Treatment of synthetic and battery industry wastewater by electrocoagulation

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ABSTRACT

The applicability of electrocoagulation process for the treatment of battery industry wastewater and synthetic wastewater containing copper, lead, nickel and zinc was investigated in this work. The electrocoagulation experiments were carried out in an electrochemical reactor using a bipolar aluminum electrodes arranged in parallel. Experiments were carried out at voltage of 9, 12 and 15 volts, pH of 3, 7 and 10, initial ion concentration of 50, 150, 250 mg/l and contact time of 5, 10, 20, 30, 40 and 60 minutes. Effects of operating parameters such as contact time, pH, voltage, initial metal concentration were studied. For the single treatment of the synthetic wastewater, the optimum pH was 3 for copper, 10 for zinc and 7 for lead and nickel. The efficiency of removal increased with the increase in voltage, time and initial metal ion concentration. The process was successfully applied in the treatment of an industrial effluent from a local battery producing company where the concentrations of copper, lead, zinc and nickel were reduced below the permissible limits at 60 minutes. The result of this study shows that electrocoagulation process is a reliable and efficient method of removing heavy metals from industrial wastewater.

Keywords: Electrocoagulation, copper, zinc, lead, nickel, wastewater

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INTRODUCTON

Water pollution by heavy metal ions has become one of the world wide environmental problems due to population explosion, urbanization and industrialization. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [1]. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms causing health problems in animals, plants, and human beings [2].

Effluents generated from these waste generating industries contain metal ions whose concentrations are higher than the permissible limits and are regarded as toxic or carcinogenic. As a result of their high toxicity, industrial wastewater containing these heavy metals must be treated before being discharged in the environment. Examples of toxic heavy metals are zinc, copper, nickel, mercury, cadmium, lead, chromium, etc. Wastewater containing heavy metal ions are generated in several industries such as metallurgical, electroplating, photo development processes, paint, battery technologies, mining operations, fertilizer, tanneries, paper, pesticides, pharmaceuticals etc.

Zinc is a trace element essential for human health. It is important for the physiological functions of living tissue and regulates many biological processes. However, too much zinc can cause eminent health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia [3]. Copper as an element does essential work in animal

metabolism but the excessive ingestion brings out serious toxicological concerns such as vomiting, cramps, convulsions, or even death. Lead is a pollutant that is present in drinking water and in air. Lead is known to cause mental retardations, reduces haemoglobin production necessary for oxygen transport and it interferes with normal cellular metabolism [4]. Lead has damaging effects on body nervous system. Nickel, exceeding its critical level might bring about serious lung and kidney problems. And it is known that nickel is human carcinogen [5]. Heavy metals are the more environmental priority pollutant and should be removed from the wastewater to protect the people and environment. Consequently, many techniques have been used in the removal of heavy metal from aqueous solutions containing them. The current techniques for the removal of heavy metal ions from wastewater are broadly non electrochemical and electrochemical methods. The non electrochemical methods are adsorption, chemical precipitation, ion exchange, membrane, membrane filtration (ultrafiltration, nanofiltration and reverse osmosis), flotation, coagulation and flocculation. The electrochemical treatment methods are electrocoagulation, electrodialysis, electrowinning, electrodeposition, electroflotation and electrodeionization. Although all the heavy metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations. The drawbacks other techniques have necessitated the search for a low cost effective method, a close recycle system or so-called effluent free technology such as electrocoagulation [6].

Electrocoagulation (EC) is an alternative technology for wastewater treatment and recovery of valuable chemicals from wastewater [7, 8]. Electrocoagulation uses no chemicals as coagulating agents. These are generated during the electrolysis process by electro-dissolution of a sacrificial anode made up of aluminium or iron [6]. The main advantages of electrocoagulation over other conventional techniques are "in situ" delivery of reactive agents and compactness (Phalakornkule, 2010). Electrocoagulation process is attractive because of its simplicity of operation, control and effective removal efficiency. Electrocoagulation technology has successfully being used in the treatment of heavy metal containing solution. It has been successfully used for the treatment and remediation of textile waste water [9, 10], suspended solids [11], heavy metals [12, 13], leachate [14, 15], Electroplating wastewater [16], Olive oil wastewater [17], Biodiesel wastewater [18] etc. This paper reports the efficiency of electrocoagulation in removing metallic ions from aqueous solutions and battery industry wastewater.

