Electrochemical degradation of a real silk textile wastewater using iron electrodes

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Abstract: *The electrochemical degradation of a raw real silk textile wastewater was carried out using iron electrodes in bipolar arrangement to remove chemical oxygen demand (COD), color and to reclaim clean water. Batch studies with four plate iron electrodes were identified as an optimal operating condition. 70-88% COD removal efficiency was achieved from its initial value of 1270 mg/L. The presence of chloride increased COD degradation. Iron electrode showed good settling and filterability. Water quality improved considerably after electrochemical coagulation (ECC) treatment achieving reduction in other water quality parameters viz., hardness, alkalinity, TS and chlorides.*
Keywords: *Chemical oxygen demand (COD); electrochemical coagulation; electrocoagulation; electrolysis time; silk textile wastewater*

I. Introduction

Textile industries consume huge quantities of water and consequently produce highly contaminated wastewater. Wastewater from textile industry consists of high organic and inorganic loads, unreacted dyestuff, pH and temperature variations (Vlyssides et al. 1999). Synthetic compounds, especially dyes are mainly responsible for the recalcitrance of textile effluents. Discharging untreated wastewater containing synthetic dyes to the fragile environment leads to serious complications like interference with the penetration of sun light and also causes carcinogenic effect in human beings (Lima et al. 2007). Changes of the dyestuff employed in the process cause considerable variation in the wastewater characteristics showing intense color, high chemical oxygen demand (COD), dissolved solids and highly fluctuating pH (Cerqueira et al. 2009). Natural degradation of synthetic dyes in the aquatic environment is a slow process and because of its persistence, it is necessary to eliminate synthetic dyes from wastewater before disposing it in water bodies or streams. At present, there is no single technology universally applicable for the treatment of textile wastewater (Mondal, 2008). Hence, the proper treatment of such wastewaters might be an economical and technical challenge.

The conventional treatment methods are ineffective for clean water reclamation displaying high hydraulic retention times (HRT). Electrochemical treatment is known for its smaller and environmental foot prints. Electrochemical coagulation (ECC) is considered to be efficient and simple method for the treatment of many types of wastewater such as pulp and paper mill wastewater (Mahesh et al. 2006a), restaurant wastewater (Chen et al. 2000), poultry slaughter house wastewater (Kobya et al. 2006a). EC removes many pollutants and contaminants from wastewater that chemical coagulation cannot remove (Khandegar et al. 2013) and plays an important role in superior oxidation (Aquino et al. 2014). High oxidation power and removal rates consequently lead to improvement of the current efficiency (Zhao et al. 2010). Electrocoagulation is considered to be capable of having high removal efficiencies of color, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and suspended solids. EC helps in achieving a more efficient treatment process quicker than traditional coagulation and inexpensive than other methods of treatment such as ultraviolet (UV) and ozone (Elnenay et al. 2017).

In ECC, low solubility of the neutral metal hydroxides, mainly at pH values 6.0-7.0, promotes the generation of sweep flocs inside the treated waste and the removal of the pollutants by their enmeshment into these flocs (Gregor et al. 1997; Duan and Gregory, 2003). The charge of the metal hydroxide species promotes

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the neutralization of the charged pollutant particles, minimizing the electrical repulsion between them, and favoring their later flocculation (Chen et al. 2002; Sour et al. 1996). Through in situ generation of coagulants, electrocoagulation processes do not require any addition of chemicals. Other advantages of electrocoagulation include the promotion in the flocculation process caused by the electric field generated in the electrochemical cell (Rajeshwar and Iba´nˇez, 1997; Yousuf et al. 2001), the promotion in the separation process caused by the improvements in the flotation of the flocs with the hydrogen bubbles generated on the cathode, and the easy automation of the process, as the dosing of coagulant reagents depends directly on the cell potential (or current density) employed.

This work was carried out to treat raw wastewater by electrochemical coagulation in batch mode. The effect of electrolysis time (ET), initial temperature and pH of the bulk solution were investigated.

II. Materials And Methods

All the chemicals and reagents used for analysis and experimentation were of analytical grade. All parameters were analyzed as per Standard methods (APHA, 2005)**.** Raw textile wastewater for use in all the batch ECC experiments was collected from textile dyeing unit in Mysore city using 20L polyethylene containers before the equalization tank of the existing effluent treatment plant.

