

Simultaneous Photo-Oxidative Degradation of EDTA and Extro-Oxidative Recovery of Copper from Industrial Effluents

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ABSTRACT: *The objectives of this investigation are the studies on the effect of copper ion on photolytic degradation of ethylenediaminetetraaceticacid (EDTA), the effect of EDTA on electrolytic recovery of copper as well as the introduction of a novel combined photolytic and electrolytic cell system for simultaneous recovery of copper and the degradation of EDTA.*

In this experimental study, a photolytic cell, an electrochemical system, and a combined photolytic - electrochemical (photoelectrolysis) system with and without an activated carbon cathode were used. Analysis was carried out using atomic absorption spectroscopy, and high performance liquid chromatography (HPLC).

The results show that a single electrochemical cell can be used to recover copper (82.1% after 9 hours) without achieving complete mineralization of EDTA by anodic oxidation (49.9 % after 9 hours). On the other hand a single photolytic cell can achieve 99.9% degradation of EDTA after 9 hours at pH 3.5 but leaves copper in solution. However, a combined photoelectrolytic system using an activated carbon concentrator cathode achieves a rapid simultaneous degradation of EDTA and recovery of copper. The amount of degradation of EDTA was 99.9% while recovery of copper was 98.8% after 9 hours.

KEY WORDS: *Copper, EDTA, Degradation, Industrial effluent, Photolytic cell, Recovery of copper, Photoelectrolysis.*

INTRODUCTION

The efficiency of removal of metals from industrial effluent can be reduced by the presence of organic species in it. Such wastes are found in many industries.

There are many examples of industrial effluents that contain chelating ligands such as EDTA, which are

deliberately added to some process stream to sequester metal ions.

The chelating agent ethylenediaminetetraaceticacid (EDTA) normally used in wastewater treatments is not degraded by conventional biological and physicochemical

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methods [1]. On the other hand the presence of organic compounds in the industrial effluent can reduce the recovery or removal of metals. A successful treatment of effluents of this type to achieve legislative compliance will depend upon whether the heavy metals affect the process of degradation of the organic species and whether the presence of organic molecules hinders the process of removal of the heavy metal. Industries for which this type of effluent occurs include: cleaning, agricultural and textile.

EDTA and related ligands such as nitrilotriacetate (NTA) are beginning to come under increasing environmental scrutiny. The main concern about these ligands is their poor biodegradability. Many ligands and their metal complexes are found to be persistent and present 15 year following their disposal, with EDTA being among the most persistent [2]. EDTA is now banned in parts of the USA, severely restricted in some countries and carefully controlled in many others by setting maximum levels for rivers.

Although there are many possible methods which can be used to destroy and reduce the levels of EDTA including treatment with activated sludge [3,4], biological degradation [5-8] and photo-oxidation with ultraviolet radiation [9-11]. For these methods, the efficiency is often reduced in the presence of heavy metal ions because of complex formation between the metal and the organic species. Similarly different methods have been used to remove or recover metals from effluent streams including chemical precipitation [12,13], solvent extraction [14,15], ion exchange [16,17], cementation [18,19], membrane separation [20,21], liquid membrane separation [22], reverse osmosis [23] and fluidized bed electrolysis [24,25]. There are practical limitations arising from failure to remove organic pollutants in using most of these methods. We now report on the effect of copper on the photolytic degradation of EDTA, the effect of EDTA on the electrolytic recovery of copper (II) ion and describe a novel combined photolytic and electrolytic cells for the simultaneous removal of copper and the degradation of EDTA to achieve total effluent clean-up.

EXPERIMENTAL

The photolytic cell was designed and used (Fig. 1) consists of a UV probe [1] surrounded by a reaction chamber [2] of 3.5 dm³ capacity through which the fluid

to be treated is pumped from a reservoir [3] via an inlet [4] and back to reservoir via an outlet [5]. The fluid was circulated at a flow rate of 10 dm³ min⁻¹ and controlled by valves. Compressed air is used as the oxidant in the photolysis and supplied through inlet [6] and exits through outlet [7]. The temperature in the system can be measured by a digital thermocouple probe [8]. The temperature in the reaction chamber is maintained at 25-30 °C by passing water through an external jacket [9] surrounding the UV probe. The UV-source was a 400 W mercury vapor lamp. The effects of pH, copper ion, hydrogen peroxide and TiO₂ (Degussa P25 which has a surface area 50 m²/g) on the degradation of EDTA were studied.

