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Treatment of tannery wastewater by electrocoagulation technology

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Abstract

Treatment of tannery wastewater by electrocoagulation (EC) process was investigated in this study. Treatment of the wastewater was carried out by an electrochemical batch reactor equipped with aluminum electrodes, which were connected parallel to each other. The optimum operating conditions were determined and applied to the process. The maximum obtained values for COD, color and turbidity removal efficiencies were 100%, 84%, and 85%, respectively, for an operating time of 21 minutes.The obtained results indicate that EC reactor is the applicable option to treat tannery industry wastewater in terms of removal efficiency and operating cost.

Keywords: Tannery Wastewater, Electrocoagulation, COD, BOD, Operating Parameters.

INTRODUCTION

The major challenges for the 21st century are water and energy. The world is very competitive where the basic concern of manufacturing companies is to increase their customers' satisfaction by constantly improving their delivery yet to keep quality at its best level [1]. Due to increased pollution from point and non-point sources quality of the water become a crucial problem, particularly for the Third-World Countries. Electrocoagulation (EC) is an electrochemical technique for treating polluted water using electricity instead of expensive chemical reagents. It has been successfully applied for treatment of soluble or colloidal pollutants in various industrial effluents [2].

The increasing economic growth in Bangladesh encourages the growth of Leather sector [3]. The tanning industry is one of the oldest manufacturing sectors in our country [4]. It is among the most polluting industries in terms of the volume and the complexity oftreatment of its effluents discharge [5]. Leather tanning consumes a huge quantity of water which ultimately goes to the environment as wastewater and degrades the environment [6]. Major chemicals used in leather manufacturing are lime, sodium and ammonium salts, fat liquors, bacteria and fungicides, tannins, dyes etc. [7]. Wastewaters generated by tannery industry are known to contain large amounts of potentially toxic wastewaters containing both organic and inorganic compounds [8, 9]. Tanneries effluents are also characterized by high wastewater generation in the range of 30–35 L/ Kg skin/hides process with a variable pH, the high concentration of suspended solids, BOD, chromium, COD, and sulfides as well as low biodegradability [10, 11]. The wastewater generated by the tanning, liming, and pickling processes in particular, as well as by the other processes, contains elevated amounts of chromium and dissolved chemical salts. Before discharging this wastewater into a river or other receiving waters, it is necessary to treat the effluent to meet the government's fixed allowable limits [12]. Tannery wastewater treatment represents a serious environmental and technological problem. In fact, after conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as COD, salinity, ammonia and surfactants [13]. Conventional physicochemical treatment methods for tannery wastewater consist of chemical oxidation/precipitation, sedimentation, coagulation/flocculation, adsorption, ion exchange, etc. [14, 15]. Conventional biological treatment methods are often inadequate to completely remove pollutants in tannery wastewater [13]. Due to the limitations of the primary and biological wastewater treatment processes, alternative processes have been pursued [7].

In recent years, there has been increasing interest in the use of electrochemical methods in the purification of various industrial wastewaters. Although electrochemical methods are available for more than a century, it now appears to be one of the most effective approaches having the features of low operational cost and high treatment efficiency [16-18]. One of these processes is electrocoagulation (EC) which has achieved much attention due to its attractive advantages as the simple, reliable, and cost-effective operation for the treatment of wastewater. Infact, it involves the dissolution of metal from the anode with simultaneous formation of hydroxyl ions, and generation of hydrogen gas at the cathode which can be recovered for use as the energy source or a reactant for other industrial applications [19]. There are vital advantages of EC as a low sludge production technology; secondly, the EC flocks are relatively large, contain less bound water, more stable, and amenable to filtration [20]. The fitting choice of EC material is an essential electrode materials generally, are aluminum and iron. They are cheap, readily available, and have been proven effective [21]. EC has satisfactory been utilized decades to treat wastewater of olive mill, restaurant, metal plating, domestic, tannery, rose processing, textile industry, etc. [18]. The continuous mode of the EC process has however been less investigated, except in a few studies [5].