Characterization of raw silk textile wastewater (TWW)

Raw real silk TWW samples were characterized for their physico-chemical parameters following Standard methods (APHA, 2005). The physico-chemical characteristics of the raw wastewater before treatment are shown in Table 1.

Table 1: Physico-chemical characteristics of raw real silk textile wastewaters

Parameters	Units	Values	CPCB discharge standards (Inland surface water)
pH	-	6.3-6.90	5.5-9.0
COD	mg L^{-1}	1100-4800	250
BOD, 3 days at 20^0 C	mg L^{-1}	211-254	30
COD:BOD	-	5.15-6.30	-
Nitrates	mg L^{-1}	106.58	10
Phosphates	mg L^{-1}	17.22	5
Chlorides	mg L^{-1}	899.74	1000
Conductivity	Mmho/cm	3.1	-
Turbidity	NTU	210	-
Total solids	mg L^{-1}	2600	-

Batch ECC treatment

Lab scale electrochemical reactor (ECR) of 1.8L capacity made up of perspex is used to carry out the experiments to incorporate a SA/V ranging from 22-88 m^2/m^3. A direct current (DC) power supply unit is used as a source of power supply across the electrodes using copper wires. ECC reactor was placed on a magnetic stirrer for continuous stirring. Fig. 1 shows batch ECC schematic experimental setup used in laboratory scale ECC studies.
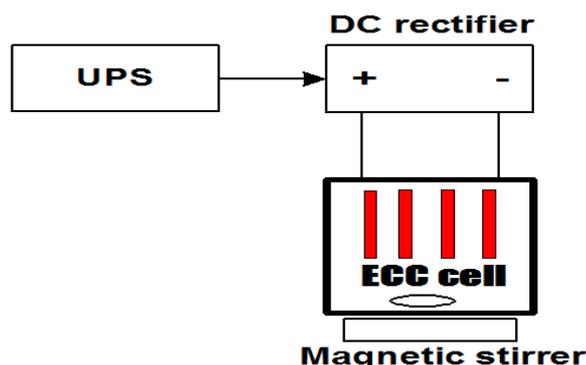

Fig. 1 Laboratory bench scale ECC setup

Electrode material selection is important in EC process. Iron is the material that most commonly used in EC process as it is economic, readily available, and proven to treat wastewater effectively (Nasrullah et al. 2017; Nandi and Patel, 2017; Pirkarami and Olya, 2017). Iron sheets were used as plate electrodes (anodes and cathodes) arranged in bipolar configuration. The ECR was filled with 1.5L of raw sample. Electrodes were connected to the positive and negative terminals of the DC power supply. Batch experiments were carried out at different cell voltages and at 430 rpm. Electrode spacing of 1cm was maintained using separating stand. Aliquot samples were retrieved from the reactor, filtered using Whatman 42grade filter paper and analyzed for various quality parameters.

III. Results And Discussion

COD degradation
Batch ECC experiments were carried out using 2 Fe electrodes for different operating conditions with 1V, 2V, 4V, 6V & 8V and 90min ET.
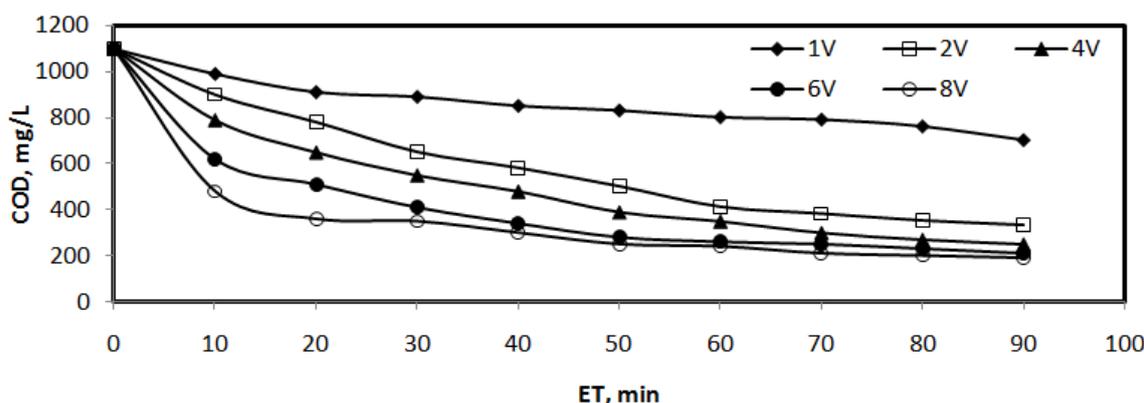