The electrochemical cell was designed and used (Fig. 2) consists of an electrolytic chamber (A) of 1.5 dm³ capacity through which the fluid to be treated is pumped from a reservoir (B) via inlet (C) and back to the reservoir via outlet (D). The fluid flow rate (15 dm³ min⁻¹) was adjusted by valves and fluid flow rate was measured by a liquid rotameter. The cell contains two mixed metal oxide coated titanium mesh anodes (E) and a single stainless steel plate cathode (F). The effect of EDTA on the deposition of copper was studied.

The photolytic and the electrochemical cells were combined to achieve the simultaneous destruction of EDTA and the recovery of copper. The combined system had a common reservoir and the fluid was pumped through the electrolytic chamber and the UV-irradiation chamber using two separate pumps. The electrochemical process was carried out at a constant current of 1.00 A. Periodically during the process samples were collected from the reservoir tank for analysis of metal ions and the degradation of EDTA.

Model solution (10 dm³) containing known concentrations of copper and EDTA were prepared by dissolving reagent grade CuSO₄.5H₂O and disodium salt of EDTA in distilled water. Reagent grade sulphuric acid and sodium hydroxide were used to adjust the pH of the solution when required. All of these materials were provided from Merck GmbH (Darmstadt, Germany). The analysis of copper was carried out using atomic absorption spectroscopy (AAS) and the degradation of EDTA was followed by HPLC method. The degradation was followed by reverse phase high performance liquid chromatography (HPLC) using Cecil 1200 HPLC UV

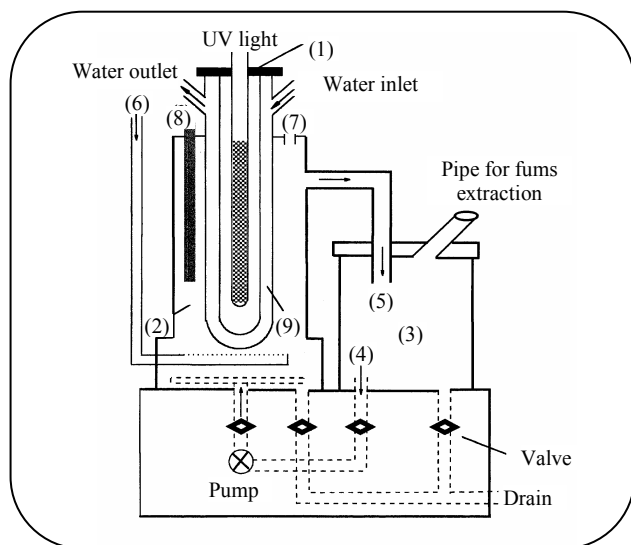


Fig. 1: The designed potolytic cell

absorbance detector linked to Gilson Model pump 303. Monitoring was carried out at wavelength of 300 nm. The reverse-phase separation column used was a 12 cm PLRP (a polystyrene-divinyl benzene packing) μm particles with 25:75 and acetonitrile: water (pH=6) containing 3gdm^{-3} tetrabutyl ammonium bromide as the mobile phase.

RESULTS AND DISCUSSION

Photo-oxidation of EDTA

An aqueous solution of EDTA (50mgdm^{-3}) has a natural pH of 4 – 4.3 at room temperature. Experiments were carried out to investigate the effect of pH over the pH range (1.5 – 11.5) on the photo-degradation of EDTA. The results show that no significant change in the degradation of EDTA is observed over the pH range studied (Fig. 3). The rate of degradation is, however, reduced at the initial stages of the reaction especially at higher pH values. pH= 3.5 was found to be the optimum for the degradation of EDTA because complete mineralization can be achieved with minimum time at this value.