MATERIALS AND METHODS

Preparation of synthetic solution
Analytical grade reagents were used in preparing stock solutions from which the various working solutions were obtained by diluting to the required concentration. The stock solution of the different metallic salts were prepared by dissolving 1.485, 4.56, 4.397 and 3.250g of $PbSO_4$, $CuSO_4$, $ZnSO_4.7H_2O$ and $Ni(NH_4)_2SO_4$ respectively in $1000cm^3$ of distilled water.

Experimental setup
The electrocoagulation reactor was fabricated using a 400ml cylindrical glass beaker. Aluminum rods with diameter of 0.8cm, length of 12.2cm and electrode distance of 1.5cm were used as electrodes for the experiments. EC reactor with monopolar electrodes connected in parallel and a regulated direct current supply (0-15V, 1.5Amp) shown in Figure 1 was used for the electrocoagulation process. The sacrificial electrodes were placed between the two parallel electrodes without any electrical connection. This cell arrangement provides a simple set up which facilitates an easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive rods will be transformed to charged sides which have opposite charges compared to the parallel side beside it.

Experimental procedure
The experiment was carried out at room temperature in a 400ml beaker in which the synthetic solution samples were filled up to 200ml and slowly stirred with a magnetic bar stirrer at 150 rpm. The working solutions were prepared from the stock solutions with their pH adjusted by either adding dilute HCl or NaOH. The electrodes were cleaned with sand paper to remove the passivation layer and rinsed with deionized water and also dipped into 1M of HCl for 1minute to energize them. The electrodes were weighed before and after each run. 0.5g of KCl was added to every treated solution to prevent passivation on the aluminium electrode surface and decrease the ohmic drop, thus increasing the conductivity of the water been treated. The polarity of the cell was reversed every 30minutes to reduce the formation of the passivation layers on the electrodes. Direct current (DC) power supply was used to pass 0.9, 1.2 and 1.5amp currents at 9, 12 and 15V respectively. After each experiment, the treated wastewater was filtered using Whatman No.1 filter paper. The residual heavy metals concentrations were determined using Atomic

Absorption Spectrophotometer (AAS). After each run, the electrodes were dipped in acetone for 5min to remove impurities.
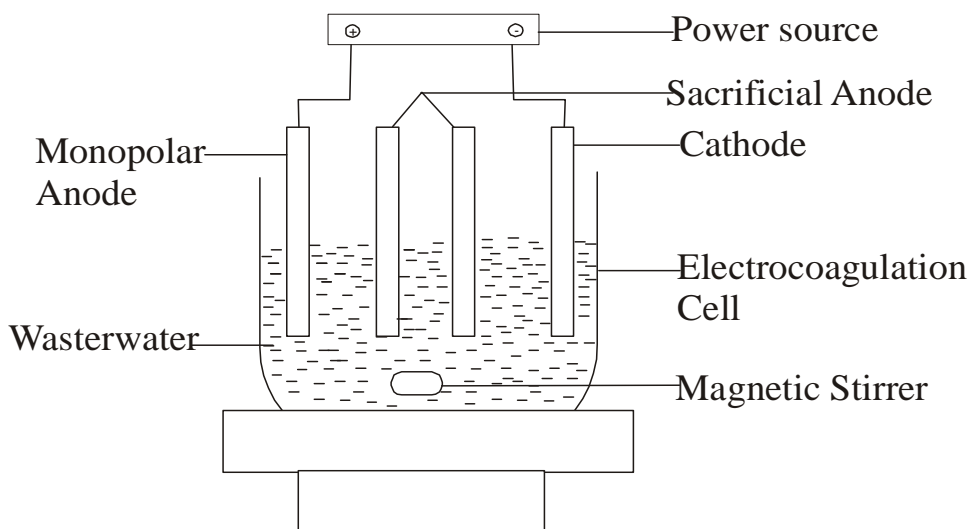

Figure 1: Electrocoagulation reactor

Effect of pH

EC process is highly dependent on the the pH of the solution [19, 20]. The pH of the the medium changed during the process. This change is dependent on the type of electrode material, initial pH and the alkalinity. pH measurements are important in showing the type of dominant reactions at the anode and cathode electrodes. This decrease was attributed to the formation of soluble Al^{3+} cations at strong acidic pH and to the formation of monomeric anions $Al(OH)^-_4$ at strong alkaline pH, therefore, the formation of these species are not constructive for water treatment process. The pH increases at low initial pH of less than 7 owing to the evolution of hydrogen and generation of OH^- ions at the cathodes. But at pH greater than 7, the final pH does not change significantly because the generated OH^- ions at the cathode are consumed by the generated Al^{3+} ions at the anode forming the needed $Al(OH)_3$ flocs.