Fig. 2 COD degradation as a function of electrolysis time at different applied voltage using two Fe electrodes configuration

Fig. 2 shows COD removal rates as a function of electrolysis time at different applied voltage. At 1V, 2V, 4V, 6V & 8V and 90min ET, COD removal was 35.54%, 71.6%, 76%, 80% and 83% respectively. For an applied voltage of 8V, COD degradation was stable after 70 min ET.

During ECC, Fe^{2+} ions get added into the solution by the anodic reactions and some of the organic molecules and suspended solids are captured by the in situ generated iron hydroxide. COD degradation by iron electrode during ECC is as given in equations (1 to 10).

$$Fe \longrightarrow Fe^{2+} + 2e^- \tag{1}$$
$$2H_2O + 2\ e^- \longrightarrow 2OH^- + H_{2(g)} \tag{2}$$
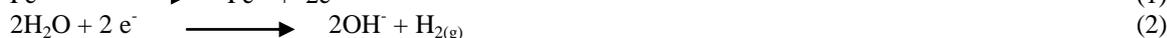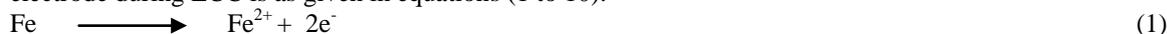
Fe^{2+} ions then react with the OH^- ions produced in the vicinity of the cathode which yields insoluble iron hydroxides.

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_{2(S)} \tag{3}$$

And at higher pH values, $Fe(OH)_2$ remains in equilibrium with Fe^{2+}. Fe^{2+} oxidation in the presence of dissolved oxygen releases insoluble $Fe(OH)_{3(S)}$ as given in the below reaction.

$$4Fe^{2+} + 10H_2O + O_{2(g)} \longrightarrow Fe(OH)_{3(S)} + 8H^+ \tag{4}$$

At cathode H^+ reduces to H_2 gas by reaction,

$$8H^+ + 8e^- \longrightarrow H_{2(g)} \tag{5}$$

The overall reaction in the electrolytic cell is given in equation 6,
$$4Fe + 10H_2O + O_{2(g)} \longrightarrow Fe(OH)_{3(S)} + H_{2(g)} \tag{6}$$

Higher chloride concentration (~1980mg/L) in the wastewater is an additional advantage as it improves the performance and effectiveness of the electrochemical process and also reduces the energy consumption. Presence of Cl^- influences the COD removal efficiencies in ECC as given in equations (7-10).

$$2\ Cl^- \longrightarrow Cl_2 + 2e^- \tag{7}$$

$$2H_2O + 2\ e^- \longrightarrow 2OH^- + H_{2(g)} \tag{8}$$

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \tag{9}$$

$$HOCl \longrightarrow H^+ + OCl^- \tag{10}$$

Remaining organic compounds in the wastewater is oxidized by the Cl_2 in ECC. The presence of chloride containing electrolytes increased the COD degradation efficiency. Hence, chlorine or hypochlorite generated in EC play a vital role in COD degradation.