Electrocoagulation process provides a direct current source between metal electrodes immersed in wastewater. The electrical current causes the dissolution of metal electrodes, and the dissolved metal ions form coagulated species and metal hydroxides, at an appropriate pH. Metal hydroxides, which destabilize and aggregate the suspended particles, precipitated by adsorbing dissolved contaminants. Main processes that occur during electrocoagulation can be given as follows:(i) migration to an oppositely charged electrode and aggregation due to charge neutralization;(ii) formation of cation or hydroxyl ion (OH-) precipitate with pollutant;(iii) interaction of metallic cation with OH- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant; (iv) formation of larger lattice-like structured hydroxides which sweep through the water; (v) oxidation of pollutants to less toxic species; (vi) removal by electro-flotation or sedimentation and adhesion to bubbles [22, 23].

In this study, treatability of tannery industry wastewaters by electrocoagulation (EC) was experimentally evaluated. Effects of pH, current density and electrolysis time were analyzed to EC process with the aluminum electrode. The optimum operating conditions were determined and applied to the process.

MATERIALS AND METHODS

Materials

Samples used in this study were collected from Tannery More, Hazaribagh Tannery area during the time from August 2016 to December 2016. The composition of the tannery wastewater is determined using APHA Standard Methods and are presented in table 1.

Table 1: Characteristics of raw tannery wastewater

Parameters	Value
Total dissolved solids (TDS)	2130 mg/L
Total solids (TS)	2750 mg/L
Turbidity	24 FAU
pH	7.40
Chemical oxygen demand (COD)	2200 mg/L
Biochemical oxygen demand (BOD)	903 mg/L
Color	275 units Pt-Co
Cadmium (Cd)	Less than 1.0 ppb
Iron	8.44 mg/L
Chromium (Cr)	235 mg/L
Aluminum (Al)	No detectable
Chloride (Cl)	104 mg/L

Experimental Setup

A batch process has been considered for the experimental studies. The batch experimental setup consists of the following components:
1. A four-liter tank made of acrylic plastic sheet (6 mm thickness)
2. Two MS plate electrodes (140 mm × 120 mm × 1.5 mm) [one anode and one cathode]
3. DC power source (30 V)
4. Insulated copper wire

The auxiliary instruments used are:
1. Multimeter (EXCEL DT9205)
2. Clamp multimeter (VICTOR 6056B)
3. pH meter (HANNA HI96107)
4. TDS meter (HANNA HI 98302)
5. Conductivity meter (EZODO COND5021)
6. Stirrer (JENWAY 1002; V = 230 V, Power = 50 W, Frequency = 50 Hz)
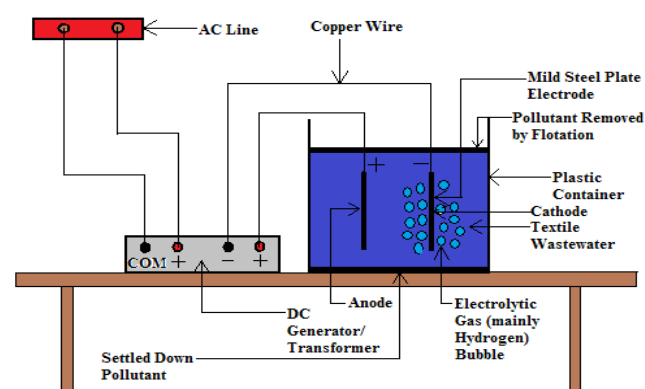7. Weight machine (AND Korea Ltd., BH300A)

Figure 1: Schematic diagram of the experimental setup

Experimental Procedure

i) The reactor configuration was assembled appropriately and the circuit was closed.

ii) DC current flowed through the wastewater in the electrocoagulation chamber for a specific operating time by virtue of the oxidation and reduction reactions occurring at the anode and cathode, respectively.

iii) In the meantime, the DC voltage and DC current was measured by using the multi-meter and clamp multi-meter.

iv) Immediately after DC current had been switched off, treated clear water was collected in a 2000 mL beaker.

v) The collected treated wastewater sample was allowed to settle down overnight.

vi) After 24 hours, clearer treated wastewater sample was collected by manual decantation for determination of chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), turbidity, conductivity and pH in the laboratory.

Analytical Procedure

The wastewater analyses such as pH, conductivity, COD and total suspended solids (TSS) were carried out in accordance with the Standard Methods for Examination of Water and Wastewater. The supernatant was filtered with cellulose acetate filter paper before COD analyses. The removal efficiency (E) was calculated using the following equation:

$$E = \frac{Y_0 - Y}{Y_0} \times 100$$

Where E is the removal efficiency (%), Yo and Y were initial and final values of COD and suspended solids, respectively.

