

## Electrochemical recovery of silver from waste aqueous Ag(I)/Ag(II) redox mediator solution used in mediated electro oxidation process

Thasan Raju, Sang Joon Chung, and Il Shik Moon<sup>†</sup>

Department of Chemical Engineering, Sunchon National University, Sunchon 540-742, Korea  
(Received 8 May 2008 • accepted 25 January 2009)

**Abstract**—The paper presents a process for the electrochemical recovery of silver(Ag) by electro deposition on the electrode surface from the waste solutions of Ag(I)/Ag(II) redox system in nitric acid medium used for the mediated electrochemical process. Electrochemical recovery was carried out in an undivided cell with DSA-O<sub>2</sub> electrodes at room temperature condition. At an optimized current density of 12 A/dm<sup>2</sup>, 99% of Ag recovery efficiency was achieved with high yield and low energy consumption. Experimental runs were made in order to observe the performance of the Ag recovery process. The operating conditions like current density, temperature and Ag(I) concentration of the electrolyte, the acid concentrations, agitation rate and inter-electrode distance were optimized.

Key words: Electrochemical, Mediated Electro Oxidation, Electro Deposition, Recovery, Undivided Cell

### INTRODUCTION

The electrochemical deposition of silver has been intensely studied for the last several decades on the fundamental side covering various aspects such as kinetics and mechanism of deposition from various electrolytes and deposition baths on diverse substrates, nucleation and growth. From the application point of view, the electrochemical silver deposition method is widely used in the industry for the removal and recovery of the valuable metal from waste and dilute solutions.

Cruz et al. [1] studied selective recovery of silver by electro deposition from spent cyanide leaching solutions used in the hydrometallurgy industry, which contained very small quantities of silver and gold but high quantities of copper, all in the form of cyanide species. Experiments in a batch electrochemical reactor with recirculation and with a reticulated vitreous carbon electrode indicated that silver at low concentration was recovered without reducing Cu(I). In a study by Fourcade et al. [2], the overall electrochemical process of recovery of silver from “iodized silver derivatives,” dissolved, or adsorbed on solid industrial waste or embedded in mineral matrices silica and alumina, was optimized.

Chen and Lim [3] studied the simultaneous electrochemical removal of silver, copper, lead and organic waste. The rates of recovery for the three metals were found to be slower under competing conditions than when under in a single metal ion bath, and the competitive metal recovery followed the order of silver>lead>copper. A removal of 33 to 50% of HA and 40 to 50% of EDTA was also achieved depending on their initial concentration.

Among various hydrometallurgical processes, electrochemical recovery of metal ions is the most common from the waste solutions of processes. Cementation, precipitation, ion exchange, solvent extraction, reverse osmosis, electro coagulation and electro dialysis are the various hydrometallurgical and electrochemical pro-

cesses for recovery of reusable material from the dilute solutions or effluents. These methods, however, are not always suitable as they recover the metals as concentrated solutions or impure sludge that requires refining through further treatment [4]. The ion exchange method can recover the metal at low concentrations, but the cost of the ion exchanger and maintenance is high [5]. The electrolytic method can be a single step process for recovering metals in elemental form [6,7].

Metal deposition is an electrochemical process that has been studied extensively and is widely used in the industry for the removal of heavy metal ions [8-12]; the recovery of valuable metal ions from waste and dilute solutions was reviewed by Mubarak et al., Choi and Kim [13,14]. The above processes were also applied to purification of solutions or electrolytes from impurities before electrolysis [15,16].

In electro deposition of metals from solutions, the mass transfer takes place by convection, migration and diffusion. In general, mass transfer plays a role for the recovery of metals with high efficiency. Mass transfer can be improved by circulation of the electrolyte, increasing the bath temperature, good and uniform agitation, and movement of the electrodes that is rotating electrodes. However, in dilute solutions, the deposition kinetics is mainly controlled by diffusion. Hence, the efficiency of any electrolytic recovery system can be maximized by minimizing the thickness of the diffusion boundary layer.

