Treatment of Tannery Wastewater by Electro-coagulation

[1]Nurul Amin, [2]Shafiqul Islam

[1]*Department of Civil Engineering, Institute of Science and Technology*

[2]*Department of Electrical Engineering, Institute of Science and Technology*

Corresponding author email: aminrana90@gmail.com[1]

Abstract

The tannery industries located at Hazaribagh are one of the major polluting industries in Dhaka. Treatment of tannery effluent is a challenging task as it is a biogenic matter of hides and a large variety of organic and inorganic chemicals. Electro-coagulation (EC) is becoming a popular process to be used for wastewater treatment. In this study the application of EC technique in the treatment of tannery effluent has been investigated. The experiments were carried out in an electrochemical reactor using aluminum electrode. Different operating time and electrode spacing has been studied in an attempt to achieve a higher removal capacity. Tannery wastewater sample was collected from a CarsasTannery Industry located at Hazaribagh. Operating time varied from 15 to 90 minutes and 4cm and 6cm electrode spacing was used. The results show that the effluent wastewater is very clear and its quality exceeded the direct discharge standard. Color removal efficiencies were found to be 88% at 75 minutes with 4cm electrode spacing and 93% at 90 minutes with 6cm electrode spacing. COD removal efficiencies were found to be 53.2% at 30 minutes with 4cm electrode spacing and 61.6% at 90 minutes with 6cm electrode spacing. The obtained results indicate that the EC technology can enhance the settling velocity of suspended particles and removal of COD and color.

Keywords: Electro-coagulation, electro-flotation, wastewater treatment, sacrificial electrodes.

1. INTRODUCTION

The important industries in Bangladesh includes textile, paper and pulp, leather tanning, fertilizer, cement, sugar, oil refining, chemical, pharmaceutical etc. Surface and groundwater pollution from tannery industries is a particular concern in Hazaribagh area. Wastewater from lagoon and finishing processes, with a chemical oxygen demand (COD) concentration exceeding 14385 mg/l and a strong dark color, is categorized as high strength wastewater. It is a significant source of environmental Pollution. The combination of strong color and highly suspended solid content results in high turbidity of the waste effluent. Due to the characteristics of tanneries wastewater, COD, Cr and turbidity removals exhibit similar trends. Conventional treatment methods for tanneries wastewater consist of various combinations of physical, biological and chemical methods. Because of the large variability of the composition of tanneries wastewaters, most of these conventional methods are becoming inadequate and insufficient. On the other hand, due to the scarcity of space, extremely high land cost, simple and efficient treatment process for the tanneries wastewater and the complexity of handling chemicals and sludge in some countries an essentially necessary. It should require minimum chemical consumption and space.

Many experiments were done in the world. In Bangladesh also some experiments have been done. The experiment has covered the effect of electrode spacing and treatment time over the performance efficiency.

2. LITERATURE REVIEW

The objective of this research work is to assess possible parameters of tannery wastewater. Among the various parameters present in the tannery effluent, chromium is of primary concern, especially from the point of view of tannery wastewater. After completing the treatment parameters were assessed again. This chapter provides an overview of the tannery industry in Bangladesh. The Electro coagulation processes have been described.

This study is to investigate the effect of electro coagulation (EC) process. This research is mainly focused on the capability of EC technology to improve wastewater quality, such as to increase removal efficiencies of COD and turbidity. EC is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. EC is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. The mechanism of the electrochemical process in aqueous systems is quite complex. It is generally believed that there are three possible mechanisms involved in the process: electro-coagulation, electro-flotation and electro oxidation. Principles of electro coagulation process are shown in figure-1. In EC with electrical current flowing between two electrodes, coagulant is generated in situ by electrolytic $Al(OH)_n$ with n = 2 or 3 is formed at the anode. Simplified oxidation and reduction mechanisms at the anode and cathode of the aluminum electrodes are represented [5].