RESULTS

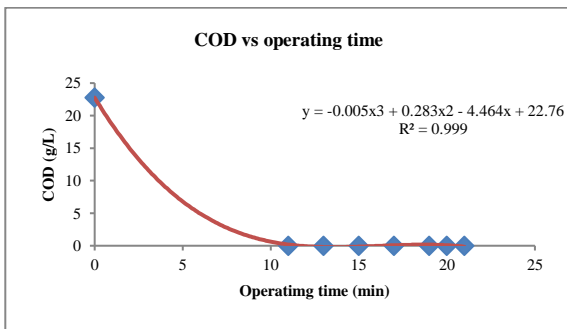### Effect of operating time on removal of chemical oxygen demand (COD)

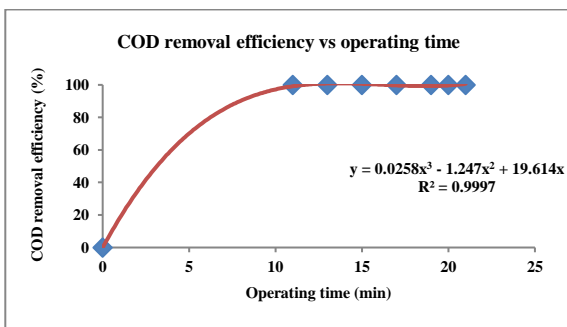**Figure 2:** Plot of COD versus operating time

Figure 3: Plot of COD removal efficiency versus operating time

From Figure 2 and 3, the equation for the variation of COD removal efficiency with operating time is as follows:

$$y = 0.025x^3 - 1.247x^2 + 19.61x; R^2 = 0.999$$

$$\frac{dy}{dx} = 0.075x^2 - 2.494x + 19.61$$

$$\frac{d^2y}{dx^2} = 0.15x - 2.494$$

Now, $\frac{dy}{dx} = 0.075x^2 - 2.494x + 19.61 = 0$

Or, x = 20.50 or 12.76

For x = 20.50, $\frac{d^2y}{dx^2} = (0.15)(20.50) - 2.494 = 0.581 > 0$

For x = 12.78, $\frac{d^2y}{dx^2} = (0.15)(12.76) - 2.494 = -0.580 < 0$

Therefore, for maximization of COD removal efficiency, operating time = 12.76 min ≈ 13 min

Corresponding value of COD removal efficiency $= \{(0.025)(13)^3 - (1.247)(13)^2 + (19.61)(13)\}$ % = 99.11%

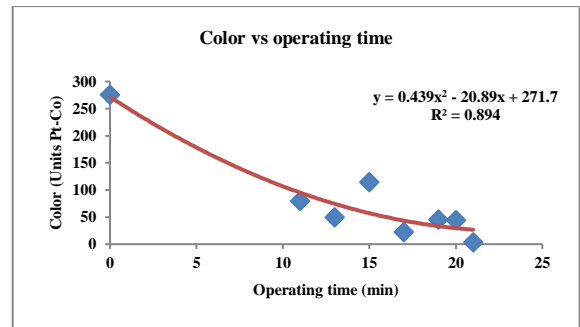### Effect of operating time on color removal

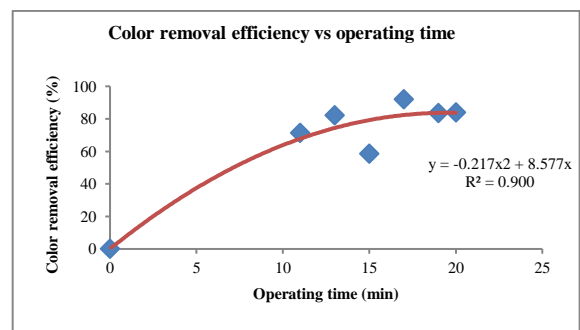**Figure 4:** Plot of color versus operating time

Figure 5: Plot of color removal efficiency versus operating time

From Figure 4 and 5, the equation for the variation of color removal efficiency with operating time is as follows:

$$y = -0.217x^2 + 8.577x; R^2 = 0.900$$

$$\frac{dy}{dx} = -0.434x + 8.577$$

$$\frac{d^2y}{dx^2} = -0.434$$

Now, $\dfrac{dy}{dx} = -0.434x + 8.577 = 0$

Or, $\quad x = 19.76$

For $\quad x = 19.76, \dfrac{d^2y}{dx^2} = -0.434 < 0$

Therefore, for maximization of color removal efficiency, operating time = 19.76 min ≈ 20 min

