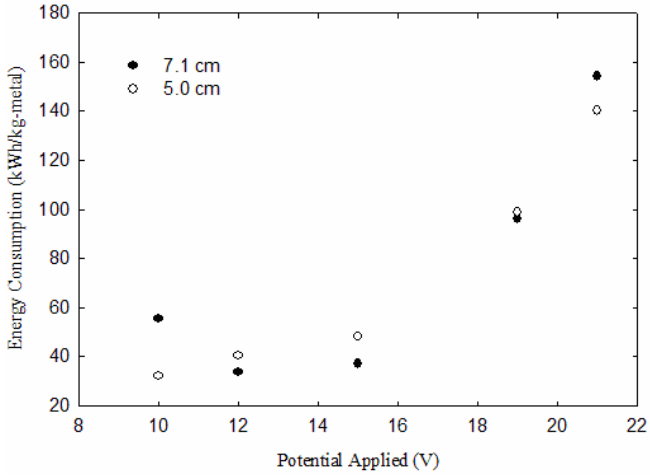

Figure 8. Effect of potential on the energy consumption using 0.25 M H_2SO_4 as anolyte and catholyte solutions and in 7.1 cm (•) and 5.0 cm (○) wide wastewater compartments.

Among all studied combination of parameters, it is found that applied potential of 15.0 V with 5.0 cm long wastewater compartment and 0.25 M H_2SO_4 as anolyte and catholyte solutions exhibited the best performance. This translates to an overall rate constant of 7.84×10^{-4} sec^{-1} and specific energy consumption of 48.18 kW-h/kg. This value of energy consumption is comparable to electrolytic cells with mechanically enhanced mass transfer at cathode, e.g., rotating barrel cathode [15]. It is anticipated that the performance of the integrated cell will improve with optimized cell design.

Conclusion

A modified electrodialytic cell that integrates electrodeposition has been used to recover metallic copper from synthetic wastewater containing copper ions. The modified cell is capable of reducing the copper ion concentration from 1000 ppm to few ppm. Unlike electrodialytic process, it does not produce any concentrated streams that would require further treatment. This work presents a study of the effect of applied potential, width of wastewater compartment and concentration of anolyte and catholyte solutions. It does not cover the optimization of the cell design. The authors are currently working to develop a mathematical model which will be used in conjunction with the experimental data to optimize cell performance.

Acknowledgment

Acknowledgement is due to King Fahd University of Petroleum & Minerals for use of their facilities.

References

1. U.S. Environmental Protection Agency Regulation. Identification and listings of hazardous wastes, Guideline 40, CFR 413, 1992.
2. L.J.J. Janssen, L. Koene, The role of electrochemistry and electrochemical technology in environmental protection, Chem. Eng. Journal 85 (2002) 137-146.
3. L. Koene, L.J.J. Janssen, Removal of nickel from industrial process liquids, Electrochimica Acta 47 (2001) 695-703.
4. K. Juttner, U. Galla, H. Schiemder, Electrochemical approaches to environmental problem in the process industry, Electrochimica Acta 45 (2000) 2575-2594.
5. R.P. Tison, Copper recovery using a tumbled-bed electrochemical reactor, J. Electrochem. 128 (1981) 317-322.
6. M. Fleishmann, J.W. Oldfield, L. Tennakkoon, Electrochemical removal of copper ions by use of fluidized bed electrode, J. Appl. Electrochem. 1 (1971a) 103.
7. D.N. Bennion, J. Newman, Electrochemical removal of copper ions from very dilute solutions, J. Appl. Electrochem. 2 (1972) 113-122.
8. P.M. Robertson, O. Dossenbach, Stirring by gas introduction and its application in the electroplating industry, Oberflaeche-Surf. 22(9) (1981) 282-287.

9. F.S. Holland, The development of eco-cell process, Chem. Ind. July (1978) 453-458.
10. M. Fleishmann, C.J.H. King, J.W. Oldfield, R.E. Plimley, C.L.K. Tennakkoon, Improvement in and relating to electrochemical cells. Br. Pat. 1419246. (1971b).
11. M. Fleishmann, R.E.W. Jansson, R.J. Marshall, Improvement in and relating to electrochemical cells. Br. Pat. 1522872. (1976).
12. R.P. Tison, B. Howie, Copper recovery from dilute solutions using a barrel plater, Plat. Surf. Fin. 71(9) (1984) 54-56.
13. C.D. Zhou, D.T. Chin, Copper recovery and cyanide destruction with a plating barrel cathode and a packed-bed anode, Plat. Surf. Fin. 80(6) (1993) 69-77.
14. C.D. Zhou, D.T. Chin, Continuous electrolytic treatment of complex metal cyanides with a rotating barrel plater as the cathode and a packed-bed as the anode, Plat. Surf. Fin. 81(6) (1994) 70-78.
15. A.A. Al-Shammari, S.U. Rahman, D.T. Chin, Copper recovery from wastewater using an electrochemical rotating barrel reactor, J. Appl. Electrochem. 34 (2004) 447-453.
16. T. Seto, L. Ehara, R. Komori, A. Yamaguchi, T. Miwa, Seawater desalination by electrodialysis, Desalination 25 (1978) 1-7.
17. S. Resbeut, G. Pourcelly, R. Sandeaux, C. Gavach, Electromembrane processes for waste treatment: electrodialysis applied to the demineralization of phenylalnine solutions, Desalination 120 (1998) 235-245.
18. A.J. Chaudhary, J.D. Donaldson, S.M. Grimes, N.G. Yasri, Separation of nickel from cobalt using elecrodialysis in the presence of EDTA, J. Appl. Electrochem. 30 (2000) 439-445.
19. H. Grib, D. Belhocine, H. Lounici, H. Pauss, N. Mameri, Desalting of phenylalanine solutions by electrolysis with ion-exchange membrane, J. Appl. Electrochem. 30 (2000) 259-262.
20. M. Davis, Use advanced methods to treat wastewater, Hydrocarbon Proc. 73 (1994) 43-46.
21. K.K. Chin, S.L. Ong, Water conservation through reclamation of sewage for reuse. Proceedings of 22nd Annual Conf. Integrated Water Resource Planning for 21st Century, Cambridge, USA. (1995) pp 73-76.
22. A.S. Bal, A.N. Vaidya, Application of membrane technology in wastewater management, Chem. Eng. World 33 (1998) 5.
23. Tokuyama Corp. Brochure, Neosepta Ion-exchange membranes, South Korea (1999).