



Trade Science Inc.

ISSN : 0974 - 7443

Volume 6 Issue 4

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 6(4) 2011 [208-213]

Removal of organics from metalworking fluids (MWFs) by batch electrocoagulation process using iron electrodes

K.C.Praveen, C.Arun, K.V.Radha*

Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai-600025, (INDIA)

E-mail: radhavel@yahoo.com

Received: 29th November, 2011 ; Accepted: 23rd December, 2011

ABSTRACT

This study elucidates the reduction of organics from metalworking fluid (MWFs) through batch electrocoagulation (EC) reactor using iron electrodes. The effect of the working parameters, such as current density (0.8-3.0 A/dm²) and electrolysis time (330 min) were investigated in this system to achieve a maximum chemical oxygen demand (COD) and color removal efficiency for MWFs effluent. A constant current density of 0.8 A/dm² was maintained throughout the process. During EC treatment the pH increases and reaches a maximum of 6.8 at 210 min where maximum COD and color removal efficiency of 85% and 95% respectively; were observed. The results were analyzed using kinetics models and a high coefficient of determination value ($R^2=0.9948$) for first-order regression model was observed. This study shows that EC technique can be employed to treat MWFs and reduce the pollutant load before biological treatment process to meet the discharge standards. The results suggest an important role of these parameters in electrochemical process for removal of organic pollutants.

© 2011 Trade Science Inc. - INDIA

KEYWORDS

Electrocoagulation;
COD;
pH;
Electrolysis time;
Color;
MWFs;
Kinetics.

INTRODUCTION

Metal finishing industries, metal processing industries, iron & steel manufacturing industries, electroplating industries etc produce a large volume of high strength MFWs that cause serious environmental problems. The effluents from these industries occupy the fifth rank with respect to discharging pollutants into local water bodies and sewage systems^[1,2]. The MFWs which are characterized by a high organic load, dark color, low pH and low biodegradability index cannot be treated by biological methods^[3]. India has a large number of metal processing industries that generate huge million liters of wastewater annually. The metalworking fluids (MWFs)

contain various pollutants (biocides, corrosion inhibitors, extreme pressure and anti wear agents, emulsifiers and surfactants) and have a high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon and a dark colour^[4].

Various methods are practiced for the last two decades to treat the effluent. Techniques such as chemical coagulation, precipitation, co-precipitation, air flotation, flocculation, adsorption, ion exchange processes, membrane processes, biological processes, phytoextraction, extraction, ozone oxidation and electrochemical processes are widely used for effluent treatment^[5-8]. Electrochemical coagulation is one of the process that can be employed to treat any kind of wastewater such as

electroplating wastewater^[9], pharmaceutical wastewater^[10], petrochemical wastewater^[11], municipal wastewater^[12], paper and pulp wastewater^[13], brackish water^[14], portable water, oil mill wastewater, nitrite effluent, textile dyes, agro industries wastewater, laundry wastewater etc^[15]. Electrocoagulation (EC) proves to be an ideal technique for effluent treatment because of its versatility, energy efficiency, amenability, cost effectiveness^[16] and environmental compatibility^[17].

During EC process it produces a series of active ionic species like Fe^{2+} and Fe^{3+} that destabilize fine dispersed particles in the solution and these destabilized particles are aggregated to form floc^[18, 19]. These Ferric ions have a distinct advantage over aluminum ions (Al^{3+}) because of its harmless property and are not toxic like aluminum ions^[20].

The dissolved contaminants present in the effluent are removed by sorption, coagulation and other processes by applying electric current^[21, 22]. Electrocoagulation (EC) is not only used for removing COD but also a wide range of pollutants from various synthetic and industries effluents^[23, 24]. However there are only few studies about EC treatment of metal processing effluent. Muszyński et al^[4] observed a maximum COD removal of 82% for spent MWFs. Kabdasli et al^[25] in his study, attained a maximum TOC and organic removal of 66% for electroplating effluent by using stainless steel electrodes with an applied current density of $9mA/cm^2$.

The objective of the present study is to investigate the COD and color reduction of MWFs in a batch EC reactor using iron electrodes. The effect of several parameters, namely current density, initial pH and electrolysis time on COD and color removal efficiency were studied and the kinetics of the EC process was also analyzed.