Effect of initial temperature on COD removal
Raw TWW have a high temperature in the dyeing section of about 75^0C. By the time it reaches the equalization tank, it is ~ 30^0C. Batch ECC experiments were carried out at two different initial temperatures. Sample having initial temperature of 6^0C and 26^0C were used in the experiments. Iron electrodes were used for the experiments at different operating parameters viz., 2 electrode configurations, 9 Volt, 430 rpm and 60 minutes electrolysis time. The samples were taken out at time intervals of 5, 10, 15, 20, 30, 45 and 60mins during each run and the samples were filtered using Whatman 42 filter paper. The filtered samples were used for analysis of COD. The Fig. 3 shows the COD degradation curves as a function of electrolysis time at initial wastewater temperature of 6^oC and 26^oC respectively.
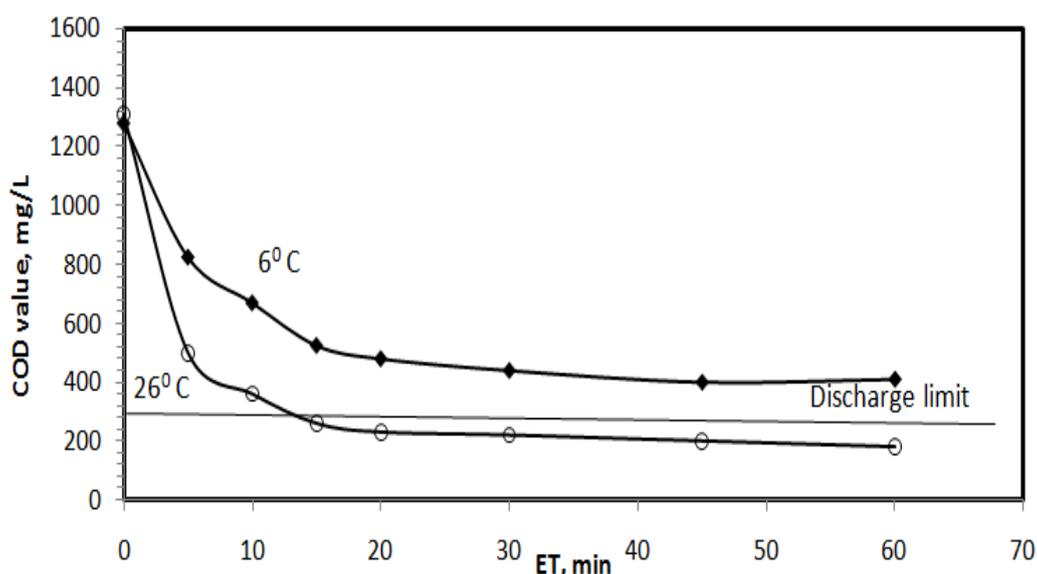

Fig. 3 COD degradation curves as a function of electrolysis time at initial wastewater temperature of 6^oC and 26^oC

Before ECC the COD values of the wastewater for the initial temperature of 6^oC and 26^oC were 1280mg/L was 1310mg/L respectively. From the Fig 3, it can be observed that COD removal was favoured at wastewater temperature of 26^0 C compared to lower initial wastewater temperature of 6^0C. Maximum COD removal was observed at 20min ET for the sample having ambient operating temperature of 26^oC. The rest 40min was allowed for floc formation and aggregation.

Sludge analysis for ECC treated wastewater
Separate batch ECC experiments were carried out at electrolysis time of 5, 10, 15, 20, 30, 45 and 60min using iron electrodes with operating parameters of 4E, 9Volt and 430rpm. ECC treated slurry was kept under observation for sludge formation. Treated wastewater was analyzed for total solids both in slurry samples and supernatant. Electrodes were weighed before and after treatment. Initial and final pH of the wastewater before and after treatment was noted for each set of experimental run. Fig. 4 shows the effect of electrolysis time on sludge floc formation.