In this work, experiments were conducted using solutions of Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} of 250mg/l each in the initial pH range of 3-10. From the figure 2, the removal efficiency of the metals at 20mins of electrolysis time, constant voltage of 15V was above 92%. For copper the highest removal efficiency of 99.67% was recorded at pH 3. Subsequently the efficiency deceased as pH increased. For lead and nickel, the removal efficiency increased as pH increased from 3 to 7 and finally it slightly decreased at pH of 7. The highest removal efficiency was recorded at pH 7. Other researchers recorded decrease in removal efficiency at strong acidic and a slight increase in weak alkaline solution [6, 16]. It was ascribed to an amphoteric behavior of $Al(OH)_3$ which leads to soluble Al^{3+} cations (at acid pH) and to monomeric anions $Al(OH)_4^-$ (at alkaline pH). The removal efficiency of zinc increased as pH increased from 3 to10. The highest removal efficiency of 98.55% was obtained at pH of 10.

Effect of Voltage

The voltage is the product of the current delivered to the electrode and its resistance to flow. It determines the coagulant dosage rate, the bubble production rate and size and floc growth resulting in a faster removal rate [21]. In order to evaluate the effect of voltage on the efficiency of removal of the heavy metals from the waste water, a number of experiments were carried out at different voltage of 9, 12 and 15V at constant initial concentration of 250mg/l for 20 mins, and pH of 7 for lead and nickel, pH of 3 for copper and pH of 10 for zinc. From figure 3, it can be seen that the removal rates of the heavy metals increased with increasing voltage. As the voltage increased the efficiency removal also increased for all the metals, as shown in fig.3. The removal efficiency of 99.67, 98.66, 98.26 and 98.55% was recorded for copper, lead, nickel and zinc respectively at 15volts.This also is due to the oxidation and reduction reactions which take place in the reactor. This is attributed to the fact that at high voltage, the extent of anodic dissolution increased and the amount of hydro-cationic complexes resulted in increase of the removal efficiency [6].
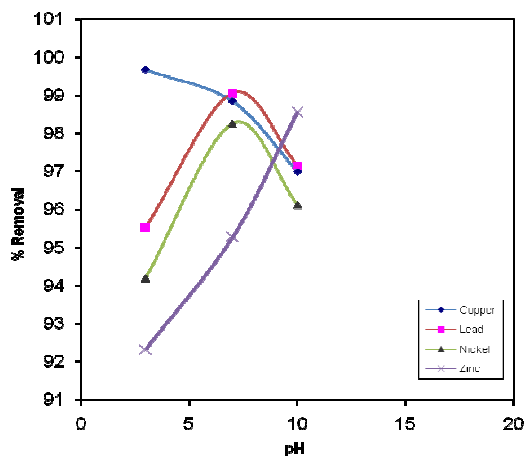
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Fig. 2 : Effect of pH on heavy metal removal
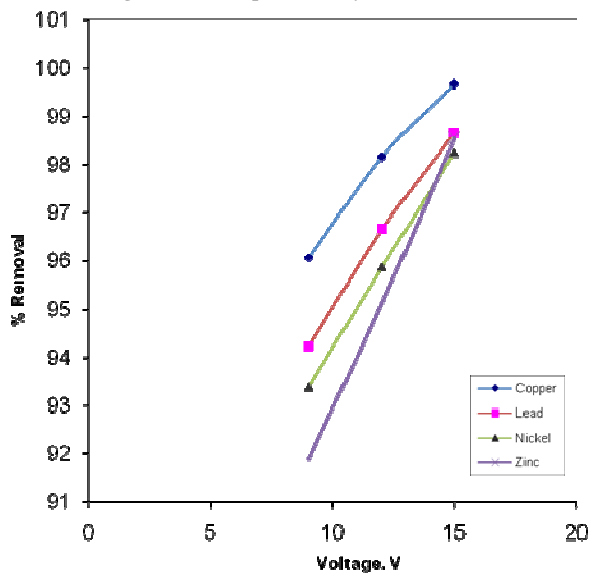