MATERIALS AND METHODS

Metalworking fluid effluent

The spent MWFs used for the study, was collected from a real metal processing/working factory (Chennai). The effluent comprised of the exhausted emulsifiers, surfactants, oils & grease. The wastewater was characterized using standard methods^[26] and the waste water characteristics such as COD, pH, total dissolved sol-

ids, BOD, dissolved salts and color are summarized in TABLE 1.

TABLE 1 : Characterization of the MWFs

Parameter	Value
pH	1.5
Conductivity	15.67 ms/cm
Iron	6.54 mg/l
Chemical oxygen demand	3400 mg/l
Total hardness as $CaCO_3$	570 mg/l
Sodium	122 mg/l
Potassium	Nil
Calcium	53 mg/l
Copper	Trace
Magnesium	127 mg/l
Sulphate	86 mg/l

Experimental set-up: electro coagulation unit

The Electro coagulation unit consists of a cylindrical reactor of height 9 cm and diameter 6 cm made of glass. The electrolytic cell contains 2000 ml MWFs as working liquid, fitted with a wooden cell cover with slots to introduce the electrodes vertically. Mild steel sheet of surface area $12cm^2$ is used as anode. A stainless steel cathode of the same dimensional was used. It was placed at an inter-electrode distance of 1 ± 0.2 cm. Before electrolysis the electrode surface was cleaned manually by abrasion with sand paper and treated with 0.1N sulphuric acid, followed by washing with pure water, thereby activating the electrode surface by removing impurities. After each experimental run, the EC reactor and electrodes were cleaned with 50% (v/v) nitric acid solution for 2-4 min and several times with distilled water to remove the precipitated impurities such as hydroxides. When the anode material consumption reaches 8- 10% the electrode was renewed.

Experimental protocol

The effect of electrolysis time and current density on percentage removal was analyzed. The electrocoagulation experiments were run at room temperature. TABLE salt was used commonly in EC to increase the conductivity of the effluent and also to decrease the power consumption of the process^[27]. Hence in this present investigation $2 gL^{-1}$ of sodium chloride was added to the wastewater as supporting electrolyte.

Full Paper

Effect of electrolysis time

To determine the effect of electrolysis time the experiment was carried out at different time intervals (30, 60, 90, 120, 150, 180, 210, 240, 270 and 300min) by maintaining a constant current density. In order to maintain uniform concentration the solution was constantly stirred at 300 rpm with a magnetic stirrer. Regulated direct current was supplied to the electrode from a rectifier in mono-polar mode to maintain a constant current density of 0.8 A/dm². The electrolyzed samples were collected and centrifuged at 4000 rpm for 15 min. The supernatant was filtered using Whatmann No.1 filter paper of pore size 11 micron and percentage removal was calculated.

Effect of current density

The current density was varied from 0.8 to 2.6 A/dm² and the effluent was treated for an hour as mentioned earlier.

Analytical techniques

COD, pH and color were analyzed for the raw and EC-treated MWFs in order to follow the process performance. The COD was determined by the Open Reflux Titrimetric method according to Standard Methods. The color removal measured by Spectrophotometer (ELICO scanning mini SPEC SL177) and pH was measured (STLAP-1PLUS). Percentage COD removal was calculated using the following relationship^[23].

$$\text{Percentage COD removal} = \frac{(COD_i - COD_f) \times 100}{COD_i}$$

$$\text{Percentage colour removal} = \frac{(A_i - A_f) \times 100}{A_i}$$

Where COD_i is the initial COD (mg/L) and COD_f is the final COD (mg/L) after electrolysis time (min). A_i is absorbance of the effluent before treatment and A_f is the absorbance of the effluent after treatment at 580nm.

RESULT AND DISCUSSION

Effect of electrolysis time on COD and color removal

EC process involves the generation of coagulants in-situ by dissolving iron ions from iron electrodes. At the anode Fe²⁺ ions were evolved by the electrochemi-

cal reaction; some of the Fe²⁺ ions were oxidized into Fe³⁺ by the dissolved O₂ in the solution. The free Fe³⁺ and Fe²⁺ ions from the anode combine with the free OH⁻ ions from the cathode to form Fe(OH)₂ and Fe(OH)₃.

