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Electrocoagulation (EC) for Reduction of Chemical Oxygen Demand (COD) of Surface Water

S. H. Rahman*, S. M. N. Islam, N. Kaiser and Md. M. Rahman

Department of Environmental Sciences, Jahangirnagar University, Dhaka 1342, Bangladesh

Abstract

Karnopara Canal water containing high COD values (1050 mg O_2/L) was treated by electrocoagulation (EC) method covering a wide range of operating conditions such as, water pH, internal electrode distances, final pH, supplying 30V electricity for constant time period (30 minutes) through same electrode material (Al electrode). The effects of different operating parameters on the efficiency of the process were examined. Targeting to reduce the COD value within the recommended limit (200 mg O_2/L), this research work was emphasized on EC treatment at the simplest and cheapest way. The batch experiment results showed that the high COD contained canal water can be effectively treated using electrocoagulation. The overall COD removal efficiencies have been obtained at 87.3%, under optimum operating conditions. Taking all the factors into account, it was found that polluted Karnopara canal water can be treated using EC consisting of Al electrodes without pre-adjustment of pH at laboratory. Therefore, EC technique to reduce high COD from canal surface water is found effective, cheaper and environmental friendly.

Key words : Dissolution, Textile effluents, Aluminum electrode, pH adjustment, Internal electrode distance

Introduction

A number of dyeing and textile industries have been established around Karnopara Canal (from 23°49'16'' N, 90°15'58"E to 23°49'31"N, 90°14'58"E) of Savar Upazilla under Dhaka district since 1984. Dyeing and textile industries use large quantities of water in their production process, and release highly polluted toxic effluents, originated from sizing, bleaching, mercerizing, fancy dyeing, screen printing, khaki dyeing, yarn dyeing and finishing stages of production (Rahman *et al.* 2008). Although these textile and dyeing industries must have ETP (Effluent Treatment Plant) and should discharge the effluents after treatment, but unfortunately most of the industries directly release the effluents into the water bodies. Hence the canal water becomes polluted. Usually polluted water contains suspended particles and shows high pH, BOD and COD. This polluted water has adverse effect on surrounding land, groundwater and aquatic ecosystems, as well as on the livelihood of the local community since people living on the bank of the canal use water for their household washing, bathing and other necessary works (Rahman *et al.* 2008).

Chemical Oxygen Demand (COD) is the indirect measure of the amount of oxygen used in the chemical oxidation by the organic and inorganic compounds present in water. Major compounds contribute to COD are biodegradable organic compounds, non-biodegradable compounds and inorganic oxidizable compounds (Moreno-Casillas *et al.* 2007). As COD determines the amount of organic pollutants found in surface water, it provides a useful measure of surface water quality (Wikipedia, 2010).

Electrocoagulation (EC) is a relatively simple and inexpensive electrochemical technique for the treatment of effluents (Mollah *et al.* 2004). EC has been used to treat various industrial effluents such as oil mill wastewater (Inan *et al.* 2004); textile industries (Can *et al.* 2003); landfill leachate (Tsai *et al.* 1997); restaurant wastewater (Chen *et al.* 2000); laundry wastewater (Ge *et al.* 2004) with some limitations of its own. Electrocoagulation mechanism for COD removal from synthetic water has been reported by Moreno-Casillas *et al.* (2007) where they mentioned the factors that affect COD removal. This paper aims to justify the utility of EC technique using Al electrode to reduce COD from wastewater samples of Karnopara Canal under various operating conditions. In addition, the mechanism of electrocoagulation and the effect of individual parameters on the removal efficiency of electrocoagulation have also been examined.

*Corresponding author. E-mail: hafizsr@yahoo.com

Mechanism of Electrocoagulation (EC)

During EC process, anode produces coagulating agent to dose the wastewater while gases are generated at cathode end. General EC process involves three successive steps (Chen, 2004):

i.   Formation of coagulants by electrolytic oxidation of anode

ii. Destabilization of the contaminants, particulate suspension and breaking of emulsions and

iii. Aggregation of the destabilized phases to form flocs.