Fig. 4 shows no formation of sludge floc till 20min ET. The floc begins to form at 30min ET with a final dried weight of 0.5421g. Sludge formation and COD removal was higher at 45 min ET and 60min ET with a final dried sludge weighing 1.7921g and 1.9201g respectively.
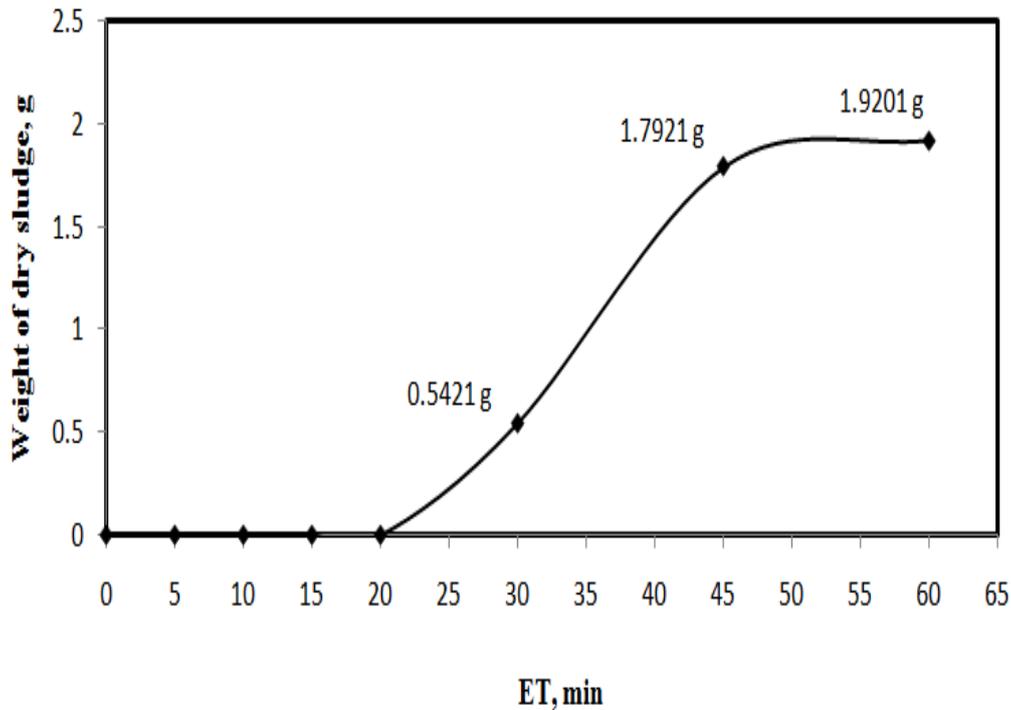
Fig. 4 Effect of electrolysis time on sludge floc formation

Batch ECC studies on total solids removal at different ET

Fig. 5 shows effect of electrolysis time on total solids removal. Total solids were seen to increase in the bulk solution during EC treatment from its initial value of 1425mg/L to 2457mg/L at the end of 60 min ET. Sludge formation begins at ~ 45min ET to reach stable levels at 60min. Total solids concentration in the supernatant after 60min ECC was 706mg/L showing a removal of ~51%.
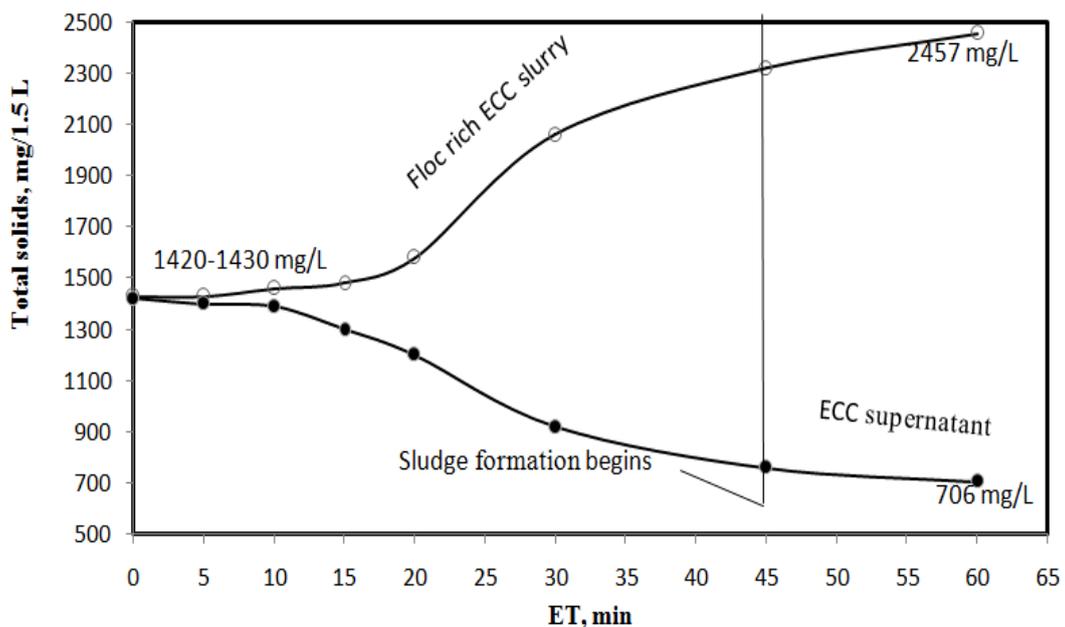
Fig. 5 Total solids removal as a function of electrolysis time