The following reactions take place in the EC cell^[28]

Anode reaction (oxidation): Fe → Fe²⁺ + 2e⁻

Cathode reaction (reduction): 2H₂O + 2e⁻ → H₂ + 2OH⁻

Co-precipitation: Fe³⁺ + 3OH⁻ → Fe(OH)₃

Fe²⁺ + 2OH⁻ → Fe(OH)₂

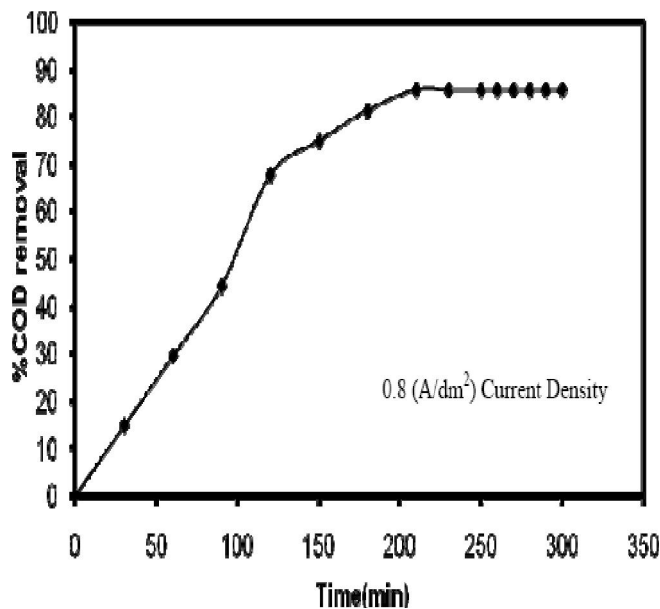


Figure 1 : Effect of time on the COD removal

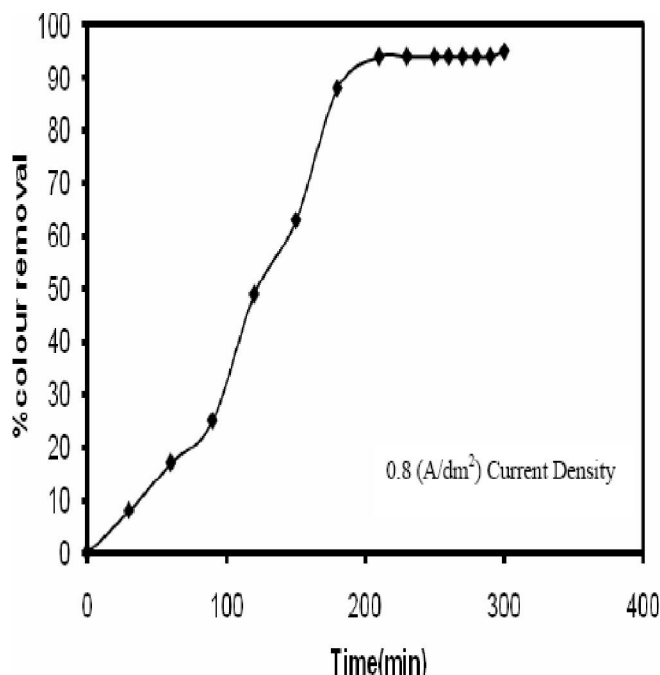


Figure 2 : Effect of color removal with respect to time

Where $\text{Fe}(\text{OH})_3$ & $\text{Fe}(\text{OH})_2$ act as active coagulating and co-precipitating agents in removing pollutants from MWFs by adsorption and absorption or either by complexation or electrostatic attraction, followed by EC.

Figure 1 & 2 elucidate the change in removal efficiencies during the treatment of MWFs by EC at different electrolysis time and a constant current density of 0.8 A/dm^2 . It was observed that the percentage removal increased with electrolysis time. COD and colour removal efficiency reaches a maximum of 85% and 93% respectively at 210 min. the process attained equilibrium at 210 min and on further increase in electrolysis time no significant change in percentage removal was observed.

Effect of pH

During the treatment process, the OH^- ions liberated at the cathode, due to the splitting of water molecules increases the pH of the working solution. The pH increased with the electrolysis time and reached a maximum of 6.8 as shown in Figure 3. With further increase in electrolysis time the pH remained constant.

