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Destruction of Cyanide in Aqueous Solution by Electrochemical Oxidation Method

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This work was to investigate the electrolytic oxidation of cyanide solution with the Ti/SnO_2-Sb-Ce anode under different conditions, such as initial pH, current density and flow rate. The results show that the destruction of cyanide on the anode is more favorably and completely conducted in strong alkaline solution. The conversion of cyanide and COD removal are 98.2 % and 84.2 % at initial pH 13 at reaction time of 4 h, but 69.5% and 48.2 % at initial pH 6, respectively. The conversion of cyanide, COD removal and current efficiency (CE) increase as the flow rate and applied current density increase, respectively, but the higher flow rate, the smaller is the increment extent of conversion of cyanide, COD removal and CE. The CE for destruction of cyanide was proved to be inversely proportional to the applied current density.

Keywords: Electrochemical oxidation; Destruction of Cyanide; pH; Current density

1. INTRODUCTION

It is well known that cyanide is able to poison the respiratory system and strongly inhibit the cellular metabolism and highly toxic for animals and humans [1], so many countries have imposed severe regulations to prevent contamination of surface and ground water caused by cyanides [2,3]. There are both natural and artificial sources of cyanide in the environment, and the most important sources of cyanide are industrial wastes. Some industries, such as plastics, electroplating, pharmaceutical production, metallurgy and photographic developing, discharge containing cyanide wastewater [4,5]. For example, the wastes from electroplating operations contain 0.5 % to 20 % cyanide by weight. Cyanides are not ready adsorbed or retained within soils, so they remain in the aqueous phase and often form complexes with others [6]. The cyanide is exceptionally stable and difficultly degraded in the environment, and liquid effluent from plants employing cyanides industrially must be effectively treated. Numerous conventional treatment methods, such as alkaline chlorination [7], hydrogen peroxide [8], ozonation [9,10], air oxidation [11], ion exchange [12,13], sulphur-based technologies and biological processes [14,15], have been used in treatment process of containing cyanide wastewater. The operating costs for destruction of cyanide by some chemical and physical technologies are typically expensive. For example, oxidants and catalysts used for alkaline chlorination and hydrogen peroxide techniques are usually high cost and harmful residue [16]. The most common technique for the destruction of cyanide is alkaline chlorination, however, this method has many disadvantages such as formation of cyanogen chloride, chloride contamination, and incomplete decomposition of some metal cyanide complexes [17,18]. The operating costs are lower by biological processes, but their practical use in the destruction of cyanide wastes is limited due to very slow detoxification and susceptive to temperature upsets [19].

The method of electrochemical oxidation for the treatment of industrial wastewater has become a hot focus in recent years because of its better effect than traditional chemical, physical and biological methods [20-22]. The electrochemical decomposition of cyanide represents an attractive alternative because of its strong oxidation performance, non-selective oxidation, environmental compatibility and no secondary pollutants. Complex cyanide and concentrated cyanide solutions can also be treated using this method [23]. The purpose of the present work is to investigate the applicability of the electrochemical destruction of cyanide in a reactor equipped with Ti/SnO_2-Sb-Ce anodes, and grope for the optimal conditions for the efficient degradation of cyanide. The effects of pH, current density and flow rate on the cyanide destruction by electrochemical oxidation were studied.

2. EXPERIMENTAL METHODS

The electrochemical degradation of cyanide was carried out under batch continuous recirculation mode. The schematic diagram of the experimental setup is shown in Figure 1. The setup mainly consists of an electrochemical cell, controlled DC unit (10 A / 30 V), a reservoir, a pump, a flow meter and flow regulator. Six Ti/SnO_2-Sb-Ce electrodes with dimensions of 5.0 cm × 4.0 cm × 0.07 cm, prepared according to the method described by our previous reports [24], was used as the anodes and six stainless steel electrode with the same area as the cathodes, and the distance between an anode and an adjacent cathode was 15 mm. Cyanide solutions were prepared by dissolving NaCN, and 2 dm^3 for each experimental run was used. Different initial cyanide concentrations were obtained by dilution of the stock solution. The experiments were conducted in the pH range of 6-13, and the pH of the solution was adjusted by adding either nitric acid or sodium hydroxide. All of the experiments were conducted at room temperature and under galvanostatic conditions at anodic current densities of 10-50 mA cm^{-2}.