The effect of the presence of copper (500mgdm^{-3}) on photo-degradation of EDTA at pH 3.5 is shown in table 1. The presence of copper leads to a reduction in the efficiency of the degradation of EDTA. The extent of degradation being 46.4% and 32.3% after one hour in the absence and in the presence of copper ions respectively. The corresponding values after 9 hours are 99.9 and

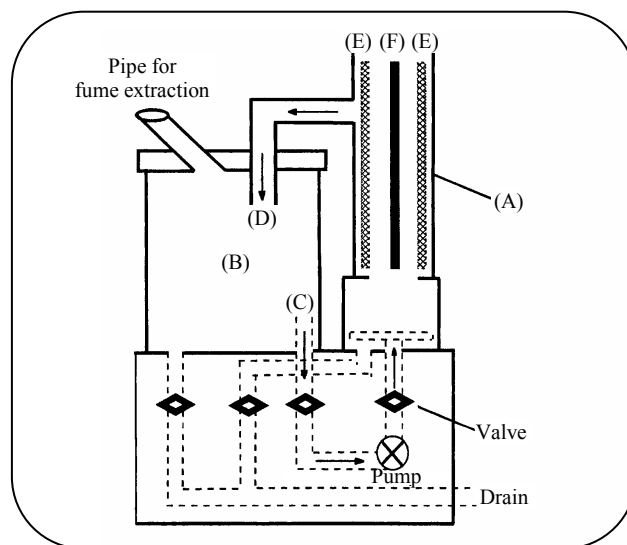


Fig. 2: The designed electrochemical cell

88.1%, respectively.

The reduction in the extent of EDTA photo-degradation in the presence of copper (500mgdm^{-3}) can be largely overcome by the addition of hydrogen peroxide as an oxidant and titanium dioxide as a heterogeneous catalyst. The effect of hydrogen peroxide was determined by adding different volumes ($5\text{--}15\text{cm}^3\text{dm}^{-3}$) of 30 % hydrogen peroxide to a solution containing the same initial concentration of EDTA in the presence or absences of copper or catalyst. The addition of H_2O_2 ($5\text{cm}^3\text{dm}^{-3}$) increase the extent of degradation of EDTA and a complete mineralization is achieved after 7 hours. No further advantage in the degradation rate is observed by increasing the hydrogen peroxide volume above $5\text{cm}^3\text{dm}^{-3}$. Addition of TiO_2 (1gdm^{-3}) accelerated the degradation of EDTA (Table 1).

Electrochemical oxidation of EDTA and recovery of copper

An electrochemical system can be used for both metal recovery and electro-oxidation of organic contaminants. The electrodeposition of metal ions from an aqueous solution is a pH-dependent process. In some cases, the pH of the solution must be kept constant to achieve the highest recovery of copper. The results obtained show that the recovery of copper is independent of the $\text{pH} \leq 4.5$ of the solution and similar recovery of copper is achieved by carrying out experiments at

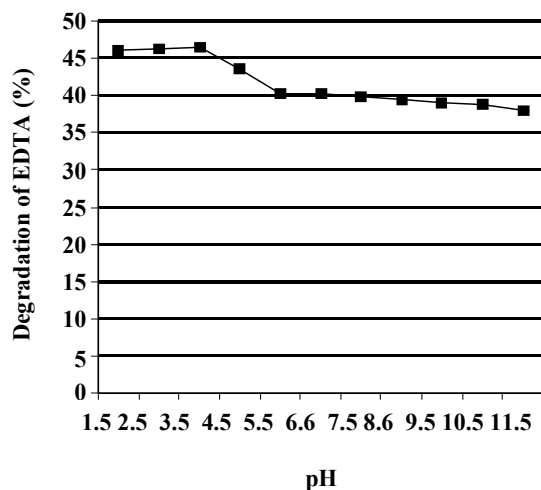


Fig. 3: The effect of pH on the photolytic degradation

pH 1.5, 2.5, 3.5 and 4.5. The effects of EDTA, hydrogen peroxide and titanium dioxide on the recovery of copper and the electrooxidation of EDTA were, therefore, studied at pH 3.5 (the optimum value for the photo-oxidative degradation of EDTA). The results show that the recovery of copper decreases in the presence of EDTA. In the absence of EDTA, the hydrated copper ions move towards the cathode surface under the influence of the electric field where they are reduced to deposit as metal at the cathode surface. In the presence of EDTA, the copper ions are complexed with EDTA and hence more energy is required to break this complex (Fig. 4).