Mechanism 1:

Anode: $Al\ (s) \rightarrow Al^{2+}\ (aq) + 2\ e^-$

$Al^{2+}\ (aq) + 2\ OH^-\ (aq) \rightarrow Al(OH)_2\ (s)$

Cathode: $2\ H_2O\ (l) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$

Overall: $Al\ (s) + 2\ H_2O\ (l) \rightarrow Al(OH)_2\ (s) + H_2\ (g)$

Mechanism 2:

Anode: $4Al(s) \rightarrow 4Al^{2+}(aq) + 8e^-$

$4\ Al^{2+}\ (aq) + 10\ H_2O\ (l) + O_2\ (g) \rightarrow 4\ Al(OH)_3\ (s) + 8\ H^+\ (aq)$

Cathode: $8\ H^+\ (aq) + 8\ e^- \rightarrow 4\ H_2\ (g)$

Overall: $4\ Al\ (s) + 10\ H_2O\ (l) + O_2\ (g) \rightarrow 4\ Al(OH)_3\ (s) + 4\ H_2(g)$

Waste water containing Cr^{6+} ($CrO_4^{\ 2n}$) ions can be removed by this
Electro Coagulation Technique using aluminum as the sacrificial anode. The
($Al^{\ 2+}$) generated by electro oxidation of the aluminum anode can reduce Cr^{6+} to Cr^{3+}
Under alkaline conditions and itself oxidized to (Al^{3+}) ion according to:

Mechanism 3:

$CrO^{2-}{}_{4(aq)} + 3Al^{2+}\ (aq) + 4H_2O\ (l) \rightarrow 3Al^{3+}\ (aq) + Cr^{3+}\ (aq) + 8OH^-\ (aq)$

Or

$CrO^{2-}{}_{4(aq)} + 3Al^{2+}(aq) + 4H_2O(l) + 4OH^-(aq) \rightarrow 3Al_3(aq) + Cr(OH)_3$

The $Cr^{3+}{}_{(aq)}$ ion is then precipitated as $Cr(OH)_{3(s)}$ by raising the pH of the solution.

Principle of EC is as shown in Fig 1. Dissolving of metal anodes are used to continuously produce metal ions close to the anodic surface. The generation of aluminum hydroxides ($Al(OH)n$) is followed by an electro phonetic

Concentration of Colloids (usually negatively charged) which are swept by the Electric field into the region close to the anode. Particles interact with the aluminum
Hydroxides and can be removed either by surface complication or electrostatic attraction. The electric field increases the probability of charges in suspension coming into contact with each other compared to chemical dosing and stirring. Therefore, the EC process improves coagulation.

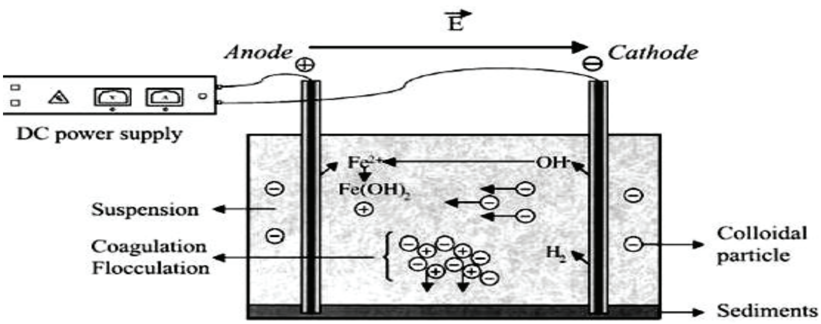

Figure 1: Principle of electro coagulation process.

3. TANNERY INDUSTRIES IN BANGLADESH

The migration of leather tanning activity from developed to developing countries over the past four decades has helped the leather industry in Bangladesh register an impressive growth rate in the last two decades. Being an exporter of wet blue in the seventies, Bangladesh now exports crust and finished leathers and leather products. Currently, leather industry is the fourth largest foreign exchange earner for the country. Special attention is given to development of infrastructure aimed at modernization and self-sustenance and for maximizing the foreign exchange earning potential of the Bangladesh leather industry [6].

Before the birth of Bangladesh in 1971, the leather industry in the erstwhile East Pakistan consisted of only about 35 medium-to-large and 25 Cottage-to-small-scale

Tanneries and they were mainly engaged in the production of wet blue for export. The cottage and small-scale units were also making some kind of low-grade finished leathers for domestic consumption. With the emergence of Bangladesh in 1971, the non-Bengali tanners disappeared as a result of which the leather making activity in the country came to a virtual standstill. The government came to the rescue and formed tanneries Corporation under which all the existing tanneries were nationalized. Later on, the nationalized tanneries were disinvested to private entrepreneurs during the late seventies and early eighties.