Several works have shown that the use of planar electrodes [17, 18] eliminates the disadvantages by increasing the specific area and thus the mass transfer. Some authors have studied [18,19] the reduction of precious metals at concentrations within the range 20-1,000 ppm in cyanide solutions as an electrolyte using planar or porous electrodes. However, the recovery of precious metals at very low concentrations from cyanide leaching solutions has received little attention. Today, innovations in electrochemical reactor design (such as turbulence promotion and high specific area) have allowed the electrolytic process to be considered as an alternative for Ag recovery from dilute solutions and are reviewed by Sulka and Jaskula,

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: ismoon@sunchon.ac.kr

Lehmani et al. [19,20].

Mediated electro oxidation [MEO] processes have been developed for the destruction of organic wastes and liquids and following this approaches for mineralization of organic compounds have been studied extensively by our group [21-30] using the Ag(I)/Ag(II) redox system in nitric acid medium. In these types of MEO processes using Ag(I)/Ag(II) redox solution, the final used solutions are aqueous solutions with nitrate complexes of Ag(I)/Ag(II) metal ions. Hence, this approach allows the selective recovery of Ag(I) from waste solutions of MEO process containing higher concentrations of Ag(I)/Ag(II) metal ions.

This work presents the recovery of Ag from waste aqueous solution of Ag(I)/Ag(II) redox system in nitric acid medium employed in mediated electrochemical destruction reactions. The purpose is to determine the selective recovery of Ag in waste aqueous solution of Ag(I)/Ag(II) redox system in nitric acid used in the mediated electrochemical oxidation process before disposing the waste solution as effluent. For this purpose, the process parameters were optimized in this present work for the recovery of Ag, and our studies show that this process can be used for the waste solutions containing Ag(I) ions for the recovery of silver.

## EXPERIMENTAL

A 600 ml Pyrex cell with a two mesh type DSA electrodes of geometric area of 34 cm<sup>2</sup> were used in the Ag recovery study in undivided configuration in aqueous nitric acid medium. Experiments were performed galvanostatically using constant current source. The solution mixture was stirred well with a mechanical stirrer. The anode and cathode were placed in the solution with inter electrode distance in the range of 2-8 cm.

For this study, solutions of silver nitrate with known concentration were prepared in 3-6 M nitric acid medium. All solutions were prepared with deionized water using analytical grade reagents. The total Ag(I) concentration in the experimental solution was deter-

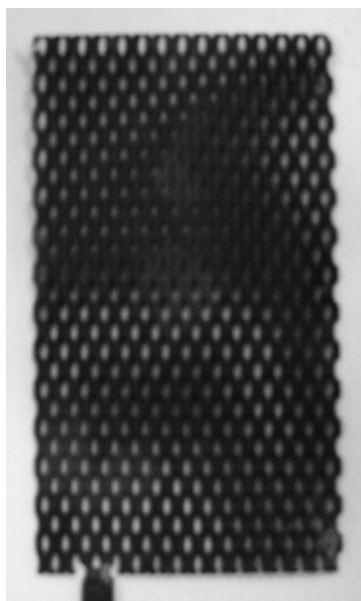


Fig. 1. Electrode (cathode) before electro deposition.

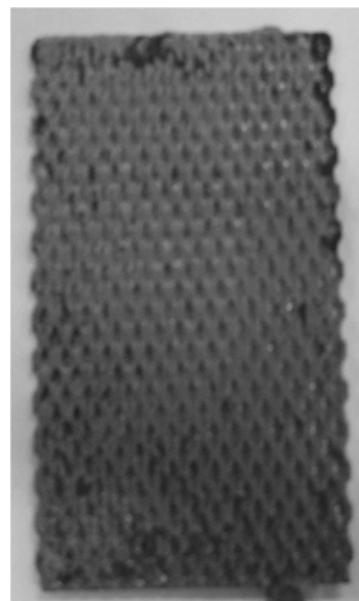


Fig. 2. Electrode after electro deposition of silver.

mined during the electrolysis with respect to time. The Ag(I) solutions were analyzed by Volhard method using KSCN and FeSO<sub>4</sub> as a indicator described elsewhere [31].