In this study, aluminum has been used as anode and cathode. Following Chen (2000), the electrode reaction can be written as:

Anode: $Al(s) \rightarrow Al_3 (aq) + 3e^-$ (1)

Cathode: $3H_2O(l) + 3e^- \rightarrow 3/2 \ H_2(g) + 3OH^-(aq)$ (2)
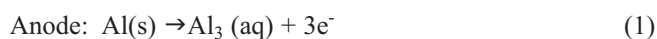
Al^{3+} and OH^- ions generated during the electrochemical reactions react to form various monomeric and polymeric species and transform into $Al(OH)_3$ according to the following reaction:
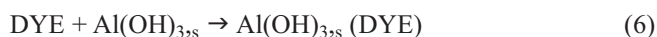
$Al^{3+} (aq) + 3H_2O (l) \rightarrow Al(OH)_3(s) + 3H^+(aq)$ (3)

These $Al(OH)_3$ flocs capture the dye molecules present in the solution by the following reaction mechanism:

Precipitation:

$DYE + Al_m \rightarrow [DYE \ Al_m]_s$ (4)

$DYE + Al_p \rightarrow [DYE \ Al_p]_s$ (5)

Adsorption:

$DYE + Al(OH)_{3,s} \rightarrow Al(OH)_{3,s} (DYE)$ (6)

$[DYE \ Al_p]_s + Al(OH)_{3,s} \rightarrow [Al(OH)_3 DYE \ Al_p]_s$ (7)

Sample was placed between parallel aluminum plates connected to a DC power supply. Aluminum dissolved from the anode and hydrogen gas generated at the cathode. The mixing between water and dissolved aluminum occurring between the electrodes results in coagulation and flocculation. Hydrogen gas formation results in pH increase and flotation of the sludge formed.

Fig. 1: View of Karnopara Canal, Savar, Dhaka.

Materials and Methods

Sampling

Karnopara Canal water was collected in 2L pre-washed plastic container during daytime. The canal water was black in color with noxious odor (Fig. 1). After collection, sample was immediately transferred to the laboratory and stored at 4°C until further analyses.

Experimental

Treatment was carried out in a two-electrode static electrocoagulation reactor of 250 mL capacity (Fig. 2) containing aluminum as electrodes (5cm×3cm×0.1cm). Prior to the experiment, the electrodes were properly scrubbed and rinsed with dilute acid to remove surface grease/other impurities on the metal surface. Samples were subjected to electrocoagulation in an EC apparatus containing the electrode assembly, DC power supply unit, a voltage stabilizer and an ammeter under potentiostatic conditions covering wide range of operating conditions. Here 140 mL filtered canal water was treated through EC under various pH (1, 3, 5, 7, 8) maintaining the distance between the electrodes at 2.5 cm and 4 cm. 30 V with 4.0 A current was applied for 30 minutes. The pH of the samples was adjusted at these ranges using concentrated HCl or NaOH as required. The electrodes were weighed before and after each experiment to estimate the electrode consumption. COD determinations were made using standard closed reflux titrimatric procedure (HACH, Water Analysis Handbook, Method 8231). The pH of the sample solutions was recorded before and after EC treatment.
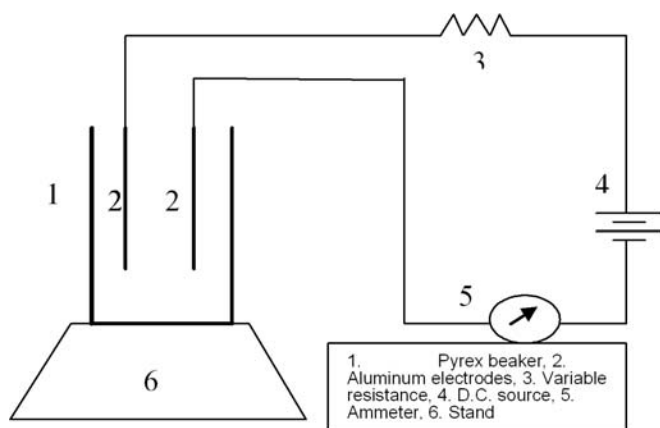
Fig. 2: Schematic diagram of the electrochemical cell.

Results and Discussion

Removal of COD

COD removal at two separate electrode distances under different pH conditions are given in Table I where COD value of inland surface water quality from industrial effluent (DoE, 2003) was taken as reference. In most of the operating conditions, COD attained within acceptable limit for Bangladesh. But, for achieving maximum efficiency different operational conditions were applied.

Aluminum dosing

In EC, the electrodes of electrochemical cell were connected to an electrical power source. Faraday's law can be used to describe the relationship between current density and the amount of aluminum involved in the reaction (g Al cm^{-2}).