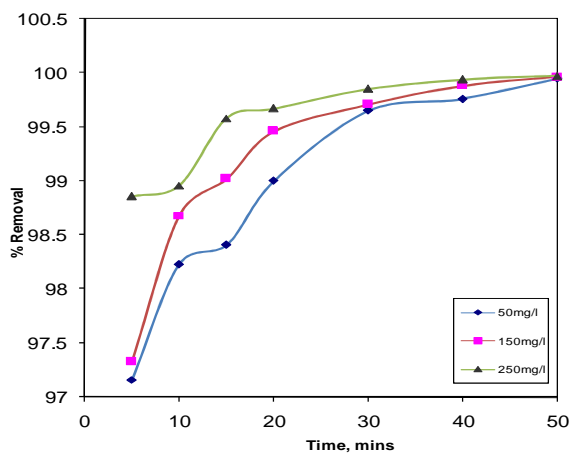**Fig. 3: Effect of voltage on heavy metal removal**

Fig. 4: Effect of time on the removal of copper

Effect of initial metal ion concentration and time

To examine the effect of initial metal ion concentration on the removal rate at varying time, several experiments with different initial concentration of 50, 150 and 250mg/l of zinc, lead, copper and nickel at a constant voltage of 15V and different times of electrolysis was carried out. Figures 4 to 7 show the change in the removal rate of heavy metals with varying initial concentration. They all showed the same trend. The removal efficiency increased with increase in contact time. At 250mg/l, which is the highest initial metal ion concentration, the metal ion concentration reduces significantly in relatively less than lower concentration, as was observed during the experiment. But lower initial metal ion concentration requires longer time for an effective removal. The electrocoagulation process is more effective at the beginning than at the end when the concentration is low.
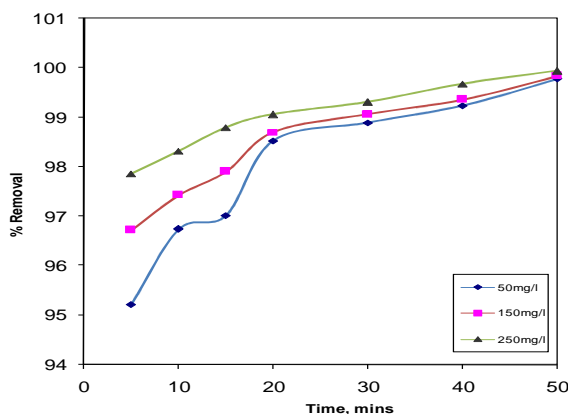
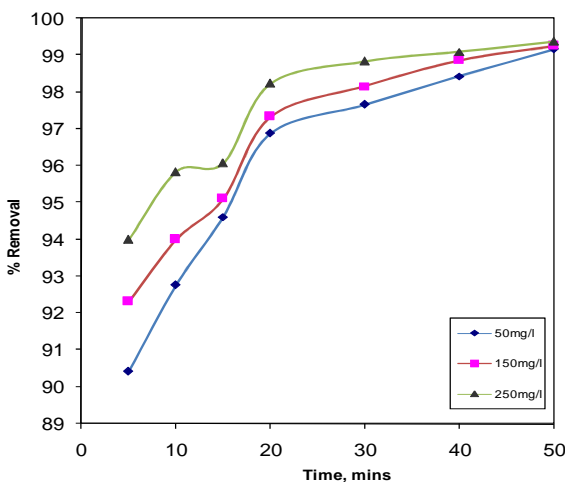**Fig. 5: Effect of time on the removal of lead**