The performance of the process was followed by analysis of the cyanide concentration and COD, and the cyanide solution was sampled at each 30 min interval from the reservoir. The concentration of cyanide in the aqueous solution during electrolysis was determined by standard titration with $AgNO_3$. COD was measured with the standard potassium dichromate method. The concentration of CNO^- was determined by a Shimadzu UV-2450 spectrophotometer at 400 nm with

$FeCl_3 \cdot 6H_2O$ in the presence of buffer solution (0.2 M KC1 and 0.2 M HC1) [15]. Ammonia-nitrogen (NH^{4+}) was measured by using a Microprocessor Ammonia Meter (HI 93700).

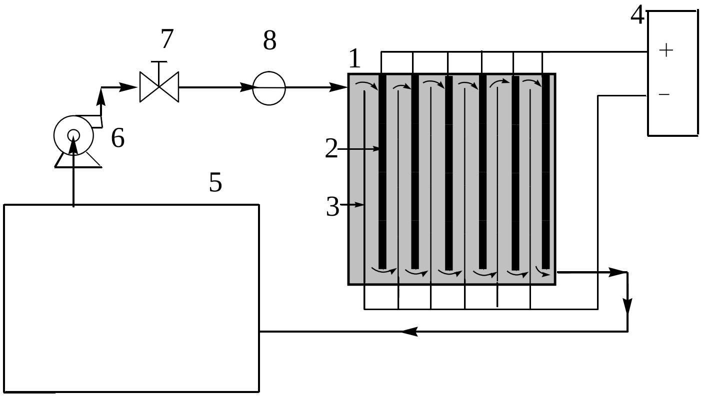

Figure 1. Schematic diagram of the experimental setup. (1) electrochemical cell; (2) anodes; (3) cathodes; (4) controlled DC unit; (5) reservoir; (6) pump; (7) flow regulator; (8) flow meter

3. RESULTS AND DISCUSSION

Experiments have been conducted by varying the operating conditions, such as initial pH, applied current density and flow rate, in order to investigate the applicability of the electrochemical destruction of cyanide with the Ti/SnO_2-Sb-Ce anode, and this new electrode was prepared in our previous work. The conversion of cyanide, COD removals of cyanide, the change of intermediates concentration and current efficiency in the electrochemical process were discussed to explore the optimal conditions for the degradation of cyanide with the Ti/SnO_2-Sb-Ce electrode.

3.1 Effect of pH

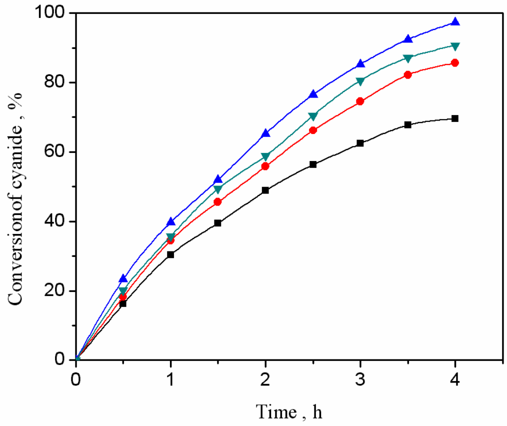

Figure 2. Effect of the initial pH on the conversion of cyanide with electrolysis time. (■) pH 6; (●) pH 8; (▼) pH 13; (▲) pH 13. $[CN^-]_0$ = 250 mg/L; applied current density = 30 mA cm^{-2}; flow rate = 80 L/h.