Wet blue remained the main exported commodity until the government imposed an export duty on wet blue in 1977-78. To encourage the export of crust and finished leather, government introduced in 1980-81 many incentives in the form of duty drawback, export performance benefit, income tax holiday including reduced import duty on leather machinery. Further, to promote rapid development of leather sector, government imposed a ban on export of wet blue leather in 1990. Simultaneously, efforts were initiated by the government for modernizing the leather industry through up gradation of infrastructure for making finished leather through BMRE (Balancing, Modernization, Rehabilitation and Expansion) and offering fiscal and non-fiscal assistance. This has really enabled many units to upgrade their leather processing facility and installation of modern machinery for the production of crust and finished leather of international quality.

4. ENVIRONMENTAL IMPACT OF TANNERY INDUSTRIES

Reviewing the waste streams described in the previous sections it is evident that tannery waste can cause severe damage not only to human beings but to the environment and ecology, if the waste is discharged without any treatment. The tannery industries discharge their total emission to the surrounding environment including the river Buriganga, nearby land and in the surrounding air without any treatment or taking any preventive measure to abate or reduce the adverse effects. The waste streams of all the tanneries have a significant contribution to the destruction of the environment around Hazaribagh. The following section describes the adverse environmental effects of tannery waste [6].

4.1 Effect on Surface Water:

The wet land and surface water bodies on the south-west, west and north-west of the tannery industrial area at Hazaribagh are already polluted and has been turned into tannery waste lagoon, and is unacceptable for any kind of use. The wastewater from the lagoon was collected during a survey by the DOE and analyzed in the DOE laboratory. High level of pollution load detected in the waste water samples from the lagoon. The most important surface water body outside the embankment is the river Buriganga. The regular monitoring results of the DOE provide that the river is highly polluted. And the chromium concentration at the drinking water intake point is also alarming. An investigation was conducted to assess the effects of tannery waste on the dissolve oxygen (DO) of the river. The DO found was 0.15-3.00 mg/L, which is far below the BEQS 6mg/L (DOE, 1992).

4.2 Effect on Land:

In the tannery industries area at Hazaribagh, the soil on both sides of the flood protection embankment is highly contaminated with tannery waste. The soil has significantly increased concentration of different organic and inorganic pollutants and heavy metals.[2] Chloride concentration is very high. There is also increased concentrations of nitrogen, NH_4-N, NH_3-N, Phosphorus and sulfur on the surface of soil (DOE, 1992). Even at depth of 1.2 meter accumulation of nitrogen was found. It was also found that the tannery industries are not only discharging chromium as heavy metal, which is inherent to the tanning process, but significant amounts of Zn, Mn, Cu and Pb as well. Other heavy metals such as Zn, Mn, Cu and Pb also have been found at high concentrations. Phenols hydrocarbons, available N (NH_4^+, NH_3) chloride, SO_4, TOC and EC have also been found exceeding critical limits in soil for agricultural production and general use [4] .

4.3 Effects on Ground Water:

According to Bangladesh Environmental Quality Standard (EQS), the standard for chromium in the ground water is .05 mg/l. The Concentration of Chromium in groundwater in DWASA water in and around Hazaribagh area is between .02 - .04 mg/l (DOE, 1993-94). Although the groundwater pollution by chromium still has not exceeded the EQS, but it is very close to the limit and the situation is very alarming.

4.4 Effects on Air Quality:

Biological decomposition of organic materials as well as sulfide emissions from waste water is responsible for the characteristic objectionable odors from the tanneries and their wastes. The following are important sources of odors:

- Sulfide emissions from de-hair and waste treatment;
- Ammonia emissions from de-liming; and
- Fleshing

4.5 Effects on Human Health:

Health problems of the workers of tanneries found that, continuous handling of chemicals cause cumulative effect in the human body. The study found that, Clinical manifestations similar to chromium toxicity like abdominal discomfort/gastritis, skin, ulcer, dermatitis, nausea, ulcer/loss of smell, erosion and discoloration of teeth and asthma were found among the people who worked in the tannery industry and also those who lived in and around the tannery industrial area for more that 10 years [1].