The initial pH of the effluent was 1.5. The effect of pH on EC treatment was analyzed by varying the pH using 1% NaOH. Experiments were carried out by varying the pH (2, 4, 6, 6.8, 8 and 10) and maintaining a

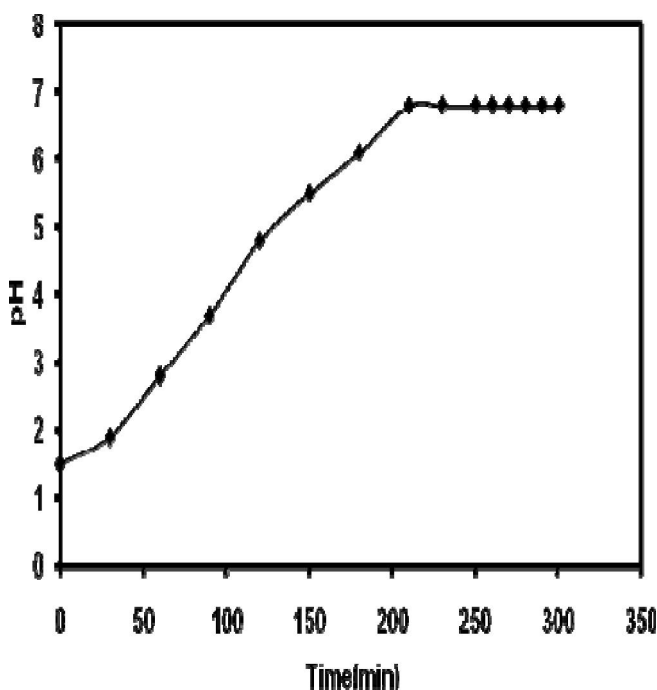


Figure 3 : Effect of Electrolysis time on pH

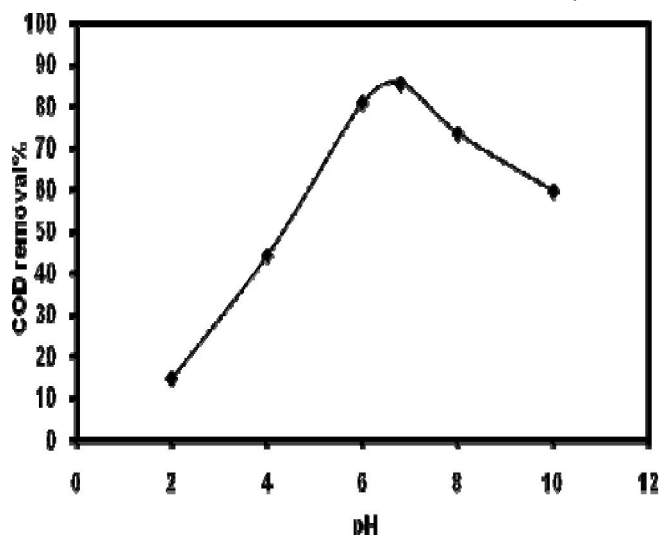


Figure 4 : Effect of pH on COD removal

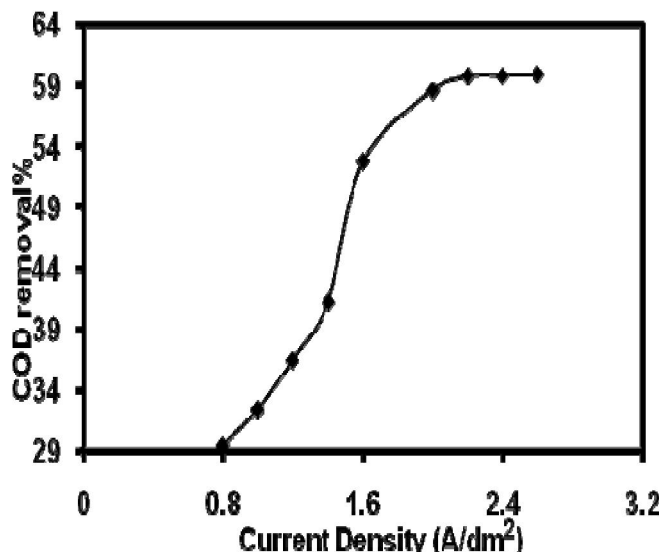


Figure 5 : Effect of current density on the removal of COD.

constant current density of 0.8 A/dm^2 . Figure 4 shows a maximum COD removal efficiency of 85% at pH 6.8. With further increase in pH the efficiency was found to decrease.

Effect of current density

The current density is an important parameter in electro coagulation processes. In the present investigation, to analyze the effect of current density on EC treatment various samples of MWFs were treated for an hour at different current densities ($0.8, 1.0, 1.2, 1.4, 1.6, 2.0, 2.2, 2.4$ and 2.6 A/dm^2) and the COD was measured. On a lesser value of current density the time taken for COD reduction was much more than three hours even though there appeared to be COD reduc-

Full Paper

tion of 12-25%. Hence experiments were conducted for a value of 0.8 and above. Figure 5, clearly indicates that with increase in current density the removal percentage increases and it reaches a maximum of 60% at a current density of 2.2. A further increase in current density only resulted in power loss due to heat generation without any increase in removal efficiency.