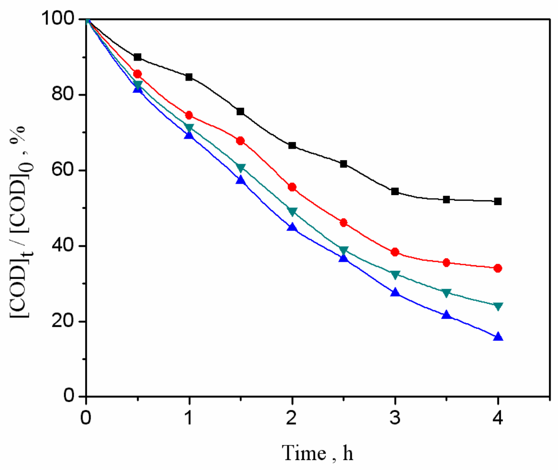

Figure 3. Effect of the initial pH on the variation of $[COD]_t/[COD]_0$ with electrolysis time. (■) pH 6; (●) pH 8; (▼) pH 11; (▲) pH 13. $[CN^-]_0$ = 250 mg/L; applied current density = 30 mA cm^{-2}; flow rate = 80 L/h.

The conversion of cyanide in the experiments conducted with initial values of pH varying from 6 to 13 is shown in Fig. 2. It has been noticed that the conversion of cyanide increases with electrolysis time at the different pH values, especially in strong alkaline solution. The rate of conversion of cyanide is larger in the beginning of the process, and that is a lower value at the end of the process. There was a notable influence of the initial pH on the oxidation of cyanide. With increasing initial pH of the solution, a noticeable improvement in the degree of CN^- conversion can be seen. The results display that the most effective oxidation is achieved at pH 13 and the main part of CN^- have been oxidized before the second hour. The conversion of cyanide is 69.5, 85.6, 90.7 and 97.4 % at initial pH 6, 8, 11 and 13 at reaction time of 4 h, respectively, which implies that the basic pH conditions are more favorable for conducting the oxidation of cyanide.

Fig. 3 shows COD removals of cyanide solution at the different pH values in electrochemical oxidation. The same trend was obtained for COD removal, but degradation of cyanide was faster by anodic oxidation at high initial pH than that at low initial pH. At initial pH 6, 8, 11 and 13, the rates of $[COD]_t/[COD]_0$ are 51.8, 34.0, 24.2 and 15.8 % (COD removal, 48.2, 66.0 75.8 and 84.2 %) at 4 h, respectively. This decrease of the COD in strong alkaline solution could be accounted for an increase in the mineralization rate of cyanide involved in the process. With continuous electrolysis, at high pH more cyanides were eventually mineralized to come into carbonate or CO_2 and N_2, however, at low pH more cyanides were oxidized to form intermediates. These results further reveal that cyanide is more effectively decomposed in strong alkaline solution.

In the electrochemical treatment of the wastewater that contains cyanide, the reaction pathways of cyanide decomposition depend heavily on the alkalinity. It is generally accepted that cyanide is oxidized to cyanate ion (CNO^-) at the anode in strong alkaline solution, which is further oxidized to carbonate or carbon dioxide and nitrogen [25-27]. The reactions may be as follows.

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^- \qquad (1)$$

$$2CNO^- + 4OH^- \rightarrow 2CO_2 + N_2 + 2H_2O + 6e^- \quad (2)$$

However, in the neutral solution the cyanate ion may continuously undergo hydrolysis to produce ammonium and carbonate ion [28],

$$CNO^- + 2H_2O = NH_4^+ + CO_3^{2-} \qquad (3)$$

In addition, cyanide ion is oxidized at the anode by first forming cyanide radical in the weak acidic solution, and C_2N_2 is further formed by the coupling of CN radicals and subsequently hydrolysed to produce the oxamide ($(CONH_2)_2$).