4.6 Effects on Vegetation and Structure:

Hagaribagh is a densely populated area with a lot of residential holdings. There are homestead gardens and residential holdings from where seasonal vegetables are grown besides permanent plantation. It was gathered from the inhabitants of the area that decades ago the quality and quantity of fruits, vegetables etc. grown in the homestead gardens were much higher compared to the present condition. According to the inhabitants, this deterioration has taken place gradually and at present many of the fruit plants do not bear any fruit at all. It is important to ascertain whether the vegetables grown here contain any constituents, which are harmful for human health. During a visit to the Hagaribagh area, the leaves of some of the trees were observed to be yellowish and some of the rooftop CI sheets were found to be rusted. Some buildings located close to the tanneries were found to have blue stains on them.

4.7 Toxicity of Chromium:

Chromium is not acutely toxic to humans. This is due to the high stability of natural chromium complexes in abiotic. In addition, the hard acidic nature of chromium imparts strong affinity for oxygen donors rather than sulfur donors present in bio-molecules. However, $Cr^{(+3)}$ because of its high rate of adsorption through intestinal tracts. In the natural environmental, $Cr^{(+6)}$ is likely to be reduced to $Cr^{(+3)}$, thereby reducing the toxic impact of chromium discharges. Chromium and dichromate ware frame shift mutagens in the Salmonella plate incorporation test, through trivalent chromium did not cause an increase in reversion frequency [3]. It appears, based on experimental evidence, that hexa-valent chromium also has mutagenic properties. Although the case for trivalent chromium is not as strong, its mutagen city must be considered a possibility. Hexa-valent chromium at 10 mg/kg of body weight will result in liver necrosis nephritis, and death in man; lower doses will cause irritation of the gastrointestinal mucosa. Hexa-valent chromium has been implicated as the cause of digestive tract cancers in man and there is firm evidence that there is increased risk of lung cancer for workers who are exposed to high levels of chromium. Exposure to a mixture of chromium (vi) compounds of different solubility carries the greatest risk for human being.

5. METHODOLOGY

The primary objective of this study is to assess characterization of wastewater. By electro coagulation the wastewater is treated and the results are show. In order to determine the parameters by electro coagulation the following work were done.

- ➢ Sample collection

- Experimental setup
- Laboratory analysis
- Data analysis and presentation

5.1Sample collection:

Wastewater samples were collected from the Carsas tannery industries. The samples were collected in some bottles which are 2 liter in capacity. Water samples were used for analysis of a wide range of water quality parameters (pH, color, Chloride, COD, EC and Chromium).

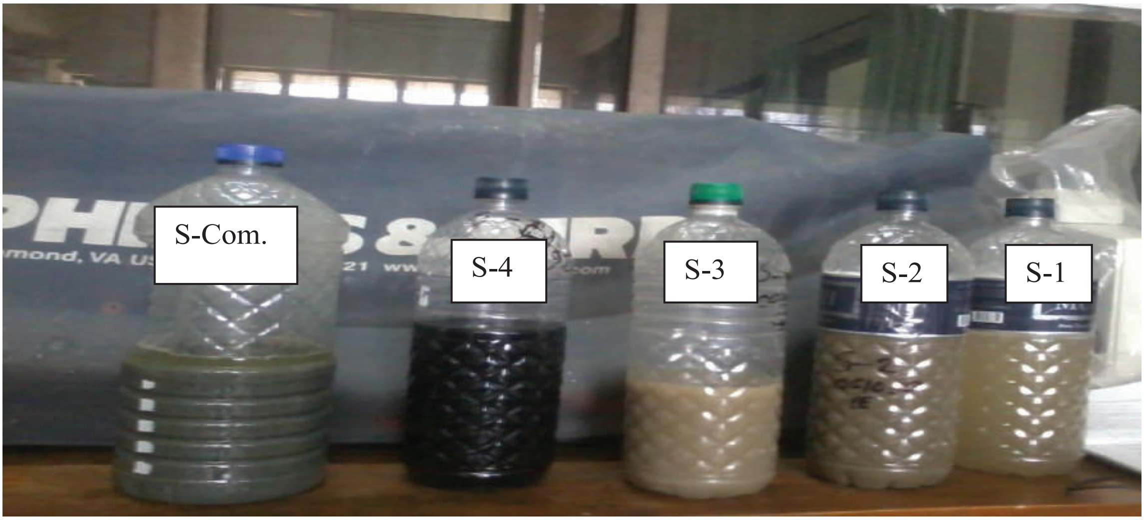

Figure 2: Different types of raw sample.