$w = itM / ZF$…………………(8)

where,

w = amount of aluminum dissolving (g Al cm^{-2})

i = current density (A cm^{-2})

t = time (s)

M = molecular weight of Al (M= 27)

Z = number of electrons involved in the oxidation/reduction reaction (Z=3)

F = Faraday's constant, 96,500 (C/mol)

The theoretical amount of Al dissolved was calculated using Equation 8, where, i and t values were same in all experiments and they were 4 A cm^{-2} and 30 minutes respectively. Then the ratio of calculated theoretical value of Al dissolved to the measured dissolved Al (Table I) were compared at various pH for 2.5 cm and 4 cm internal electrode distance (Fig. 3). Dissolution value calculated theoretically as 0.6715 g Al cm^{-2}. In both cases, the aluminum dissolution increased at slightly basic pH (pH-8) and also at strong acidic pH (pH 1 to 3) (Table I). Interesting matter is that the pH at which

Table I: COD removal at various operating conditions

Sample water COD (mg O_2/L)	Electrode distance (cm)	Sample water pH	Adjusted initial pH	Final pH after treatment	Al dissolution in the reactor (g)	COD (mg O_2/L) treatment	Standard COD for Inland surface water (mg O_2/L) (DoE, 2003)
1050	2.5	8.0	1.0	5.0	0.11	133.34	200
			3.0	8.0	0.06	166.67	
			5.0	8.0	0.04	233.34	
			7.0	9.0	0.04	233.34	
			8.0	9.0	0.20	166.67	
1050	4.0	8.0	1.0	3.0	0.11	166.67	200
			3.0	9.0	0.06	133.34	
			5.0	8.0	0.05	100.00	
			7.0	9.0	0.05	033.34	
			8.0	9.0	0.20	166.67	

maximum dissolution obtained was the collected sample water pH. One of the major aims of the research work was to identify the easiest operating condition at which COD of the polluted water attain national standard level. This issue is discussed in the subsequent section. From Figure 3, it was also found that dissolution rate was limited at pH ranges from 4 to 7.
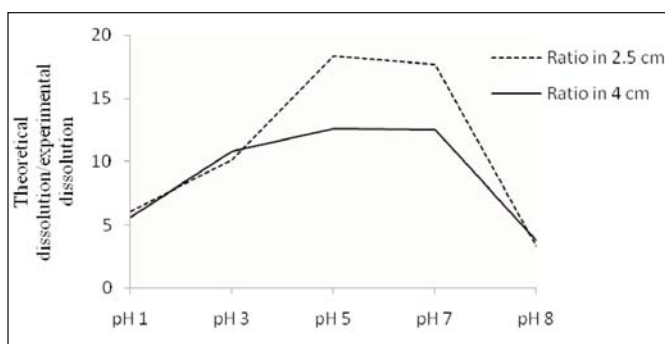

Fig. 3: Comparison of theoretical dissolution/calculated dissolution with different pH value for two separate internal electrode distances

Effect of various operational conditions on COD removal

Effect of initial pH

The importance of pH in coagulation is well known. In order to evaluate the effect of pH on COD removal, a series of experiments were performed by adjusting the raw water pH. The pH of the collected sample water was around 8 and during treatment various pH were attained which was called as initial pH. When initial pH of sample water was slightly basic (pH=8), Al dissolution was high for both 2.5 cm and 4.0 cm internal electrode distances (Fig. 4). This slightly basic pH is considered as the optimum for $Al(OH)_{3(s)}$ formation with Al electrode. In this pH, high COD creating pollutant adsorbed on $Al(OH)_{3(s)}$ according to equations 6 and 7 and causing more than 80% removal of COD for both internal electrode distance. Except initial pH of 5 and 7 for 2.5 cm internal electrode distance, in remaining all cases (Table I) COD was attained at the acceptable limit after treatment through electrocoagulation process.