Corresponding value of color removal efficiency = $\{-(0.217)(20)^2 + (8.577)(20)\}$ % = 84.74%

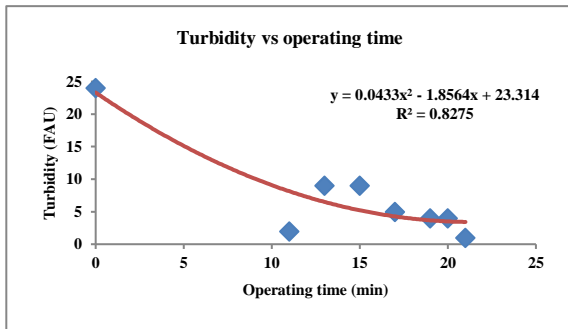## Effect of operating time on turbidity removal

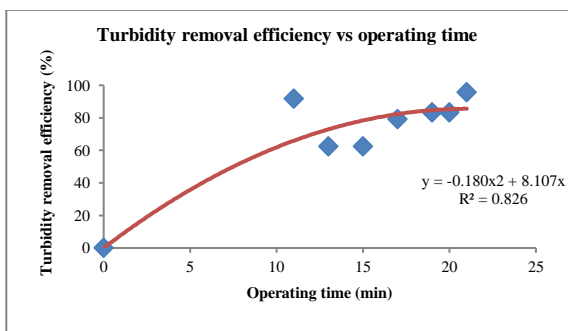**Figure 6:** Plot of turbidity versus operating time

Figure 7: Plot of turbidity removal efficiency versus operating time

From Figure 6 and 7, the equation for the variation of turbidity removal efficiency with operating time is as follows:

$$y = -0.180x^2 + 8.107x; R^2 = 0.826$$

$$\dfrac{dy}{dx} = -0.360x + 8.107$$

$$\dfrac{d^2y}{dx^2} = -0.360$$

Now, $\dfrac{dy}{dx} = -0.360x + 8.107 = 0$

Or, $\quad x = 22.52$

For $\quad x = 22.52, \dfrac{d^2y}{dx^2} = -0.360 < 0$

Therefore, for maximization of turbidity removal efficiency, operating time = 22.52 min ≈ 23 min

Corresponding value of color removal efficiency = $\{-(0.180)(23)^2 + (8.107)(23)\}$ % = 91.24%

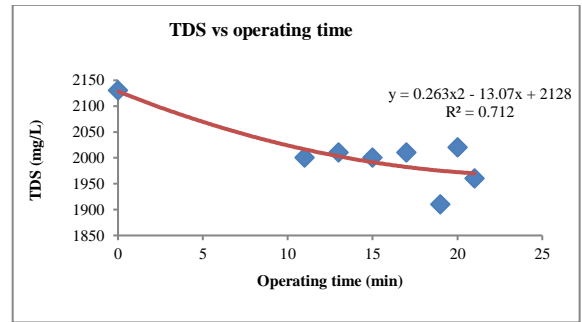## Effect of operating time on removal of total dissolved solids (TDS)

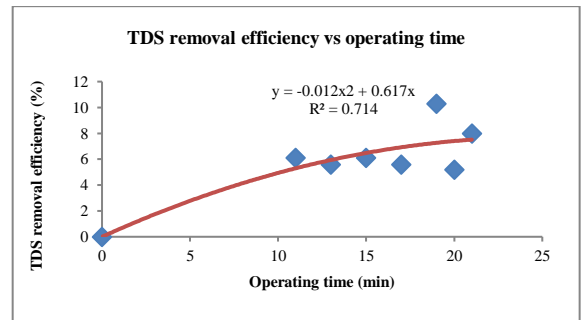**Figure 8:** Plot of TDS versus operating time

Figure 9: Plot of TDS removal efficiency versus operating time

From Figure 8 and 9, the equation for the variation of TDS removal efficiency with operating time is as follows:

$$y = -0.012x^2 + 0.617x; R^2 = 0.714$$

$$\dfrac{dy}{dx} = -0.024x + 0.617$$

$$\dfrac{d^2y}{dx^2} = -0.024$$

Now, $\dfrac{dy}{dx} = -0.024x + 0.617 = 0$

Or, $\quad x = 25.71$

For $\quad x = 25.71, \dfrac{d^2y}{dx^2} = -0.024 < 0$

Therefore, for maximization of TDS removal efficiency, operating time = 25.71 min ≈ 26 min