Settling characteristics

The mixture of sludge and supernatant from the EC process were mixed and resultant slurry was used for settling and filterability studies. Settling studies were carried using graduated cylinder. The slurry was homogenized before pouring into cylinder and was allowed to settle under quiescent conditions. The position of interface was measured as a function of time. Each settling experiments were carried out for a time interval of 45 min. Fig 6 shows the settling characteristics for Fe.
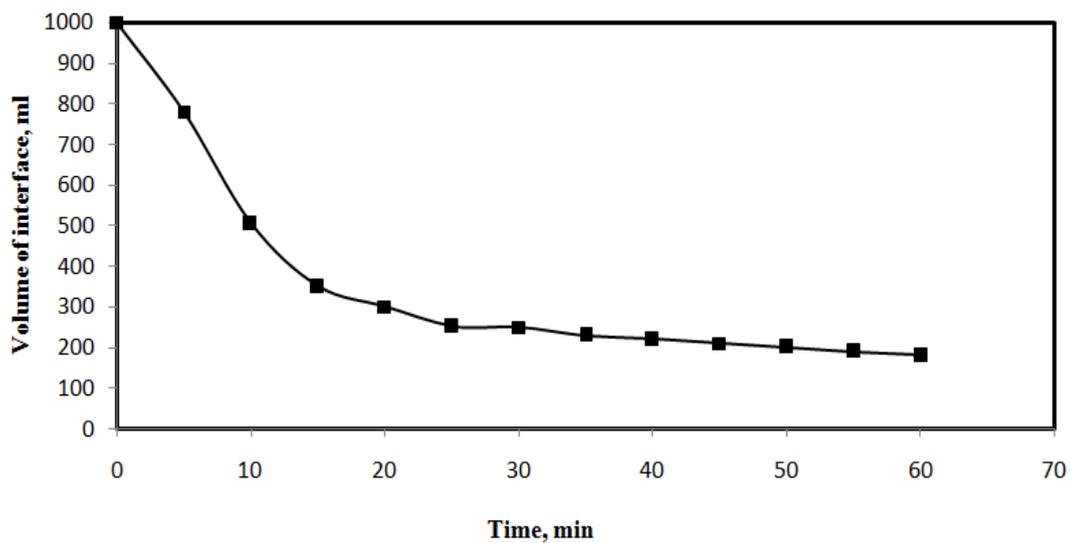
Fig. 6 Settling characteristics for Fe electrodes

Fig. 6 shows the volume of sludge settled interface vs time in minutes. Settling of sludge with Fe electrodes was quite faster due to different morphology of iron hydroxide particles, which are better defined with higher density. No settling was observed up to 5min. Discrete and compression settling is seen to dominate among all the four settling regimes.