5.2 Experimental setup:

This study is to investigate the effect of electro coagulation (EC) process. This research is mainly focused on the capability of EC technology to improve wastewater quality, such as to increase removal efficiencies of COD.

5.3 Laboratory analysis:

The wastewater samples were coagulate by aluminum electrode and filtered, then the samples were ready for analysis. In this study, P^H in the wastewater samples were measured using a P^H meter. Turbidity were measured by Turbidity meter (Hach 2100Q). Color were defined as either true or apparent color. True color is the color of water from which all turbidity has been removed. Apparent color includes any color that is due to suspended solids in the water sample. Color concentrations in the wastewater samples were determined by UV spectrophotometer (DR 2800).

BOD or biochemical oxygen demand is the measure of the oxygen consuming capabilities of organic matter. Water with high BOD indicates the presence of decomposing organic matter and subsequent high bacteria counts that degrade its quality and potential uses. BOD_5 were determined by Hoch BOD incubator machine and COD were determined by reactor digestion method.

Total solids and total dissolved solids in the wastewater samples were determined by oven dry method. Total dissolved solids or TDS characterize the general purity of water and is often largely due to soluble ions such as sodium, chlorine and sulfate. Total suspended solids in sample were determined by subtracting the total dissolved solids from the total solids.

Figure 3: Chemical laboratory for parameters test.

5. RESULTS

To determine the wastewater quality of Tannery industries, several parameters of wastewater has been analyzed. In this chapter quality of raw wastewater and removal efficiencies of electro coagulation method were discussed.

5.1 Analysis of Results:

The results obtained from the experiment of tannery wastewater have been presented through different tables and diagrams as mentioned below:

Table 1: Analysis of Hazaribagh tannery wastewater before treatment.

Parameter	Unit	Bangladesh Standard for Tannery Industry Effluent	Hazaribagh Sample 1	Hazaribagh Sample 2	Hazaribagh Sample 3	Hazaribagh Sample 4	Composite-sample
pH		6-9	7.34	12.56	9.73	3.52	9.63
BOD	mg/L	100	675	700	746	800	600
TSS	mg/L	150	185	11,910	3,059	902	7,630
TDS	mg/L	2100	20,575	69,607	24,701	68,598	40,012

Table: 2 Quality variation of different parameters of wastewater after treatment (Spacing between electrodes: 4 cm and DC power supply: 18 volts) upon times and electrodes.

Parameters	Units	0 (min)	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
pH	-	9.63	9.06	9.00	8.96	8.86	8.85	8.85
DO	mg/L	0.07	0.06	0.05	0.04	0.04	0.03	0.03
Color	pt-co	2870	840	680	505	390	345	400
TDS	mg/L	25600	25500	25700	25600	25800	25900	27400
TSS	mg/L	7630	-	-	-	-	-	-
COD	mg/L	14385	9540	6730	10330	8690	8690	8880
BOD_5	mg/L	600	-	-	-	-	-	-
Electric conductivity	mS/cm	50.9	51.1	51.3	51.4	51.5	51.8	55.2

Table: 3 Quality variation of different parameters of wastewater after treatment (Spacing between electrodes: 6 cm and DC power supply: 18 volts) upon times and electrodes.

Parameters	Units	0 (min)	15 (min)	30 (min)	45 (min)	60 (min)	75 (min)	90 (min)
pH	-	9.63	9.33	8.78	8.75	8.74	8.71	8.64
DO	mg/L	0.07	0.06	0.05	0.04	0.03	0.03	0.03
Color	pt-co	2870	1100	940	245	240	230	205
TDS	mg/L	25600	25100	28100	27800	29400	27700	27500
TSS	mg/L	7630	-	-	-	-	-	-
COD	mg/L	14385	8760	6770	6470	7250	11620	5530
BOD_5	mg/L	600	-	-	-	-	-	-
Electric conductivity	mS/cm	50.9	51.0	52.7	55.6	55.8	55.9	57.1

pH values in tannery wastewater samples varies from the range of 9.63 to 8.85 (in 4 cm spacing of electrodes) and varies from the ranges of 9.63 to 8.64 (in 6 cm spacing of electrodes).