Corresponding value of TDS removal efficiency = $\{-(0.012)(26)^2 + (0.617)(26)\}$ % = 7.93%

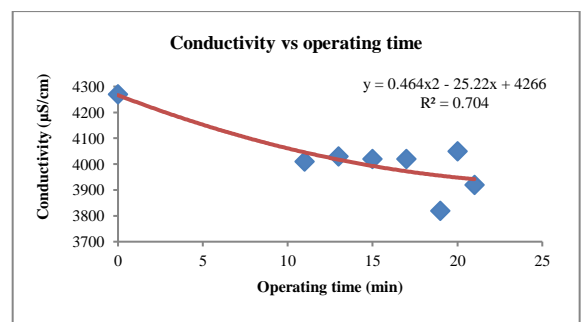## Effect of operating time on conductivity removal

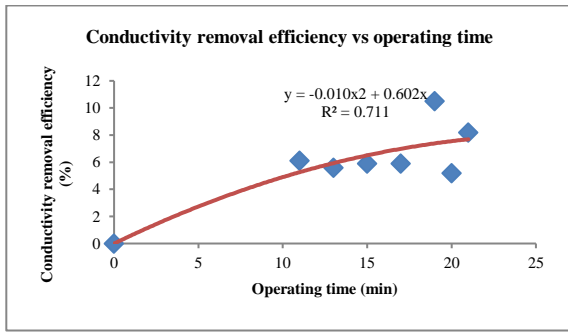**Figure 10:** Plot of Conductivity versus operating time

Figure 11: Plot of conductivity removal efficiency versus operating time

From Figure 10 and 11, the equation for the variation of conductivity removal efficiency with operating time is as follows:

$$y = -0.010x^2 + 0.602x; R^2 = 0.711$$

$$\frac{dy}{dx} = -0.020x + 0.602$$

$$\frac{d^2y}{dx^2} = -0.020$$

Now, $\frac{dy}{dx} = -0.020x + 0.602 = 0$

Or, $x = 30.1$

For $x = 30.10, \frac{d^2y}{dx^2} = -0.020 < 0$

Therefore, for maximization of conductivity removal efficiency, operating time = 30.10 min ≈ 30 min

Corresponding value of conductivity removal efficiency = $\{-(0.010)(30)^2 + (0.602)(30)\}$ % = 9.06%

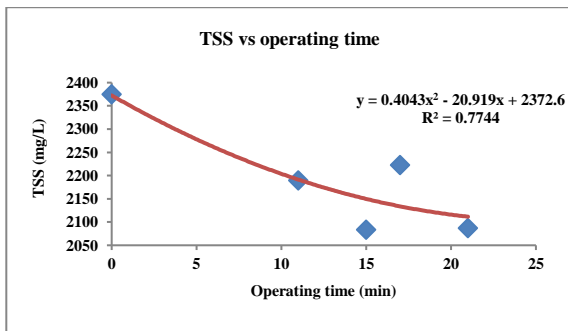**Effect of operating time on removal of total suspended solids (TSS)**

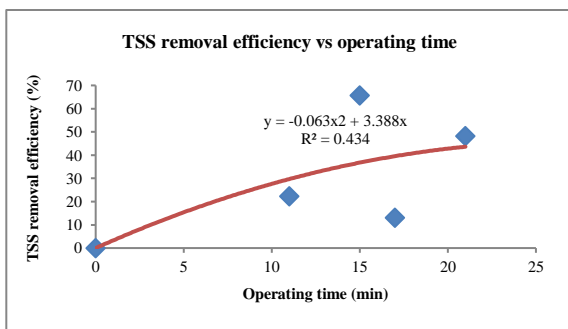**Figure 12:** Plot of TSS versus operating time