Experiments were carried out for the optimization of process parameters like current density, Ag(I) concentration, nitric acid concentration, sulphuric acid concentration, rate of agitation and the inter electrode distance of the anode and cathode for the Ag recovery system. In all the experimental study of process parameters, the recovery efficiency and energy consumption were calculated based on the Ag(I) measured in the experimental solution as a function of time. Figs. 1 and 2 show the cathode before and after electro deposition of silver, and the silver deposition is easily visible with shiny and smooth coating on the electrode surface.

## RESULTS AND DISCUSSION

Reaction scheme for electrochemical recovery of silver.

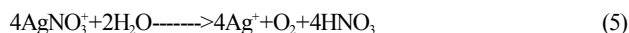
At cathode



At anode



Overall reaction



### 1. Effect of Current Density

Recovery of silver was from the used solution of Ag(I)/Ag(II) redox based mediated electrochemical oxidation processes. The solution contained Ag(I) with nitric acid and same was used as the electrolyte in an undivided cell at ambient temperature conditions. The recovery of the Ag was varied on the current density employed in the range of 1-18 A/dm<sup>2</sup>. Fig. 3 shows the effect of current den-

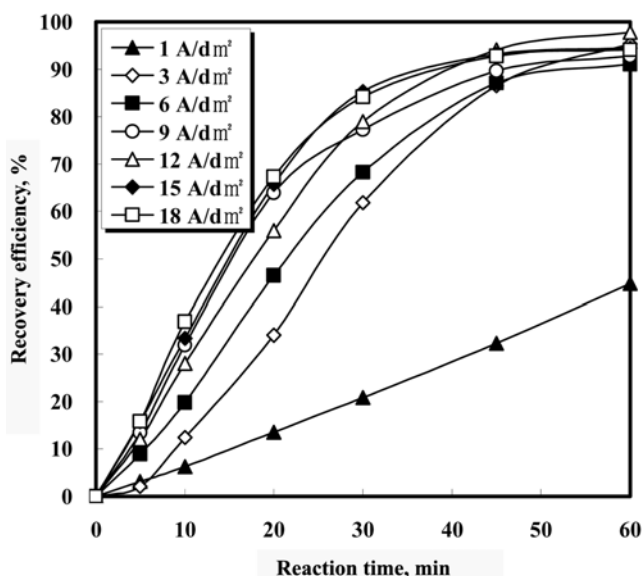


Fig. 3. Effect of current density on recovery of Ag [Ag(I)=0.1 M, Nitric acid=0.5 M, Current density=1-18 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

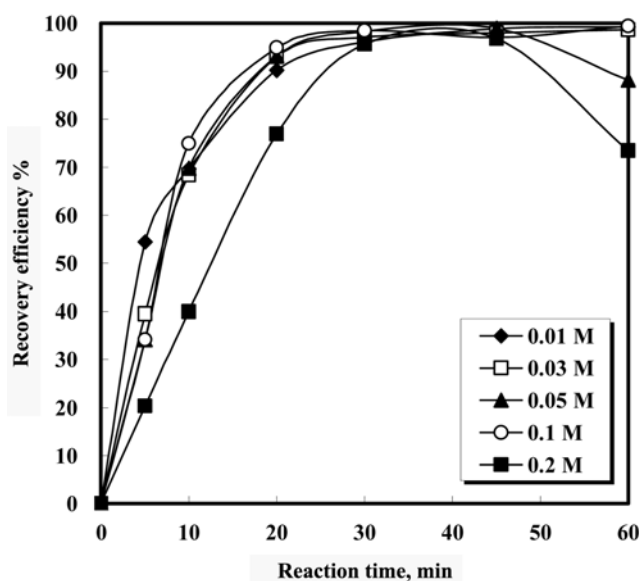


Fig. 4. Effect of Ag(I) concentration on recovery of Ag [Ag(I)=0.01-0.2 M, Nitric acid=0.5 M, Current density=12 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

sity for recovery of the Ag in an undivided cell. Current density plays a crucial role in the recovery of Ag, and increasing the current densities yields high recovery efficiency at optimum Ag(I) concentration. At lower current densities, the rate of recovery is low when compared to the high current densities.