EC values in tannery wastewater samples varies from the range of 50.9 to 55.2 (in 4 cm spacing of electrodes) and varies from the ranges of 50.9 to 57.1 (in 6 cm spacing of electrodes).

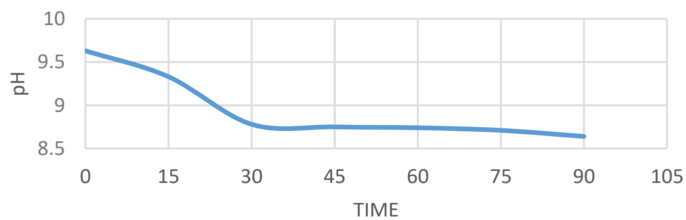

Figure 4: Effect of operating time on pH (4 cm electrode spacing).

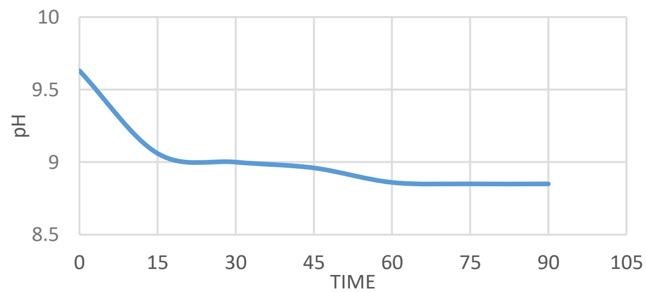

Figure 5: Effect of operating time on pH (6 cm electrode spacing).

The color removal efficiency exhibits maximum value in 75 minute in the case of 4 cm electrode spacing and also exhibits maximum value in 90 minute in the case of 6 cm electrode spacing show in below figure 6.

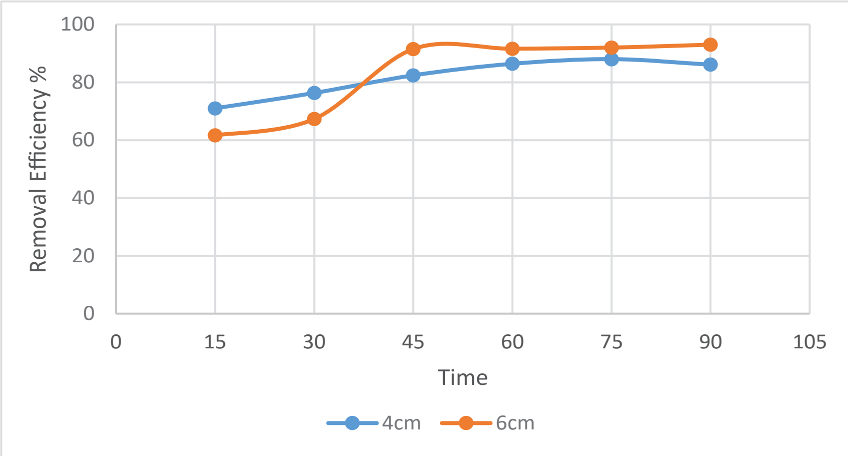

Figure 6: Effect of operating time and electrode spacing on removal efficiency of color.

COD removal efficiency is not very fast in the cases of 4 cm electrode spacing. 53.2% COD is removing in 4 cm electrode spacing in the case of 30minutes of expperiment performed but COD removal efficiency is also fast in the cases of 6 cm electrodspacing. 61.6% COD is removing in 6 cm electrode spacing in the case of 90 minutes of experiment performed.