Figure 13: Plot of TSS removal efficiency versus operating time

From Figure 12 and 13, the equation for the variation of TSS removal efficiency with operating time is as follows:

$$y = -0.063x^2 + 3.388x; R^2 = 0.434$$

$$\frac{dy}{dx} = -0.126x + 3.388$$

$$\frac{d^2y}{dx^2} = -0.126$$

Now, $\frac{dy}{dx} = -0.126x + 3.388 = 0$

Or, $x = 26.89$

For $x = 26.89, \frac{d^2y}{dx^2} = -0.126 < 0$

Therefore, for maximization of TSS removal efficiency, operating time = 26.89 min ≈ 27 min

Corresponding value of TSS removal efficiency = $\{-(0.063)(27)^2 + (3.388)(27)\}$ % = 45.55%
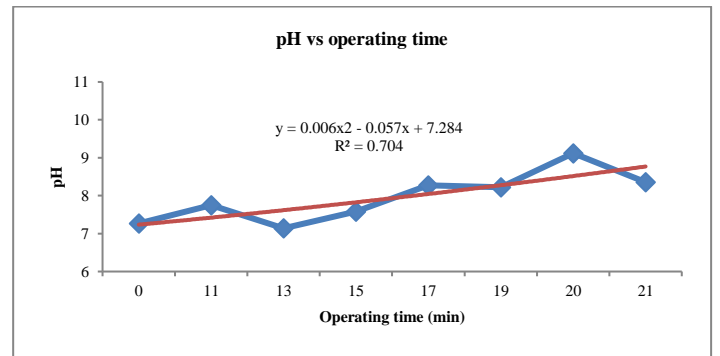
Variation of pH with operating time

Figure 14: Plot of pH versus operating time

During the decolorization of tannery wastewater by electrocoagulation, the pH quickly passed through 7 and increased to 11. Due to aphorism, aluminum hydroxide dissolves at high and low pH and has the lowest solubility at pH 6.2. When the pH reaches 6, most of the aluminum hydroxide precipitate out as Al-coagulant and adsorb the colorant. When the pH reaches 9, some of the Al-coagulant will dissolve and restore a portion of the adsorbed colorant into the solution. The restored color had an observable turbidity that did not settle after 5 minutes of centrifugation. It is believed that the turbidity is caused by the gelatin-like aluminum hydroxide that dissolves in the high pH aqueous solution. This does not occur in case of iron.

DISCUSSION

Some notable points regarding the experimental results for electrocoagulation treatment of the tannery wastewater have been furnished below:

- The sludge produced during electrocoagulation process was considerably less for them in comparison with other treatment processes.
- Some samples of water contain high levels of oxidizable inorganic materials which may interfere with the determination of COD. Because of its high concentration in most wastewater, chloride is often the most serious source of interference.

- The COD removal efficiency was found to be excellent due to the complete destabilization of the organic compounds through the formation of polyvalent polyhydroxide complexes by the highly charged cations.
- The color and turbidity removal efficiencies were also very impressive.
- Both the total dissolved solids (TDS) and conductivity removal efficiencies reached the value of only 7.6% for an operating time of 21 minutes (maximum operating time used in experimentation). The probable reason was that the electrolytic ally formed coagulants in situ the electrocoagulation reactor were not able to destabilize the dissolved salts, thereby resulting in quite low removal efficiencies for TDS and conductivity. The reasonably high concentration of Zn in the raw tannery wastewater might account for these phenomena.
- The total suspended solids (TSS) removal efficiency data obtained were quite scattered and thereby, induce high uncertainty. A removal efficiency value of almost 44% was obtained for an operating time of 21 minutes. There is a somewhat unique correlation between turbidity and total suspended solids, in many cases, this relationship may be proportional. But this was not reflected in our experimental data, probably due to the imperfect method for determining the total solids (TS) content of the treated water.
- The increasing trend of final pH with operating time was because of the increased concentration of OH^- ions along with less concentration of pollutants in the wastewater. The slight decrease in final pH for lower operating times was probably due to less concentration of free OH^- ions as a result of their involvement in the coagulating process for pollutants.

CONCLUSIONS

The present study attempted to investigate the applicability of an electrocoagulation technology in the treatment of tannery wastewater by using a fixed bed electrochemical batch reactor. It has been noted that EC is capable of having high removal efficiencies of color, chemical oxygen demand (COD), Biochemical oxygen demand (BOD), and achieving a more efficient treatment processes quicker than traditional coagulation and inexpensive than other methods of treatment such as ultraviolet (UV) and ozone. The application of EC process to tannery wastewater as an alternative pretreatment was found to be very effective.

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