$$CN^- \rightarrow CN\cdot + e^- \qquad (4)$$

$$2CN\cdot \rightarrow C_2N_2 \qquad (5)$$

$$C_2N_2 + 2H_2O \rightarrow (CONH_2) \qquad (6)$$

Part of the oxamide may be continuously hydrolysed in the weak acidic solution,

$$(CONH_2)_2 + 2H_2O \rightarrow C_2O_4^{2-} + 2\,NH_4^+ \qquad (7)$$

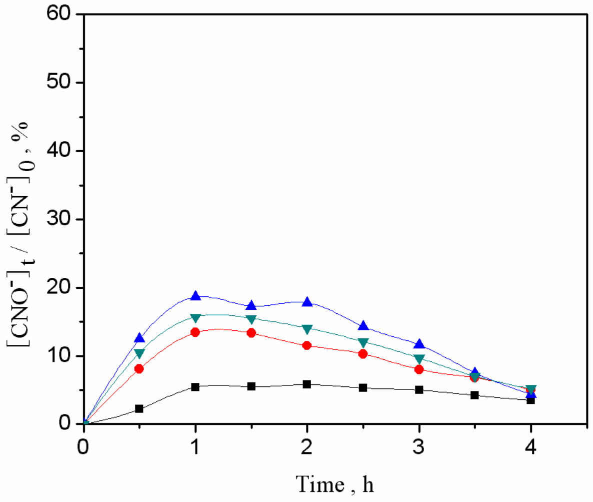

Figure 4. Effect of the initial pH on the variation of $[CNO^-]_t/[CN^-]_0$ with electrolysis time. (■) pH 6; (●) pH 8; (▼) pH 11; (▲) pH 13. $[CN^-]_0$ = 250 mg/L; applied current density = 30 mA cm^{-2}; flow rate = 80 L/h.

Fig. 4 and 5 illustrate the change in concentration of intermediates, such as CNO^- and NH_4^+ (cyanate and ammonium), at different pH values in the course of the electrochemical oxidation process. Cyanate ion was rapidly accumulated to a higher concentration level in the first 1 h of cyanide oxidation at initial pH 8, 11 and 13, however, there was a lower accumulation of cyanate at the same time at initial pH 6. It was found that cyanate ion concentration is the highest at pH 13 at 1 h. Subsequently, in 3 h of electrolysis, cyanate ion concentrations were gradually reduced at initial pH 6, 8, 11 and 13.

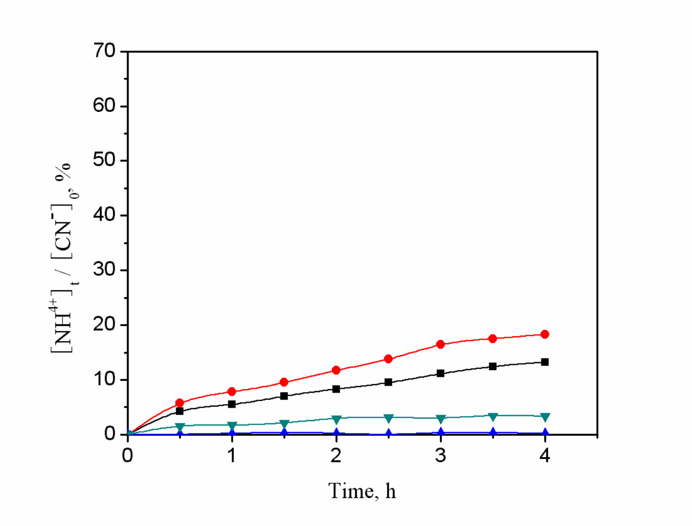

Figure 5. Effect of the initial pH on the variation of $[NH_4^+]_t/[CN^-]_0$ with electrolysis time. (■) pH 6; (●) pH 8; (▼) pH 11; (▲) pH 13. $[CN^-]_0$ = 250 mg/L; applied current density = 30 mA cm^{-2}; flow rate = 80 L/h.

The rates of $[CNO^-]_t/[CN^-]_0$ are all close to 5 % in 4 h at different pH values. The results suggest that the cyanate ion (CNO^-) is favorably generated, namely, reaction (1) occurs much more easily, in the strong alkaline solution in the electrochemical process. Fig. 5 shows the variation of ammonium concentrations ($[NH_4^+]_t/[CN^-]_0$). The conversion of cyanide and COD (in Fig. 2 and 3) removal are the highest at initial pH 13, while the ammonium concentration is very small and could almost be ignored at the same pH, which indicates reactions (3) and (7) hardly occur. The rates of $[NH_4^+]_t/[CN^-]_0$ slowly increase with time at initial pH 6, 8 and 11, but the increase of the concentration rate is the slowest at pH 11. White precipitates can be always observed in the electrolyte solution at initial pH 6 and 8, however, it began to slowly disappear after 10 min of electrolysis. They may be attributed to the formation of oxamides, oxalates and ammonium ions at low OH^- concentration (reactions (6) and (7)) [25]. These experimental results confirm that the oxidation of cyanide mainly occurs via reactions (1) and (2) in the strong alkaline solution, but via a sequence of reactions (3), (4), (5), (6), and (7) in the weak acidic or neutral solution. These findings indicate that the strong alkaline condition is optimal for the electrochemical oxidation of cyanide with the Ti/SnO_2-Sb-Ce electrode.