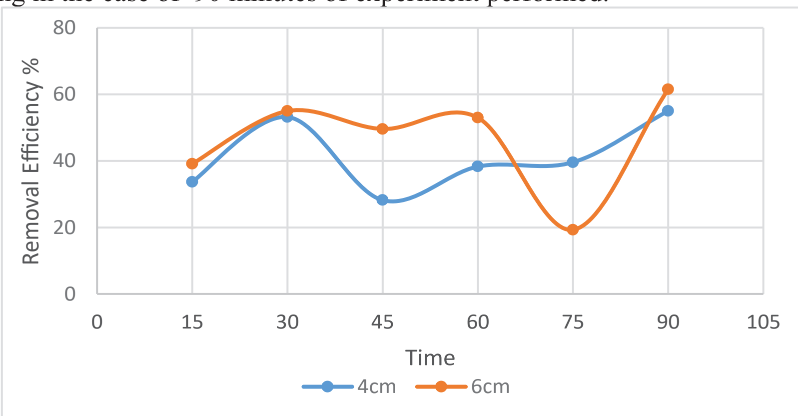

Figure 7: Effect of operating time and electrode spacing on removal efficiency of COD.

It is visible that the amount of dissolved oxygen after experiments is slightly lower than the preliminary values shown in below figure 8.

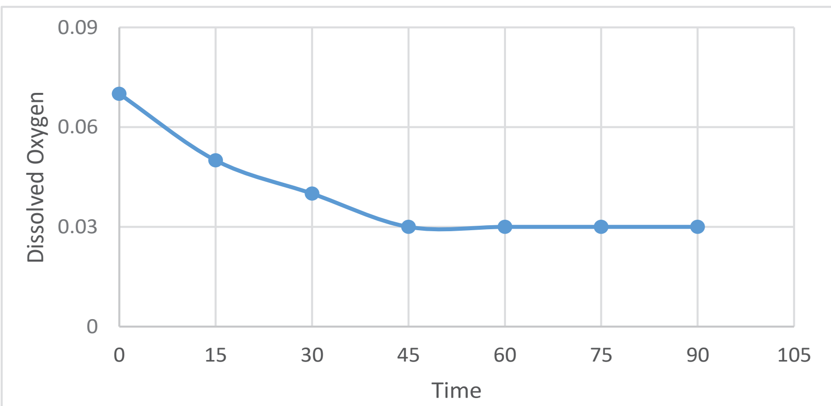

Figure 8: Effect of operating time on DO (4 cm electrode spacing).

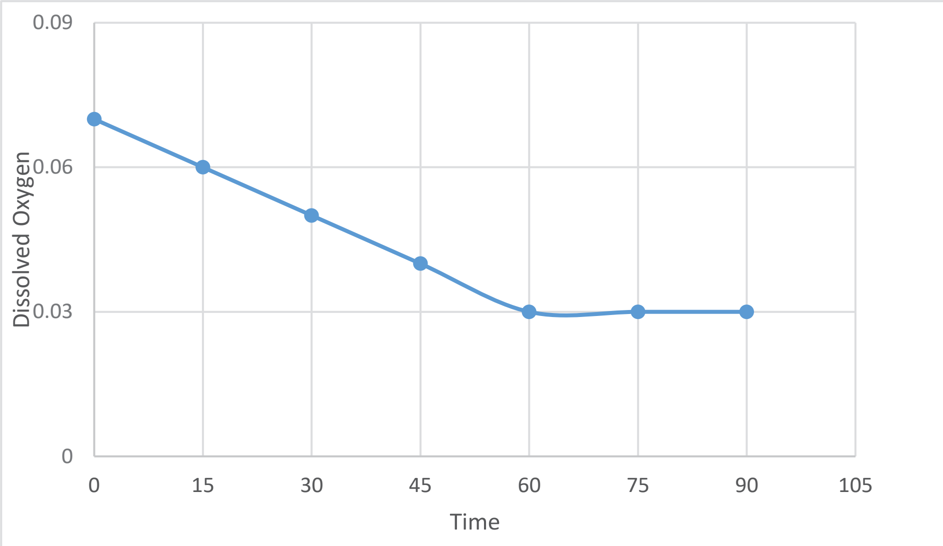

Figure 9: Effect of operating time on DO (6 cm electrode spacing).

The electric conductivity of pure water is lower than wastewater. The sample of wastewater is becoming fresh by treatment and decrease dissolved material. So the electric conductivity is becoming higher with respect to time.