Kinetic studies

Zero, first and second order models were used to evaluate the kinetic of the COD removal in the electrochemical process. The Zero-Order kinetic model is expressed as

$$C_0 - K_0 t = C \quad (1)$$

Where C (mg/l) is the concentration of COD at time t; C_0 (mg/l) is the initial concentration of COD; K_0

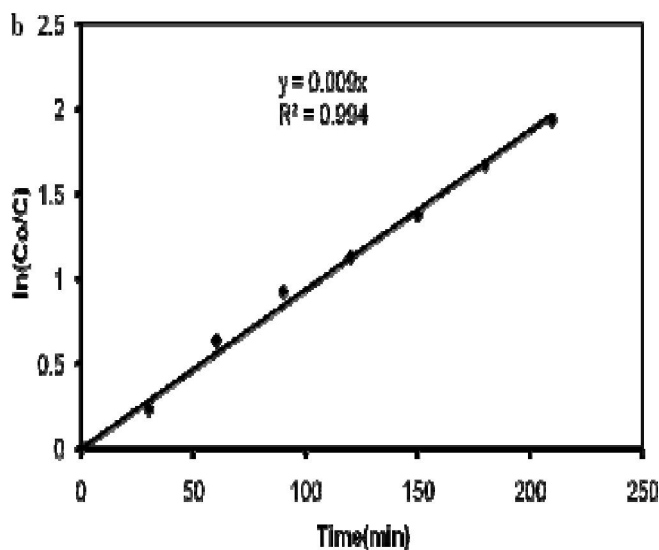
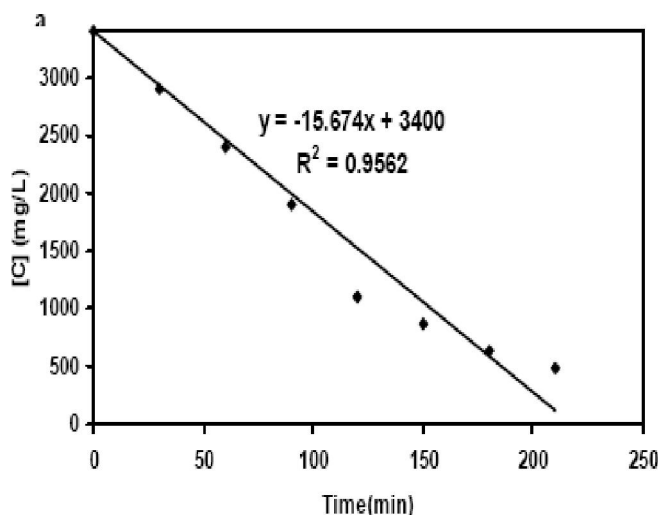


Figure 6 : (a) Zero order kinetics for COD removal and (b) First order kinetics for COD removal

($\text{mol L}^{-1}\text{min}^{-1}$) is the zero-order rate constant

The first order model is expressed as

$$\ln(C_0/C) = K_1 t \quad (2)$$

Where, K_1 (min^{-1}) is the first-order rate constant.

The kinetics of the process was further analyzed using the second order relation. The second order kinetic model is expressed as^[3]

$$(1/C) - (1/C_0) = K_2 t \quad (3)$$

Where, K_2 ($\text{L}/(\text{mol min})$) is the rate constant of second order kinetic model. K_2 and R^2 can be determined from the slope of the plot. The analysis of the results from the Figure 6 shows that the R^2 value is close to one for the First-order kinetic model. Thus the treatment of MWFs by EC follows first order kinetics.

CONCLUSION

The results show that maximum COD and color removal of 85% and 93 % were achieved at a current density of 0.8 (A/dm²) and electrolysis time of 210 min using mild steel as the anode and stainless steel as the cathode. The iron hydroxide generated in the cell removes the COD present in the electroplating effluent and reduces the COD concentration to 490 mg/L. the pH of the working solution was found to increase with increase in time and reaches a maximum of 6.8 at equilibrium condition. The kinetic study shows that the treatment of MWFs by EC follows First-order kinetics.