At current density of 12 A/dm<sup>2</sup> the Ag recovery efficiency is high in 99% and further increase in current density does not yield higher. Hence, the optimum current density for the recovery of Ag is 12 A/dm<sup>2</sup> and it is given the Table 1 with recovery efficiency and energy consumption.

## 2. Effect of Ag(I) Solution Concentration

The effect of Ag(I) solution concentration were studied for the recovery of Ag at different concentrations at optimum experimental conditions. A high recovery of Ag can be achieved at a concentration of 0.1 M solution of silver nitrate. At low concentration, the Ag recovery rate is low. Fig. 4 indicates the recovery efficiency based on concentration of Ag(I) solutions and concentration.

In practice, most of the mediated electrochemical oxidation reactions were at a low concentration, preferably 0.1 to 0.05 M concentration, and the waste recovery solutions also had the same con-

centration in the above range in the waste disposal.

## 3. Effect of Nitric Acid Concentration

Most of the mediated electrochemical oxidation reactions involving Ag(I)/Ag(II) redox system were carried out in nitric acid medium due to several advantages as compared to the other acids [25]. In this present work, the recovery of Ag was at various nitric acid concentrations from 0.5 to 6.0 M. In these studies, it is revealed that the recovery efficiency Ag is high at lower acid concentrations when compared to the higher concentrations. Fig. 5 clearly indicates the recovery efficiency of Ag is decreased while increasing the acid concentration. From these studies, at 0.5 M nitric acid concentration the recovery of Ag is high. Here again the concentration of HNO<sub>3</sub> acid plays a vital role in a mediated redox system.

## 4. Effect of Electrolysis Temperature

The effect of temperature plays a crucial role in the recovery of Ag from Ag(I)/Ag(II) redox mediated waste solutions. The experiments were conducted at temperature ranging from 20-40 °C. Fig. 6 shows that the recovery efficiency decreases with increase of temperature and also the energy consumption is high (4 kWh/kg) at 40 °C electrolysis condition.

Table 1. Effect of current density on recovery of Ag

Current density A/dm <sup>2</sup>	Current rate A/hr	Initial Ag(I) in solution g	Final Ag(I) in solution g	Recovery efficiency %	Energy consumption KWh/kg
1	0.35	3.14	1.63	48	0.31
3	1.0	3.14	0.14	96	0.80
6	2.0	3.27	0.28	92	1.80
9	3.0	3.14	0.22	93	3.20
12	4.0	3.24	0.07	99	3.81
15	5.0	3.30	0.17	95	5.47
18	6.0	3.14	0.17	94	5.77

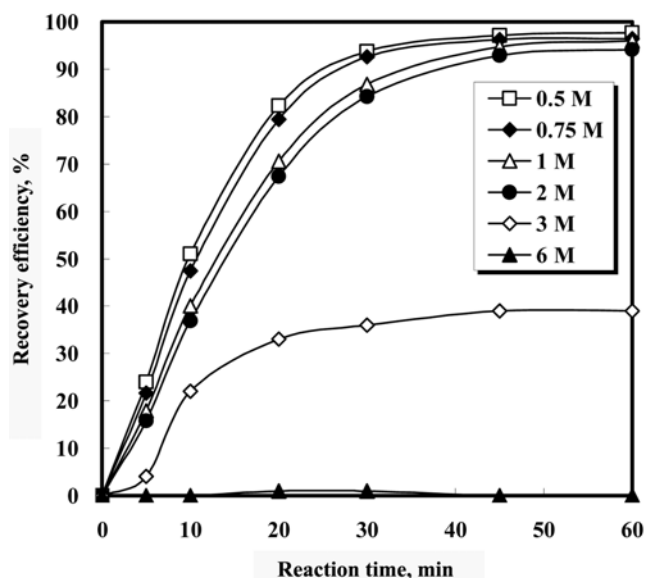


Fig. 5. Effect of Nitric acid concentration on recovery of Ag [Ag(I)=0.1 M, Nitric acid=0.5-6 M, Current density=12 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