3.2. Effect of Current Density

The cyanide wastewater (2 L) with an initial concentration of 250 mg/L was treated at the initial pH 13 at the flow rate of 80 L/h with varying current densities and electrolysis times, respectively. Figure 6 shows the extent of cyanide decomposition and COD removal with electrolysis time for various applied currents. It can be seen from Figure 6 that the higher the current density and the longer the electrolysis time, the greater is the degree of electrochemical oxidation of cyanide and COD removal. High cyanide decomposition and COD removal with increasing current density from 30 to 50 mA cm^{-2} can be always observed. 98.6 % of conversion of cyanide and 85.1 % of COD removal is obtained at current density of 50 mA cm^{-2} in the electrolysis time of 4 h. However, the higher the applied current density, the smaller is the increment extent of conversion of cyanide and COD removal.

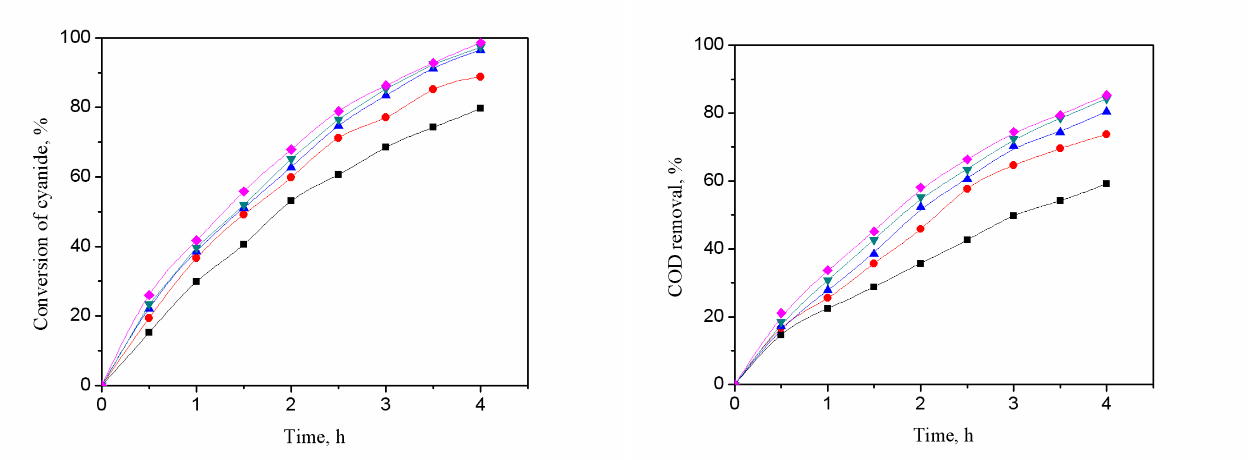

Figure 6. Effect of current density on the conversion of cyanide and COD removal with electrolysis time at initial pH 13. (■) 10 mA cm^{-2}; (●) 20 mA cm^{-2}; (▲) 30 mA cm^{-2}; (▼) 40 mA cm^{-2}; (♦) 50 mA cm^{-2}. $[CN^-]_0$ = 250 mg/L; flow rate = 80 L/h.