The addition of copper ions decreases the electro-oxidation of EDTA. A 7.3% electro-oxidation of EDTA can be achieved in 1 hour in the absence of copper but this reduces to 5.1% when the metal ions are present. The corresponding values after 9 hours are 49.9 and 43.5%, respectively. The percentage recovery of copper after 1 and 9 hours is 20 and 82.1 % respectively. The addition of H_2O_2 as an oxidant increases both the degradation of EDTA (by combined chemical and electro-oxidation) and the recovery of copper (by reducing the amount of complexing ligand). The addition of TiO_2 as a heterogeneous catalyst, however, decreases both the electro-oxidation of EDTA and the recovery of copper (Table 2 and Fig. 5) because the TiO_2 covers the surface of the electrodes and ultimately reduces the oxidation and reduction processes.

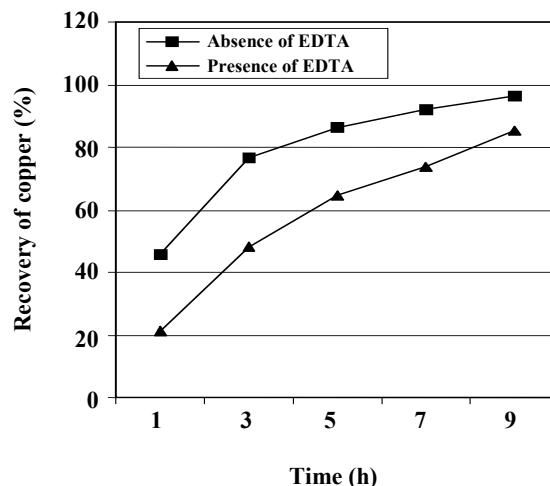


Fig. 4: Effect of EDTA (50mgdm^{-3}) on the recovery of copper (500mgdm^{-3}) using an electrolytic cell

Combined photolytic and electrolytic cell

The results show that the photolytic cell is capable of achieving 88.1% degradation of EDTA with zero recovery of copper after 9 hours whilst the electrochemical cell system is capable of achieving 85.1% recovery of copper with only 43.5% degradation of EDTA. It is thus suggestive that a combined photolytic and electrolytic cell system should achieve the simultaneous destruction of organic species and the recovery of heavy metals in a total effluent clean-up.

The combined system can be used to achieve near to complete mineralization of EDTA after 7 hours in the absence of copper ions compared to 9 hours in the photolytic cell system. The presence of 500mgdm^{-3} of copper slightly decreases the degradation of EDTA but gives 97.2% degradation of EDTA and 93.8% recovery of copper in 9 hours at pH= 3.5. The addition of hydrogen peroxide ($5\text{cm}^3\text{dm}^{-3}$) in the combined system increases the degradation of EDTA and also the recovery of copper. This increase in EDTA degradation is attributed to [1] the continuous removal of copper at the cathode surface which ultimately reduces its effect on the photolytic oxidation and [2] the photo-oxidation and electro-oxidation processes occurring simultaneously in the combined system.

The addition of TiO_2 (1gdm^{-3}) increase the degradation of EDTA but reduces the recovery of copper in the combined system as in the separate electrochemical system (Table 3 and Fig. 6).