Fig. 6: Effect of time on the removal of nickel

Competitive removal of heavy metals
The competitive removal of the heavy metals was carried out using 50mg/l of the aqueous solution containing copper, lead, zinc and nickel at pH of 7, voltage of 15V for 60min. It can be seen from figure 8 that removal efficiency of 99.45, 98.87, 97.66 and 95.87% was obtained for copper, lead, zinc and nickel respectively. The best performance was obtained with copper. After 5min of electrocoagulation process, 98.24% of copper was removed.
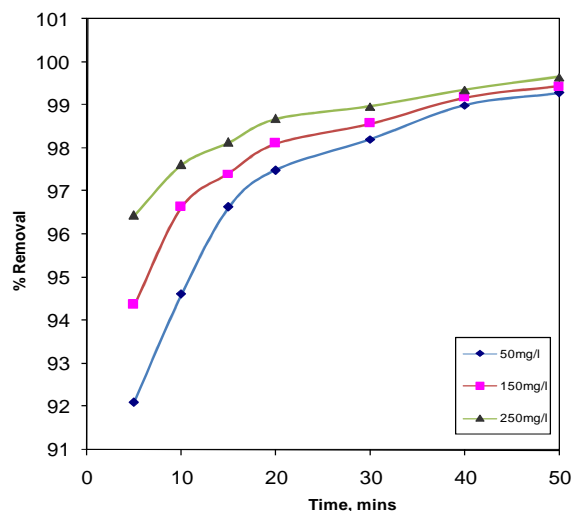
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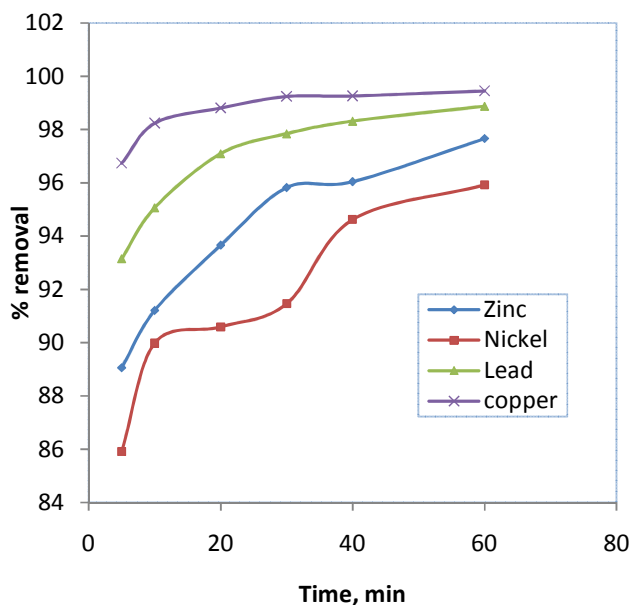**Fig. 7: Effect of time on the removal of zinc**

Fig. 8: Competitive removal of heavy metals

Treatment of battery industry wastewater

The applicability of the electrocoagulation process for actual wastewater was validated by treating an industrial effluent sample collected from a local battery producing company. The main characteristics of the effluent sample before and after the treatment are presented in Table 1. The relatively high COD content of the wastewater is indicative of the presence of organic compounds in the effluent. At a constant voltage of 15V and an electrolysis time of 60minutes, the concentration of all the heavy metals (Pb, Cu, Ni and Zn) was reduced below the permissible limits as can be seen from the figure 9. Compared to the removal efficiency from the synthetic solutions, the removal rates of the studied metals from battery wastewater was slower. This can be attributed to the presence of the organic compounds which also compete for adsorption on the $Al(OH)_3$ flocs resulting in a substantial reduction of the metals ions removal. The initial COD of 508mg/l decreased to 105mg/l, below the permissible limit after 60minutes, resulting in a removal efficiency of about 79.3%.

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During the electrocoagulation treatment of the wastewater, pH was found to increase at first few minutes of the operation and changed only slightly afterwards up to 60minutes of operation. The pH increase at the beginning could be attributed to the generation of OH^- ions dissociated from water at the cathode. The relative stability of pH afterwards could be probably due to the formation of the insoluble $Al(OH)_3$ flocs and the rest metal hydroxides
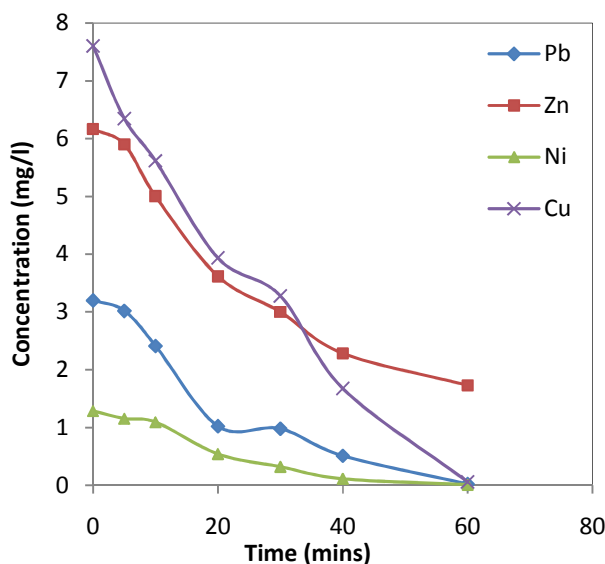

Fig. 9: Concentration variation with time during the removal of heavy metals from battery waste water.