REFERENCES

- [1] M.Ugurlu, M.H.Karaođlu, I.Kula; Polish J.of Environ.Stud., **15**, 647-654 (2006).
- [2] E.Csefalvay, V.Pauer, P.Mizsey; Desalination, **240**, 132-142 (2009).
- [3] A.M.F.M.Guedes, L.M.P.Madeira, R.A.R. Boaventura, C.A.V.Costa; Water Research, **37**, 3061-3069 (2003).
- [4] A.Muszyn'ski, M.Za'seska-Radziwi'ska, M.Lebkowska, D.Nowak; Arch.Enviro.n Contam. Toxicol., **52**, 483-488 (2007).
- [5] M.Visa, R.A.Carcel, L.Andronic, A.Duta; Catalysis Today, **144**, 137-142 (2009).
- [6] C.P.Nanseu-Njiki, S.R.Tchamango, P.C.Ngom, A.Darchen, E.Ngameni; J.Hazard.Mater., **168**, 1430-1436 (2009).
- [7] N.Meunier, P.Drogui, G.Mercier, J.Franc, O.Blais;

- Sep.Purify.Technol., **67**, 110-116 (2009).
- [8] H.R.Mortaheb, H.Kosuge, B.Mokhtarani, M.H.Amini, H.R.Banihashemi; J.Hazard.Mater., **B165**, 630-636 (2009).
- [9] D.Reddithota, A.Yerramilli, R.J.Krupadam; Indian J.Chem.Technol., **14**, 240-245 (2007).
- [10] J.Yi-zhong, Z.Yue-feng, L.Wei; J.Zhejiang University Sci., **3**, 401-404 (2002).
- [11] A.Dimoglo, H.Y.Akbulut, F.Cihan, M.Karpuzcu; Clean Techn.Environ.Policy, **6**, 288-295 (2004).
- [12] A.A.Bukhari; Bioresouce Technol., **99**, 914-921 (2008).
- [13] P.A.Soloman, C.Ahmed Basha, M.Velan, N.Balasubramanian; J.Chem.Technol.Biotechnol., **84**, 1303-1313 (2009).
- [14] N.Daneshvar, H.Ashassi, R.Rakhshaei; Iran.J. Chem & Chem.Eng., **21**, 13-20 (2002).
- [15] P.A.Soloman, C.Ahamed Basha, M.Velan, N.Balasubramanian, P.Marimuthu; Sep.Purif. Technol., **69**, 109-117 (2009).
- [16] K.Juttner, U.Galla, H.Schmieder; Electrochimica. Acta., **45**, 2575-2594 (2000).
- [17] S.Yi, Y.Ma, X.Wang, Y.Jia, Desalination, **239**, 247-256 (2009).
- [18] S.Vasudevan, J.Jayaraj, J.Lakshmi, G.Sozhan; Korean J.Chem.Eng., **26(4)**, 1058-1064 (2009).
- [19] M.F.Ni'am, F.Othman, J.Sohaili, Z.Fauzia; Water Sci.Technol., **56**, 47-53 (2007).
- [20] M.Yousuf, A.Mollah, Robert Schennach, Jose R.Parga, David L.Cocke; J.Hazard.Mater., **B84**, 29-41 (2001).
- [21] V.P.Malkin; Chemical and Petroleum Engineering, **39**, 1-2 (2003).
- [22] M.M.Emamjomeh, M.Sivakumar; J.Environ.Manage, **90**, 1663-1679 (2009).
- [23] M.Kumar, F.I.A.Ponselvan, J.RamMalviya, V.C.Srivastava, I.D.Mall; J.Hazard.Mater., **B165**, 345-352 (2009).
- [24] P.K.Holt, G.W.Barton, C.A.Mitchell; Chemosphere, **59**, 355-367 (2005).
- [25] I.Kabdaply, T.Arslan, T.Olmez-Hancý, I.Arslan-Alaton, O.Tunay; J.Hazard.Mater., **165**, 838-845 (2009).
- [26] L.S.Clesceri, A.E.Greenberg, A.D.Eaton; Standard Methods for the Examination of Water and Wastewater, 20th Edition, American Water Works Association, Washington DC, (1998).
- [27] G.Chen; Sep.Purify.Technol., **38**, 11-41 (2004).
- [28] E.Bazrafshan, A.H.Mahvi, S.Nasseri, A.R.Mesdaghinia, F.Vaezi, Sh.Nazmara; Iran.J.Environ. Health.Sci.Eng., **3**, 261-266 (2006).