As it was intended to obtain COD within standard (200 mg O_2/L) set by the Department of Environment (DoE) of Bangladesh, EC treated water was found to have COD below 200 mg O_2/L irrespective of electrode distances. At low pH (Fig. 4 and Table I), COD was also found within the standard

limit. Some researchers (Pichard *et al.* 2000 and Canizares *et al*. 2005) reported that Al electrodes show higher COD removal efficiencies at lower pH values for three possible reasons: First, aluminum has only one oxidation state, so when an organic compound reacts with aluminum to form an insoluble compound it will react almost completely. Second the solubility of aluminum hydroxide $Al(OH)_3$ is minimum at a lower pH close to 4, and last when using aluminum electrode there is oxygen evolution at the cathode which may help with the oxygen demand. Since collected sample water was slightly basic and extra acid required for lowering pH, it was realized that unadjusted pH condition (pH 8) would be the most suitable condition for EC treatment.
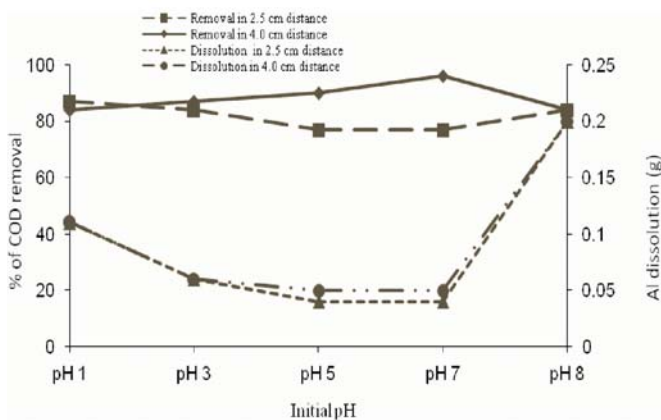

Fig. 4: Effect of initial pH value and internal electrode distance on Al dissolution and percentage of COD removal

Effect of final pH

During treatment using EC under various pre-adjusted pH conditions, final pH was also measured. During experiments, significant increment of pH were observed and these results are presented in Figures 5 and 6 for both 2.5 cm and 4.0 cm internal electrode distances respectively including the relationships between increment of pH and amount of Al dissolution as well as percentage of COD removal. Increment of pH was defined as final pH. When internal electrode distance was 2.5 cm, final pH were 5, 8, 8, 9 and 9 (Fig. 5) where initial pH were 1, 3, 5, 7 and 8 respectively. On the other hand, when internal electrode distance was 4.0 cm, final pH were 3, 9, 8, 9 and 9 (Fig. 6) where initial pH were 1, 3, 5, 7 and 8 respectively. During the EC process, hydrogen gas is generated at the cathode and might increase pH of the medium. Vik *et al.* (1984) also reported the increment of pH for elec-

trocoagulation of potable water. In all cases, except initial pH of 1 for both 2.5 and 4.0 cm internal electrode distances where final pH reached at 5 (Fig. 5 and Table I) and 3 (Fig. 6 and Table I) respectively, slightly basic pH was found which is less harmful for aquatic environment. Some researchers (Moreno-Casillas *et al.* 2007 and Vik *et al.* 1984) also studied COD removal efficiency through EC and found it depend was on the final pH. Considering final pH and COD criterion, collected sample water may be treated using EC without adjustment of pH.
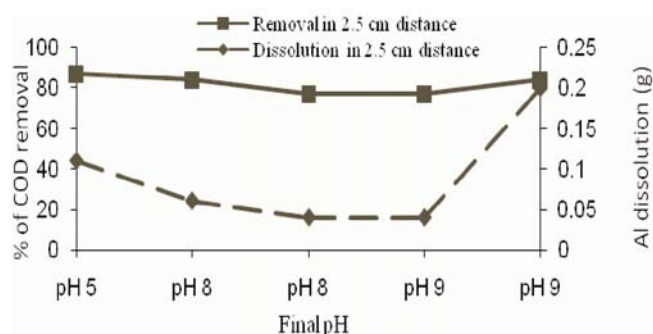

Fig. 5: **Effect of final pH value on Al dissolution and percentage of COD removal for 2.5 cm internal electrode distance**
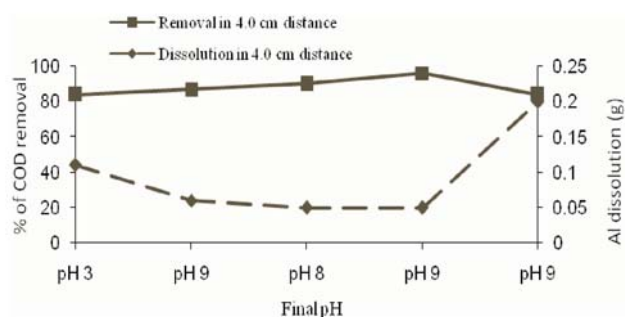

Fig. 6: Effect of final pH value on Al dissolution and percentage of COD removal for 4.0 cm internal electrode distance

Conclusion

Experiments were carried out to treat high COD contained surface water using EC. The influence of initial pH, final pH, internal electrode distance and aluminum dissolutions on coagulation efficiency for COD removal have been critically examined. Reduction of COD was significantly influenced by these parameters were observed from this study.