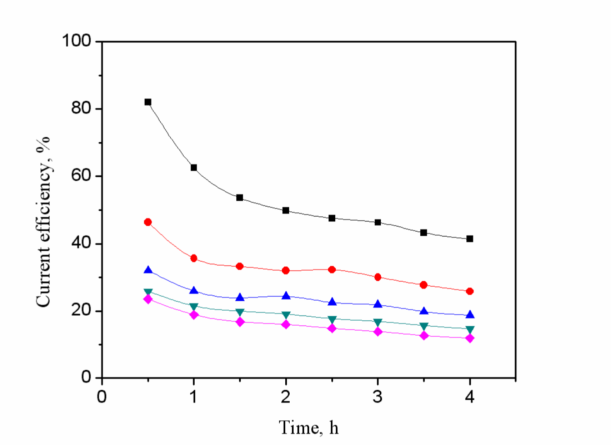

Figure 7. Current efficiency for current densities with electrolysis time at initial pH 13. (■) 10 mA cm^{-2}; (●) 20 mA cm^{-2}; (▲) 30 mA cm^{-2}; (▼) 40 mA cm^{-2}; (♦) 50 mA cm^{-2}. $[CN^-]_0$ = 250 mg/L; flow rate = 80 L/h.

Energy consumption is one of the basic parameters in electrochemical treatment of wastewater. The energy consumption is commonly evaluated with the CE, calculated as a function of the COD value of the solution. The CE related to the elimination of COD was based on the following equation [29]:

$$\mathrm{CE}(\%) = \frac{(\mathrm{COD}_0 - \mathrm{COD}_t)}{8It} FV \times 100 \qquad (8)$$

Where COD_0 and COD_t are the COD (in g of O_2 dm^{-3}) at times 0 and t (s), respectively, F is Faraday’s constant (96487 C mol^{-1}), V is the volume of the electrolyte (dm^3), I is the current (A), and 8 is the equivalent mass of oxygen (g eq^{-1}). Fig. 7 shows the CE for current densities of the oxidation of cyanide with electrolysis time. The CEs decrease with electrolysis time during the treatment of cyanide wastewater. It is also clear that the higher the applied current density for the oxidation of cyanide, the lower was the CE. When the current density is 10 mA cm^{-2}, the CEs are 82.08 % at 0.5 h and 41.32 % at 4 h. However, the CEs fall to 23.56 % at 0.5 h and 11.88 % at 4 h when the current density is enhanced to 50 mA cm^{-2}. This is because that the parasitic reaction of water electrolysis is predominant on the Ti/SnO_2-Sb-Ce anode at a high current density, and the fraction of anodic current actually was consumed in the decomposition reaction of cyanide. Current density of 20 ~ 30 mA cm^{-2} is feasible for the compositive efficiency of cyanide oxidation and energy consumption with the Ti/SnO_2-Sb-Ce electrode.

3.3 Effect of Flow Rate

Experiments were conducted at the different flow rates at initial pH 13 and the results were showed in Table 1. It can be ascertained from Table 1 that the conversion of cyanide, COD removal and CE increase as the electrolyte circulation rate increases when other parameters was kept constant. The transport of cyanide and intermediates from the bulk to the electrode surfaces increases due to a higher flow rate, and this may result in an increase destruction rate of cyanide in the process. An increase in the COD removal, conversion of cyanide and CE with an increase in the flow rate can probably be explained by mass-transfer limitation, making it difficult for cyanide to reach the Ti/SnO_2-Sb-Ce electrode surface. As the effect of current density, the higher flow rate, the smaller is the increase extent of conversion of cyanide, COD removal and CE. So the flow rate of about 120 L/h is adequate for cyanide destruction with the Ti/SnO_2-Sb-Ce electrode.

Table 1. Effect of the flow rates on the conversion of cyanide, COD removal and current efficiency.

Flow rate, (L/h)	Current density, (mA cm^{-2})	Conversion of cyanide, (%)	COD removal, (%)	Current efficiency, (%)
40	10	72.2	45.2	31.5
40	30	91.4	67.7	15.8
40	50	94.8	78.5	11.0
80	10	79.7	59.2	41.3
80	30	98.2	84.2	19.6
80	50	98.6	85.1	11.9

120	10	82.4	64.0	44.7
120	30	98.5	85.3	19.8
120	50	99.1	87.4	12.2

4. CONCLUSION

The results of the present investigation show that the process of destruction of cyanide can be achieved in an electrochemical reactor equipped with the Ti/SnO_2-Sb-Ce anode. The electro-oxidation of cyanide performed better under strong alkaline conditions, and the good effect of COD removal was also obtained. The CE of destruction of cyanide was influenced by current density, showing an inversely proportional relationship. The process of oxidation of cyanide probably is strongly mass-transfer controlled, so the appropriate applied current density and flow rate of solution are requisite for the high efficiency of cyanide elimination.