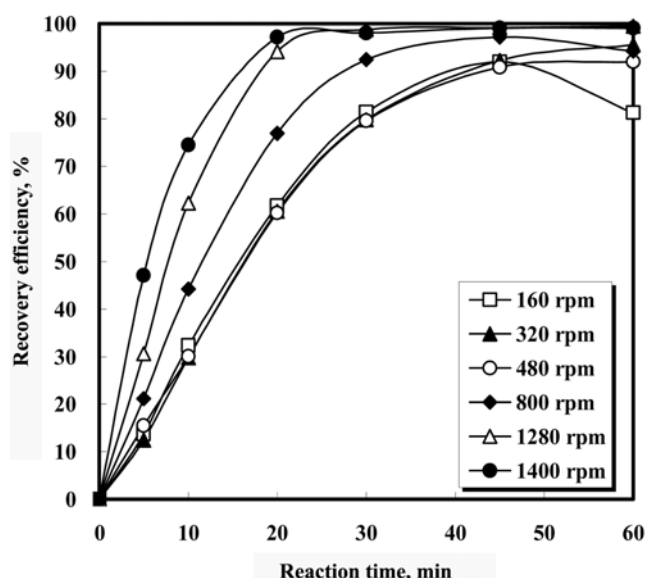


Fig. 7. Effect of agitation rate on recovery of Ag [Ag(I)=0.1 M, Nitric acid=0.5 M, Current density=12 A/dm<sup>2</sup>, agitation rate=160-1,400 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

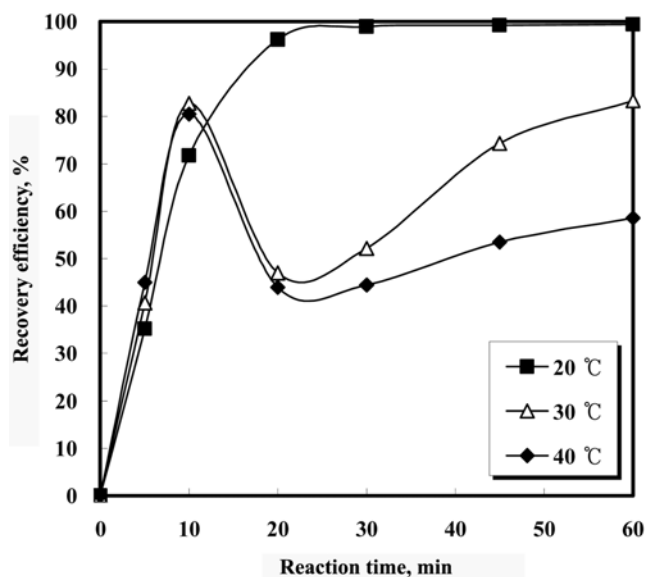


Fig. 6. Effect of temperature on recovery of Ag using batch cell [Ag(I)=0.1 M, Nitric acid=0.5 M, Current density=12 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20-40 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

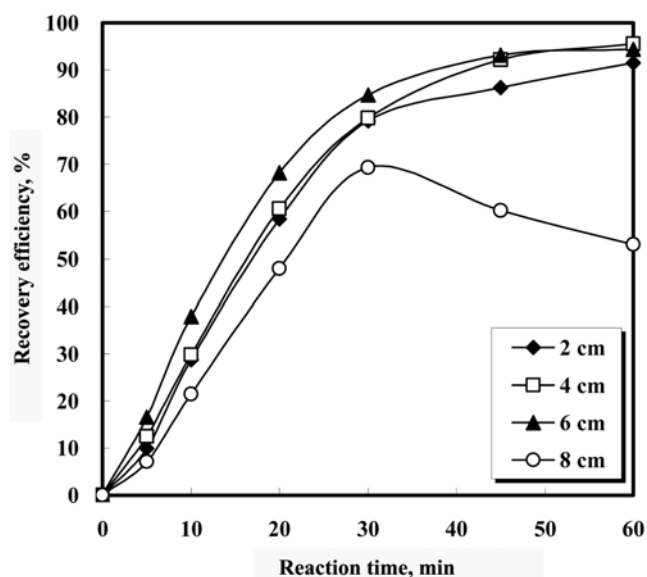


Fig. 8. Recovery efficiency of Ag for the various inter-electrode distances [Ag(I)=0.1 M, Nitric acid=0.5 M, Current density=1-18 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=2-8 cm].