Table 1: Effect of copper (500mgdm^{-3}), H_2O_2 and TiO_2 on the degradation of EDTA in pH 3.5 using a photolytic cell

Time (h)	Degradation of EDTA (%)				
	Absence of copper	Absence of copper and presence of H_2O_2 ($5\text{ cm}^3\text{dm}^{-3}$)	Presence of copper	$\text{Cu} + \text{H}_2\text{O}_2$ ($5\text{ cm}^3\text{dm}^{-3}$)	$\text{Cu} + \text{TiO}_2$ (1 g dm^{-3})
1	46.4	68.4	32.3	59.2	62.4
3	71.4	84.6	62.1	78.3	84.1
5	90.1	98.5	73.7	91.7	97.6
7	97.3	99.9	81.5	99.9	99.9
9	99.9	99.9	88.1	99.9	99.9

Table 2: Effect of copper (500mgdm^{-3}), H_2O_2 and TiO_2 on the electro-oxidation of EDTA (50mgdm^{-3}) using an electrolytic cell

Time (h)	Degradation of EDTA (%)			
	Absence of copper	Presence of copper	$\text{Cu} + \text{H}_2\text{O}_2$ ($5\text{ cm}^3\text{dm}^{-3}$)	$\text{Cu} + \text{TiO}_2$ (1 g dm^{-3})
1	7.3	5.1	28.1	9.3
3	18.1	14.9	40.2	17.9
5	27.4	21.3	50.2	22.4
7	37.3	28.1	65.5	24.8
9	49.9	43.5	83.3	27.1

Table 3: Effect of copper (500mgdm^{-3}), H_2O_2 and TiO_2 on the degradation of EDTA (50mgdm^{-3}) using a combined cell

Time (h)	Degradation of EDTA (%)			
	Absence of copper	Presence of copper	$\text{Cu} + \text{H}_2\text{O}_2$ ($5\text{ cm}^3\text{dm}^{-3}$)	$\text{Cu} + \text{TiO}_2$ (1 g dm^{-3})
1	27.1	19.3	56.1	55.8
3	60.3	42.7	79.7	72.3
5	87.4	78.5	88.1	83.4
7	98.1	91.3	94.7	89.7
9	99.9	97.2	99.6	91.0

Table 4: Degradation of EDTA and the recovery of copper (500mgdm^{-3}) using an activated carbon electrochemical concentrator and a combined photolytic and activated carbon concentrator

Time (h)	Recovery of copper and the degradation of EDTA(%)			
	Activated carbon concentrator cell system		Combined photolytic and activated carbon concentrator cell system	
	Copper	EDTA	Copper	EDTA
1	39.4	40.3	43.1	56.3
3	68.9	61.2	66.6	73.1
5	84.1	78.2	84.2	89.9
7	90.7	84.8	97.1	98.1
9	96.1	94.3	98.8	99.9

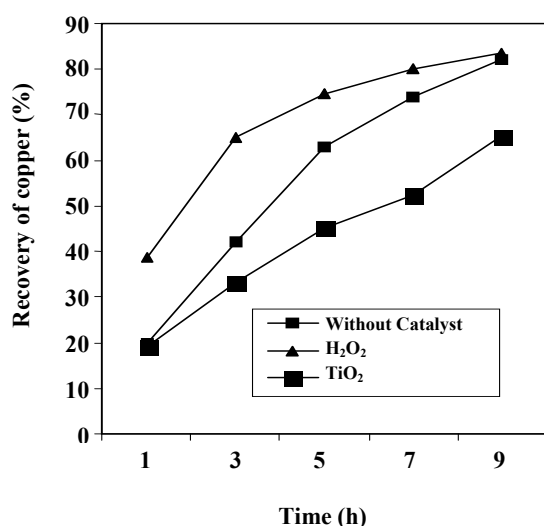


Fig. 5: Effect of H_2O_2 ($5\text{cm}^3\text{dm}^{-3}$) and TiO_2 (1gdm^{-3}) on the recovery of copper (500mgdm^{-3}) using an electrolytic cell

Activated carbon concentrator system

The simultaneous destruction of EDTA and the recovery of copper can also be achieved by using an activated carbon electrochemical concentrator system compared to a standard electrochemical cell system [26]. The data on the degradation of EDTA and the recovery of copper from solution containing 50mgdm^{-3} of EDTA and 500mgdm^{-3} of copper using an activated carbon concentrator and a combined photolytic and activated carbon concentrator cell systems are given in Table 4. The results show that activated carbon concentrator system is capable of destroying EDTA and at the same time recovering copper from