Table 1: Characteristics of the battery wastewater before and after the electrocoagulation treatment

PARAMETER	BEFORE TREATMENT	AFTER TREATMENT
pH	4.2	7.5
Conductivity(μs/cm)	$1350x10^2$	352
COD(mg/l)	508	105
Turbidity(NTU)	30	5
Pb(mg/l)	3.20	0.0231
Cu(mg/l)	7.6	0.0608
Ni(mg/l)	1.287	0.0113
Zn(mg/l)	6.1627	1.7301

CONCLUSION

The use of aluminium electrode in this electrocoagulation process is safe, effective and convenient for effective removal of heavy metals such as zinc, copper, lead and nickel from synthetic aqueous and battery wastewater. The removal efficiency was found to be dependent on initial pH of the the wastewater. Optimum pH of 3 for copper, 10 for zinc and 7 for lead and nickel of pH were obtained. Removal rate increased with increase in voltage and time. The final concentration of Zn, Ni, Cu and Pb fell below the permissible limits.

REFERENCES

[1] Volesky B, Holan ZR, *Biotechnology Progress*, **1995**, 11(3), 235-250.
[2] Ong S, Seng C, Lim P, *EJEAFche*, **2007,** 6 (2), 1764-1774.
[3] Oyaro N, Odendi J, Murago ENM, Gitonga E, *J. Food,Agric. Enviro.,* **2007,** 5 (3&4): 119-121.
[4] Qaiser S, Saleem AR, Ahmed MM, *Environ. Biotechnol.* **2007**, 10(3), 1-8.
[5] Borba CE, Guirardello R, Silva EA, Veit MT, Tavares CRG, *Biochem. Eng. J*, **2006,** 30(2), 184-191.
[6] Dermentzis K, Christoforidis A, Papadopoulou D, Davidis A, *Environmental Progress and Sustainable Energy*, **2010,** 30(1): 37-43.
[7] Phalakornkule C, *World Academy of Science, Engineering and Techn*, **2010,** 65, 278-285.

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[8] Zongo I, Merzouk B, Palm K, Wethe J, Maiga AH, Leclerc J, Lapicque F, *Adv. in Appl Sci. Res*, **2012,** 3(1), 572-582.

[9] Kobya M, Can OT, Bayramoglu M, *J. Hazard. Mater*, **2003,** B100, 163-178.

[10] Can OT, Kobya M, Demirbas E, Bayramoglu M, *Chemosphere*, **2006,** 62, 181-187.

[11] Bukhari AA, *Bioresour.Technol*, **2008,** 99(5), 914-921.

[12] Heidmann I, Calmano W, *J. of Harzard. Mater*, **2008,** 152, 934-941.

[13] Kumar CS, Khilar KC, Mahajan SP, *Chemosphere*, **2004,** 55, 1245-1252.

[14] Ilhan F, Kurt U, Apaydin O, Gonullu MT, *J. of Hardard. Mater*, **2007,** 154, 381-389.

[15] Deng Y, Englehardt JD, *Water Res*, **2006,** 40, 97-105.

[16] Adhoum N, Monser L, Bellakhal N, Belgaied J, *J. of Hazard Mater*, **2004,** B112 ; 207-213.

[17] Inan H, Dimoglo A, Simsek H, Karpuzcu M, *Water Res*, **2004,** 36, 23-31.

[18] Srirangsan A, Ongwandee M, Chavalparit O, *EnvironmentAsia*, **2009,** 2, 15-19.

[19] Chen Y and Kravet G, *Journal of the Air and Waste Management Association*, **2000,** 50, 536-541.

[20] Mollah MYA, Morkovsky P, Gomes JAG, Kesmez M, Parga J, Cocke DL, *J. Hazard. Mater.,* **2004, B**114, 199-210.

[21] Holt P, Barton GW, Wark M, Mitchell CA, *Colloids Surf. A: Physicochem. Eng. Aspects*, **2002,** 211: 233-248.