The recovery is high at 20 °C when compared to the high temperature. Hence, the optimum temperature of 20 °C, which gives high recovery efficiency and low energy consumption, has been related for all these studies.

##### 5. Effect of Agitation

In these studies, the agitation rate of electrolyte solutions improves the recovery efficiency of Ag at high rate. The solutions were agitated at various stirring rates with a mechanical magnetic stirrer. The stirring rates were varied from 160-1,400 rpm. Fig. 7 clearly indicates that the silver recovery efficiency is increased with increase

of agitation rate of the electrolyte.

##### 6. Effect of Inter-electrode Distance

In electrochemical reactions, the energy consumption is important for the feasibility of process development. For energy calculations, the cell voltage developed during the electrolysis is important and it can be reduced by keeping the working and counter electrodes at a particular distance. Experiments were performed at different inter electrode distances. The recovery efficiency of the Ag and cell voltage was measured. Fig. 8 demonstrates the trend of the agitation rate with recovery efficiency. A minimum inter electrode

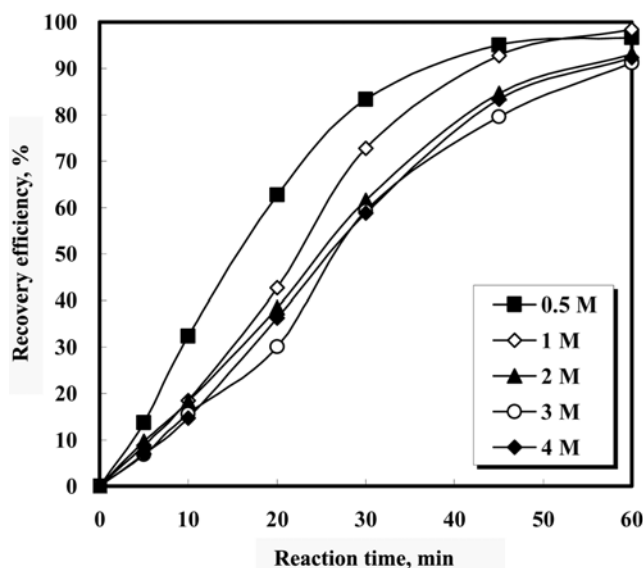


Fig. 9. Effect of sulphuric acid on recovery of Ag [Ag(I)=0.1 M, Sulphuric acid=0.5-4 M, Current density=12 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C, Cell voltage=2.6 V, inter electrode distance=6 cm].

distance of 6 cm yielded high Ag recovery efficiency at low cell voltage.

#### 7. Effect of Sulfuric Acid Concentration

In some of the mediated electrochemical oxidation systems with Ag(I)/Ag(II) redox mediated systems, reactions were carried out in sulfuric acid medium due to some benefits like high vapour pressure. Thus the present study on the recovery of Ag was done at various sulfuric acid concentrations from 0.5 to 4.0 M. Fig. 9 shows the effect of sulphuric acid concentration on recovery of Ag(I) and the recovery efficiency. In these studies the recovery of Ag is high at low acid concentrations when compared to the higher acid concentrations.

### CONCLUSIONS

The development of a process for the electrochemical recovery of silver by electro deposition method from the waste solutions of mediated electrochemical process Ag(I)/Ag(II) redox system in nitric acid medium was investigated. Electrochemical recovery was carried out in an undivided cell with DSA-O<sub>2</sub> electrodes at room temperature conditions. The optimized parameters for the electrochemical recovery of silver were Ag(I) concentration=0.1 M, Nitric acid concentration=0.5 M, Current density=12 A/dm<sup>2</sup>, agitation rate=1,200 rpm, temperature=20 °C and inter electrode distance=6 cm. At optimized process parameters like current density and other experimental conditions, 99% of recovery efficiency of Ag was achieved with high yield and low energy consumption.

### ACKNOWLEDGMENTS

This research is supported by the Korean Ministry of the Environment as "The Eco-Technopia-21 project and supported by a Korea Research foundation Grant funded by the Korean government (MOE-HRD - KRF-2007-210-D000001). This work was supported by the

Ministry of Knowledge Economy (MKE) through the project of GTFAM Regional Innovation Centre (RIC).