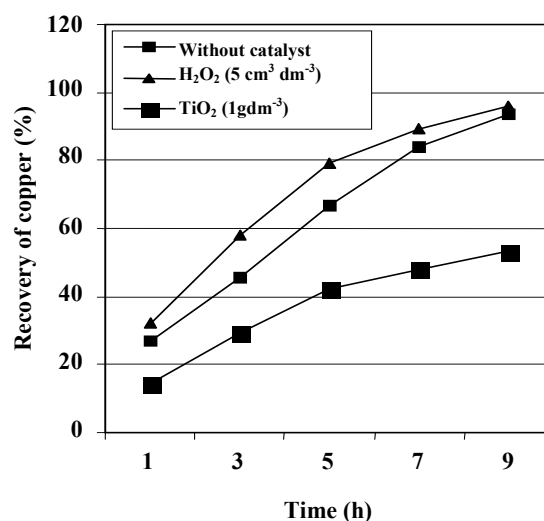


Fig. 6: Effect of H_2O_2 ($5\text{cm}^3\text{dm}^{-3}$) and TiO_2 (1gdm^{-3}) on the recovery of copper (500mgdm^{-3}) using a combined cell

mixed effluent streams. The purpose of this concentrator system is to increase the copper ions near the cathode surface, which ultimately increases the reaction efficiency. The concentrator system has three further advantages [1] in-situ regeneration of activated carbon occurs in the system due to the production of H_3O^+ ions at the anode surface, [2] the effectiveness of activated carbon concentrator material is independent of the solution and recovery of copper and the degradation of EDTA can be achieved at any pH and [3] complete effluent clean-up can be achieved rapidly without the use of an additional oxidants or catalysts.

CONCLUSIONS

The results of this study show that an electrochemical cell alone can be used to recover copper but is not capable of achieving the complete anodic oxidation of EDTA. On the other hand, making of a photolytic system alone can achieve EDTA degradation but leaves copper ions in solution. The use of a combined photolytic and electrochemical cell can, however, lead to the simultaneous destruction of EDTA and the recovery of copper. Similar results to that of the combined system can also be achieved by using an activated carbon electrochemical concentrator cell system. The degradation of EDTA and the recovery of copper can be further improved by combining the photolytic and activated carbon concentrator cell.