But considering recommended value of COD for surface water in Bangladesh, following conclusions were drawn:

* Without pre-adjustment of pH of sample water, EC process attained COD at the recommended value (200 mg O_2/L);

* Though distance between electrodes is an important factor for EC treatment, here 2.5 or 4.0 cm internal electrode distances were found effective in treating polluted surface water with regard to both COD and pH;

* In addition, no chemical is required for obtaining optimum operating condition;

* The results presented in this article prompt us to believe that EC technique is effective, cheaper and environmentally friendly.

Acknowledgement

References

Can O. T. Bayramoglu M. and Kobya M. (2003). Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes. *Ind. Eng. Chem. Res.* **42**: 3391-3396.

Canizares P. Carmona M. Martinez F. and Rodrigo M. A. (2005). Electrodissolution of Al electrodes in electrocoagulation process. *Ind. Eng. Chem. Res.* **44**: 4178-4185.

Chen G. (2004). Electrochemical technologies in wastewater treatment. *Sep. Purifi. Technol.* **38**: 11-41.

Chen X. Chen G. and Yue P. L. (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep. Purif. Technol.* **19**: 65-76.

Chithra K. Thilakavathi R. Murungan A. A. Marimuthu C. and Balasubramanian N. (2008). Treatment of Textile Effluents Using Sacrificial Electrode. *Modern Applied Science* **2**(4): 38-43.

Department of Environment (DoE), (2003). A Compilation of Environmental Laws, Department of Environment and Bangladesh Environmental Management Project. Schedule 10, P 213.

Ge J., Qu J. Lei P. and Liu H. (2004). New bipolar electro coagulation- electro flotation process for the treatment of laundry wastewater. *Sep. Purif. Technol.* **36**: 33-39.

Chen G. (2004). Electrocoagulation technologies in wastewater treatment. *Sep. Purift. Technol,* **38**: 11-41.

Inan H., Dimoglo A., Simsek H. and Karpuzcu M. (2004). Olive oil mill wastewater treatment by means of electro-coagulation. *Separat. Purif. Technol.* **36**: 23-31.

Khan M. Knapp J. Clemett A. and Chadwick M. (2006). Managing Pollution from Small Industries in Bangladesh, Technical report, Research for Development, Department for International Development (DFID).

Khan M. S., Ahmed S., Evans A. E. V. and Chadwick M. (2009). Methodology for Performance Analysis of Textile Effluent Treatment Plants in Bangladesh. *Chemical Engineering Research Bulletin.* **13**: 61-66.

Mollah M. Y. A., Morkovsky P., Gomes J. A. G., Kesmez M., Parga J. and Cocke D. L. (2004) | Fundamentals, present and future perspectives of electrocoagulation. *J. Hazard. Mater.* **114**(1-3): 199-210.

Moreno-Casillas H. A., Cocke D. L., Gomes J. A. G., Morkovsky P., Parga J. R. and Peterson E. (2007). Electrocoagulation mechanism for COD removal. *Sep. Purif. Technol.* **56**: 204-211.

Pichard T., Cathlifaud G., Mazet M. and Vandesteendam C. (2000). Cathodic dissolution in the electrocoagulation process using Al electrodes. *J. Environ. Monit.* **2**: 77-80.

Rahman S. H., Neelormi S. and Tareq S. M. (2008). Environmental Impact Assessments of Textile and Dyeing Industries on Ecosystem of Karnopara Canal at Savar, Bangladesh. *Jahangirnagar Uni. y J. Sci.* **31**(1): 19-32.

Tsai C. T., Lin S. T., Shue Y. C. and Su P. L. (1997). Electrolysis of soluble organic matter in leachate from landfills. *Water Res.* **31**: 3073-3081.

Vik E. A., Carlson D. A., Eikum A. S. and Gjessing E. T. (1984). Electrocoagulation of potable water. *Water Research,* **11**: 1355-1600.

Wikipedia (2010) http://en.wikipedia.org/wiki/ Chemical_ oxygen_ demand