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References

1. J. B. Lacy, C. W. Richard, B. Trevor Sewell & and J. B. Michael, *Appl. Microbiol. Biotechnol.* 80 (2008) 427.
2. V. Reyes-Cruz, I. González and M. T. Oropeza, *J. Solid State Electrochem.*, 9 (2005) 566.
3. E. A. El-Ghaoui, R. E. W. Jansson and C. Moreland, *J. Appl. Electrochem.*, 12 (1982) 69.
4. K. Osathaphan, P. Tiyanont, R. A. Yngard, and V. K. Sharma, *Water Air Soil Pollut.*, 219 (2011) 527.
5. B. Bozzini, D. Lacitignola and I. Sgura, *Int. J. Electrochem. Sci.*, 6 (2011) 4553.
6. S.K. Dubey and D.S. Holmes, *World J. Microbiol. Biotechnol.*,11 (1995) 257.
7. J. R. Parga, and D. L. Cocke, *Desalination*, 140 (2001) 289.
8. M. Kitis, A. Akcil, E. Karakaya and N. O. Yigit, *Miner. Eng.*, 18 (2005) 353.
9. M. D. Gurol, and W. M. Bremen, *Environ. Sci. Technol.*, 19 (1985) 804.
10. F. R. Cakrillo-Pedroza, F. Nava-Alonso and A. Uribe-Salas, *Miner. Eng.*, 13 (2000) 541.
11. A. Alicilar, M. Kömürcü and A. Murathan, *Korean J. Chem. Eng.*, 19 (2002) 273
12. S. J. Kim, K. R. Hwang, S. Y. Cho, and H. Moon, *Korean J. Chem. Eng.*, 16 (1999) 664.
13. K. Osathaphan, T. Boonpitak, T. Laopirojana, V. K. Sharma, *Water Air Soil Pollut.*, 194 (2008) 179.
14. B. R. Lim, H. Y. Hu and K. Fujie, *Water Air Soil Pollut.*, 146 (2003) 23.
15. S. Christoskova, M. Stojanova and M. Georgieva, *React. Kinet. Catal. Lett.* 67 (1999) 59.
16. E. A. Devuyst, G. Robbins, R. Vergunst, B. Tandi and R. F. Iamarino, *Mining Eng.*, 2 (1991) 205.
17. M. D. Gurol and W. M. Bremen, *Environ. Sci. Technol.*, 19 (1985) 804.
18. K. S. Virender, R. Wayne , O. S. Jeremy and O. B. Brandon, *Environ. Sci. Technol.*, 32 (1998) 2608.
19. A. Akcil1 and T. Mudder, *Biotechnology Letters*, 25 (2003) 445.

20. N. Matyasovszky, M. Tian and A. Chen, *J. Phys. Chem. A*, 113 (2009) 9348.
21. M. E. Makgae, M. J. Klink and A. M. Crouch, *Appl. Catal. B: Environ.*, 84 (2008) 659.
22. H. Q. Xu, A. P. Li , Q. Qi, W. Jiang and Y. M. Sun, *Korean J. Chem. Eng*. DOI:10.1007/s11814-012-0014-3.
23. N. S. Bhadrinarayana, C. Ahmed Basha and N. Anantharaman, *Ind. Eng. Chem. Res.* 46 (2007) 6417.
24. H. **Q.** Xu, A. P. Li and X. C. Cheng, *Int. J. Electrochem. Sci.*, 6 (2011) 5114.
25. J. Y. Hwang, Y. Y. Wang, C. C. Wan, *J. Appl. Electrochem.*, 17 (1987) 684.
26. S. Lidia, Z. G. Francesco, N. K. Santosh and M. P. Anna, *Ind. Eng. Chem. Res.*, 39 (2000) 2132.
27. P. Tissot and M. Fragnière, *J. Appl. Electrochem.*, 24 (1994) 509.
28. G. H. Kelsall, S. Savage and D. Brandt, *J. Electrochem. Soc.*, 138 (1991) 117.
29. J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz and C. Comninellis, *Electrochim. Acta*, 46 (2001) 3573.