### REFERENCES

1. V. Reyes Cruz, M. T. Oropeza, I. Gonzalez and C. Ponce-De-Leon, *J. Appl. Electrochem.*, **32**, 473 (2002).
2. F. Fourcade, T. Tzedakis and A. Bergel, *Chem. Eng. Sci.*, **58**, 3507 (2003).
3. J. P. Chen and L. L. Lim, *Chemosphere*, **60**, 1384 (2005).
4. A. V. Pethkar, K. M. Paknikar, *Process Biochem.*, **38**, 855 (2003).
5. C. L. Lasko and M. P. Hurst, *Environ. Sci. Technol.*, **33**, 3622 (1999).
6. E. F. Hradil and G. Headil, *Met. Finish*, **82**, 85 (1984).
7. E. Raub and K. Muller, *Fundamental of metal deposition*, Elsevier Publishing Company, New York (1967).
8. F. A. Lopez, M. I. Martin, C. Perez and A. Lopez Delgado, *Water Res.*, **37**, 3883 (2003).
9. B. Donmez, F. Sevim and S. C. Olak, *Chem. Eng. Technol.*, **24**, 91 (2001).
10. Y. P. Hor and N. Mohamed, *J. Appl. Electrochem.*, **33**, 279 (2003).
11. M. S. Lee, J. G. Ahn and J. W. Ahn, *Hydrometallurgy*, **70**, 23 (2003).
12. A. Dip and L. Makhoulouf, *Chem. Eng. Process*, **43**, 1265 (2004).
13. A. A. Mubarak, A. H. El Shazly and A. H. Konsowa, *Desalination*, **167**, 127 (2004).
14. J. Y. Choi and D. S. Kim, *J. Hazard. Mater.*, **99**, 147 (2003).
15. B. B. Boyanov, V. V. Konareva and N. K. Kolev, *Hydrometallurgy*, **73**, 163 (2004).
16. J. Nasi, *Hydrometallurgy*, **73**, 123 (2004).
17. Tricoli, N. Vattistas and P. F. Marconi, *J. Appl. Electrochem.*, **23**, 390 (1993).
18. M. Fleischmann, D. Pletcher and A. Rafinski, *J. Appl. Electrochem.*, **1**, 1 (1971).
19. G. D. Sulka and M. Jaskula, *Electrochim. Acta*, **51**, 6111 (2006).
20. Lehmani, P. Turq and J. P. Simonin, *J. Electrochem. Soc.*, **143**, 1860 (1996).
21. S. Balaji, S. J. Chung, M. Matheswaran and I. S. Moon, *Korean J. Chem. Eng.*, **24**, 1009 (2007).
22. S. Balaji, S. J. Chung, T. Ramesh and I. S. Moon, *Chem. Eng. J.*, **126**, 51 (2007).
23. S. Balaji, V. V. Kokovkin, S. J. Chung and I. S. Moon, *Water Res.*, **41**, 1423 (2007).
24. S. J. Chung, S. Balaji, M. Matheswaran, T. Ramesh and I. S. Moon, *Water Sci. Technol.*, **55**, 261 (2007).
25. V. V. Kokovkin, S. J. Chung, S. Balaji, M. Matheswaran and I. S. Moon, *Korean J. Chem. Eng.*, **24**, 749 (2007).
26. J. W. Lee, S. J. Chung, S. Balaji, V. V. Kokovkin and I. S. Moon, *Chemosphere*, **68**, 1067 (2007).
27. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *J. Ind. Eng. Chem.*, **13**, 231 (2007).
28. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *Electrochim. Acta*, **53**, 1897 (2007).
29. M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, *Chem. Eng. J.*, **144**, 28 (2008).
30. M. Matheswaran, S. J. Chung and I. S. Moon, *Korean J. Chem. Eng.*, **25**, 1031 (2008).
31. G. H. Jeffery, VOGEL, *Textbook of quantitative chemical analysis* 5<sup>th</sup> ed., Longman Scientific & Technical, London (1989).