Filterability Characteristics

The filterability of the sludge was tested using gravimetric filter paper, which is dry and previously weighed. Filter paper was placed on funnel supported over graduated cylinder column. A known volume of homogenized slurry was taken in a beaker and poured into the funnel. Filtrate was collected from the graduated vertical cylinder at regular interval of time. Each filterability lasted for 10-15 min. The cake formed in the funnel was removed carefully and weighed. Fig. 7 shows filterability characteristics of sludge. Sludge formed after ECC showed good filterability characteristics.
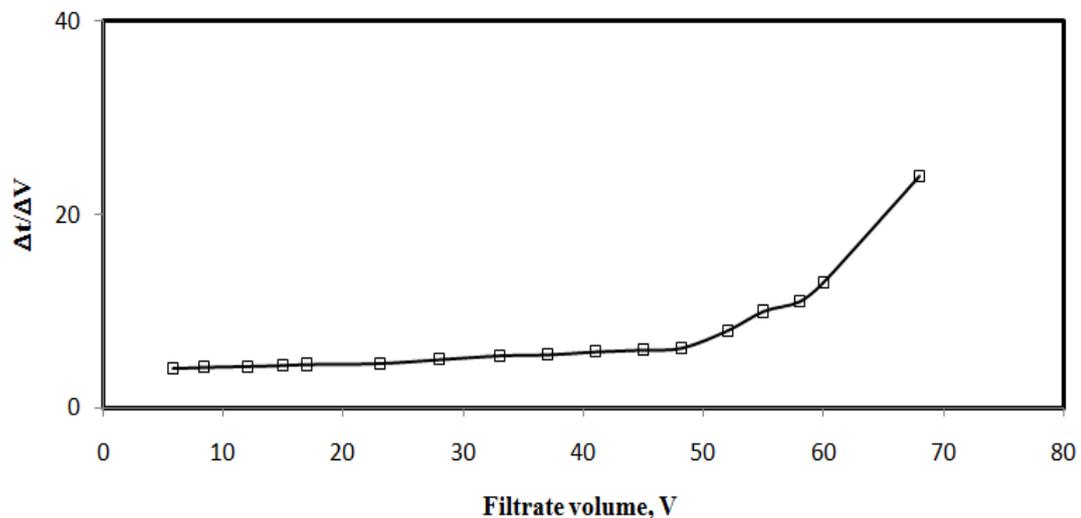

Fig. 7 Filterability Characteristics of sludge

Batch ECC studies on electrode dissolution

Fig. 8 shows the electrode dissolution as a function of ET. Electrode dissolution curve shows two plateaus namely, plateau 1 from 5 to 30 min ET; and plateau 2 from 45 to 60 min ET. Bulk solution pH shift from 7.73 to 8.84 was observed between 15 to 20min ET. Maximum electrode dissolution was observed between 30 to 60 min ET. Electrode dissolution causes increase in the solids concentration in the bulk solution during ECC.
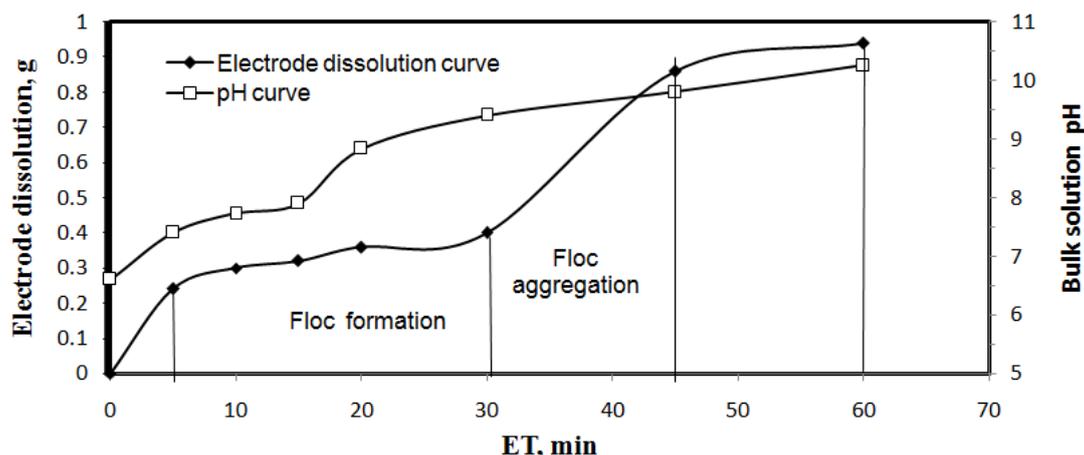
Fig. 8 Electrode dissolution and bulk solution pH as a function of ET

IV. Conclusions

Iron electrodes with 4 electrode configuration provided maximum COD removal ranging from 70-88% at initial wastewater temperatures of 6^oC and 26^oC from its initial COD value of ~1270mg/L. Maximum electrode dissolution was observed between 30 to 60 min ET. Dry sludge was of the order of 0.36, 1.19, and 1.28kg/m^3 of raw textile wastewater treated which is less compared to other treatment methods. Fe electrode showed good settling. This may likely due to, different morphology of iron hydroxide particles, which are better defined and higher density. And also use of iron ^{electrode} often results in the formation of very fine brown particles which are more prone to settling. Fe electrode showed good filterability.

Acknowledgement

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