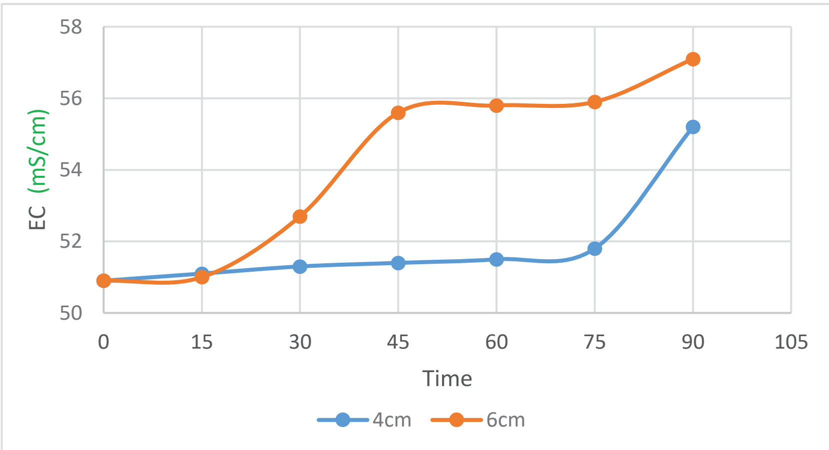

Figure 10: Effect of operating time and electrode spacing on Electric Conductivity.

CONCLUSIONS AND DISCUSSIONS

The result of pH parameter of our sample after treatment (8.64) with 6 cm satisfies with the Bangladesh standard (6-9). The Result of BOD_5 higher than the Bangladesh standard. BOD_5 result is 600 mg/L which doesn't satisfy Bangladesh standard 100 mg/L. The initial value of COD was 14385 mg/L after EC treatment the result have been changed to 5530 mg/L. We have removed 61.6 % COD from sample. But COD value of our sample doesn't satisfy Bangladesh standard effluent industry 400 mg/L. the result of EC parameter doesn't satisfy Bangladesh standard effluent industry 1200 µmhoms/cm. From data table it has visibled that total dissolved solids are increasing (25400 to 27500 mg/L) with respect to time. The initial value of TDS has been increased because suspended particle of waste water converted into dissolved solid. The result of total dissolved solid (TDS) value is doesn't satisfy Bangladesh stranded in effluent industry 2100 mg/L.

The major focus of this study was to assess the removal efficiency of COD, Color and from the results of this study it appears that wastewater from tannery industry is becoming fresh.

1. pH value varied from (9.63 to 8.85) at 4 cm electrode spacing and (9.63 to 8.64) at 6 cm spacing.
2. The Value of dissolve Oxygen were decreasing from the initial value.
3. The results of COD removal efficiency is as high as 61.6% for EC process with the constant supply of 18 volt and electrode spacing 60 mm at time 90mins.
4. Color is removing maximum in 75 minutes where the electrodes are in 60 mm in spacing and the value of removal efficiency is 92.86 %.
5. The value of EC is becoming higher with respect to time. Because of dissolved material were increased in sample.

REFERENCES

[1] M.H.A"Study on chromium Content in Water around the Hazaribagh Tannery Industries and Prevailing Health Problem," *M. Phill. Thesis, Faculty of Post Graduate Medicine and Research, University of Dhaka,*1994

[2] DoE, "Dhaka Waste Water Management Study under National Environment Pollution Control Project", *Government of the People Republic of Bangladesh, Department of Environment, Dhaka.* 1992

[3] G. Lofroth,. and B. N. Ames, " Mutagenicity of Inorganic Compounds in Salmonella Typhimurium: Arsenic, Chromium and Selenium." *Mutation Research/Environmental Mutagenesis and Related Subjects*, vol. 53, no. 1, pp. 59-65, 1978.

[4] M. N, "Industrial Pollution of Soils, Crops, Sediments and Water System around Dhaka City*," Ph.D. Thesis. Dhaka: Department of soil Science, University of Dhaka,*1995

[5] R. Babu, N. Bhadrinarayana, ,. Begum and ,. Anantharaman, "Treatment of Tannery Waste Water by Electro-coagulation", *Journal of the University of Chemical Technology and Metallurgy*, vol. 42, no. 2, pp. , 201-206, 2007.

[6] G.C.S," Assessment of Ground Water Contamination in Dhaka City from Tannery Waste*," M.sc Thesis, BUET,* 2001