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REFERENCES

- [1] Babey, P.A., Emilio, C.A., Ferreyra, R.E., Gautier, E.A., Gettar, R.T. and Litter, M.I., Kinetics and mechanisms of EDTA photocatalytic degradation with TiO₂, *J. Water Science and technology*, **44** (5), 179 (2001).
- [2] Li, Z.B., Shuman, L.M., Redistribution of forms of zinc, cadmium and nickel in soils treated with EDTA, *Sci. Total Environ.*, **191**, 95 (1996).
- [3] VanGinkel, C.G., Virtapohia, J., Steyaert, J.A.G., R., Treatment of EDTA-containing pulp and paper mill waste waters in activated sludge plants., *Tappi J.*, **82**, 138 (1999).
- [4] Virtapohia, J., Alen, R., Accelerated degradation of EDTA in an activated sludge plant study looks at a sludge plant-operating under alkaline conditions., *pulp & paper-Canada*, **99**, 53 (1998).
- [5] Henneken, L., Norte, B., Hempel, D.C., Biological degradation of EDTA: Reaction kinetics and technical approach., *J. Chem. Tech. Biotechnol.*, **73**, 144 (1998).
- [6] Kaluza, U., Kilgelhofer, P., Taeger, K., Microbial degradation of EDTA in an industrial wastewater treatment plant, *water Res.*, **32**, 2843 (1998).
- [7] Thomas, R.A.P., Lawlor, K., Bailey, M., Macaskie, L.E., Biodegradation of metal – EDTA complexes by an enriched microbial population, *Appl. Environ. Microbiol.*, **64**, 1319 (1998).
- [8] Yang X., Jiang Z., Guan Y., Deng, J., Lu, M., Biodegradation behavior of ethylenediamine-tetraethylene acid, *Huan Jing Ke Xue*, **22** (2), 41 (2001).
- [9] Davis, A.P., Green, D.L., Photocatalytic oxidation of cadmium-EDTA with titanium dioxide, *Environ. Sci. Technol.*, **33**, 609 (1999).
- [10] Sorensen, M., Zurell, S., Frimmel, F.H., Degradation pathway of the photochemical oxidation of ethylenediaminetetraacetate (EDTA) in the UV/H₂O₂ process, *Acta Hydrochimica ET Hydrobiologica*, **26**, 109 (1998).
- [11] Kagaya, S., Bitoh, Y., Hasegawa, K., Photocatalyzed degradation of metal – EDTA complexes in TiO₂ aqueous suspensions and simultaneous metal removal., *Chem. Lett.*, **2**, 155 (1997).
- [12] Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., Heavy metals in wastewater: Modelling the hydroxide precipitation of copper (II) from waste water using lime as the precipitant, *Waste management*, **16**, 717 (1996).
- [13] Gyunner, E.A., Yakhkind, N.D., Effect of a base on the precipitation of copper (II) hydrosulfates from solution, *Zhur. Neorg. Khim.*, **42**, 222 (1997).
- [14] Alguacil, F.J. Cobo, A., Solvent extraction with LIX 973N for the selective separation of copper and nickel, *J. Chem. Tech. Biotechnol.*, **74**, 467 (1999).
- [15] ElAamrani, F.Z., Kumar, A., Cortina, J. L., Sastre, A.M., Solvent extraction of copper (II) from chloride media using N- (thiocarbamoyl)benzamidine and N-benzothiourea derivatives, *Analytica chimica Acta*, **382**, 205 (1999).
- [16] Raghavan, R., Bhatt, C.V., Comparative study of certain ion-exchange resins for application in copper-bearing process solution., *Hydrometallurgy*, **50**, 169 (1998).
- [17] Maurelia, G.R., Zamora, C.R., Gonzalez, M.M., Guevara, B.M., Diaz, C.G., Copper removal from industrial solutions and effluents with quelate polymers and ion exchange resins., *Afinidad*, **55**, 57 (1998).
- [18] Hsu, Y.J., Kim, M.J., Tran, T., Electrochemical study on copper cementation from cyanide liquors using zinc., *Electrochimica Acta*, **44**, 1617 (1999).
- [19] Stefanowicz, T., Osinska, M., Napieralaskazogzda, S., Copper recovery by the cementation method.,

Hydrometallurgy, **47**, 69 (1997).

- [20] Alexandrova, I., Iordanov, G., Transport of nickel and copper against a concentration gradient through a carboxylic membrane, based on poly vinyl chloride/polymethymethacrylate-co-divinylbenzene), *J. Appl. Polymer sci.*, **63**, 9 (1997)
- [21] Juang, R.S., Chen, M.N., Removal of copper (II) chelates of EDTA and NTA from dilute aqueous solutions by membrane filtration., *Ind.eng. Chem. Res.*, **36**, 179 (1997).
- [22] Guyon, F., Parthasarathy, N., Buffle, J., Removal of copper(II) chelates of EDTA and NTA from dilute aqueous solutions by membrane filtration., *Anal. Chem.* **71**, 819 (1999).
- [23] Goel, M., Agrawal, V., Kulkarni, A.K., Cramer, S.M., Gill, W.N., Stability and transport characteristics of reverse osmosis membranes using cyanide rinse waters., *J. membrane sci.*, **141**, 245 (1998).
- [24] Cambell, D.A., Darymple, I.M. Sunderland, J. G., Tilston, D., The electrochemical recovery of metals from effluent and process stress streams. *Resources Conservation and recycling.*, **10**, 25 (1994).
- [25] Boyanov, B.S., Donaldson, J.D., Grimes, S.M., Removal of copper and cadmium from hydro-metallurgical leach solutions by fluidized-bed electrolysis. *J. Chem. Tech. Biotechnol.*, **41**, 317 (1988).
- [26] Dando. S.O.V., PhD. thesis, The removal of metals and effluent control using electrolytic techniques, Department of chemistry, Brunel university, London, (1995).