

# Electro-coagulation Treatment of Wastewater from Paper Industry

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## Abstract

The objective of this paper is to find the optimal operating conditions for the removal of Total Suspended Solid (TSS) and Chemical Oxygen Demand (COD) of wastewater from paper industries by electro-coagulation techniques. The electro-coagulation process is more effective, quick and feasible method for treatment than chemical coagulation. The effect of key operational parameters, including the type of coagulant, initial pH, current density, and duration of treatment, on the percent removal of TSS and COD were investigated. Iron (III) Sulphate  $\text{Fe}_2(\text{SO}_4)_3$  (Fe), and Calcium Carbonate  $\text{CaCO}_3$  (Ca) salts were used in this study, alone, and as an aid to the electro-coagulation technique. Under the optimal operational conditions (initial pH =8,  $t = 30$  min and  $J = 60$  A/m<sup>2</sup>), the treatment of wastewater from paper industries by electro-coagulation alone has led to a removal of TSS and COD of 82% and 84% , respectively. The electro-coagulation process was then combined with the addition of the Fe and Ca salts at the same optimal operational conditions. The addition of Fe resulted in about 95% and 96% removal of TSS and COD, respectively. The addition of Ca resulted in about 90% removal for both TSS and COD. The results indicated that the two salts when combined with electro-coagulation technique have minor effect on the % removal of TSS and COD. The two salts have similar effect on the % removal. The Fe salt, however, has slightly more effect than Ca on the percent removal of TSS and COD.

Keywords: Wastewater from paper industries; Electro-coagulation (EC); TSS; COD; Electrode

## 1. Introduction

Pulp and paper industry is one of the major water-intensive chemical processes. Paper industry generates a huge amount of wastewater and creates economical and environmental problems.

They are distinguished contributors of pollutants to the environment in the form of black liquor. The effluent from pulp and paper industry contains high organic matter, suspended solids, strong color, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). The COD concentration in wastewater from paper industries could be as high as 11,000 mg/l (2). The strong blackish color is produced due to the complex compounds derived from polymerization between lignin-degraded products and tannin during various pulping/bleaching operations. The pulp and paper industry is the second largest industrial water consumer with a usage of about 35 m<sup>3</sup>/ton paper. The paper industry generates wastewater as high as 60 m<sup>3</sup>/ton of paper produced (2). In order to reduce the amount of fresh water employed, this industrial activity is currently being forced to adopt zero liquid effluent technologies in order to close the water circuits [1].

Conventionally, physical and chemical processes, such as adsorption, chemical oxidation and biochemical treatment methods treat the pulp and paper effluent. The low biodegradability index (BOD<sub>5</sub> / COD) typically of less than 0.4 of pulp and paper effluent clearly shows that this type of effluent cannot be treated effectively through conventional biochemical methods. On the other hand, the chemical methods generate considerable amount of sludge which itself needs further treatment. The drawbacks associated with the conventional techniques forced the industries/researchers for effective treatment method for complete degradation of pollutants [2, 3].

The above subsequent biochemical processes are usually installed in treatment plants for pulp and paper effluents. However, cardboard industries do not use wood to obtain the pulp, instead they use recycled paper especially cartoons and cardboards. Therefore, the composition of the effluents is not exactly the same. Instead, the pH is less basic, and more starch related products can be found rather than lignin. In addition, the recycled paper could contain appreciable amounts of glues, sticky adhesives, fillers, some dyes and residuals of and bleaching agents. Furthermore, the circulating flow results in an accumulation of these pollutants. Therefore, the quality of

circulating water decreases and finally cannot be further used without purification. For these reasons, the type and sequence of the treatment processes used to treat recycled paper effluents are not always the same as those for effluents of for pulp and paper industry. As wastewaters from recycled papermaking process are marginally biodegradable, with BOD/COD ratios between 0.4 and 0.5, they can be treated by biological means. Nevertheless, the amount of organic matter is so high that a conventional biological reactor is not feasible. The traditional treatment processes of pulp and paper industry; however, could be modified in order to optimize the treatment process conditions for recycled paper effluents [4, 5].

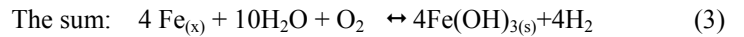
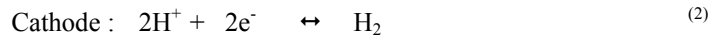
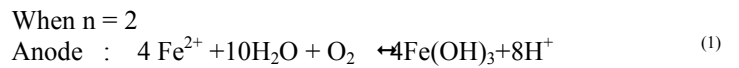
## 2. Description of electro-coagulation (EC) Technique

Electro-coagulation is an electro-chemical wastewater treatment technology. Electro-coagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium. In its simplest form, an electro-coagulation reactor may be made up of an electrolytic cell with one anode and one cathode [6]. The conductive metal plates of the cell are commonly known as 'sacrificial electrodes' and may be made of the same or different materials. This process has proven very effective in removing contaminants from water and is characterized by reduced sludge production, no use of aggressive chemicals, and ease of operation [7]. Colloid – destabilizing agents that effect the charge neutralization are produced by electrolysis in the EC process. For example, iron anodes are used to produce iron cations which have similar effect as the addition of Fe-based salt as a coagulant in conventional treatment systems.

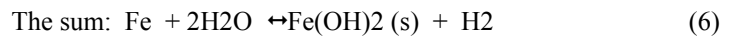
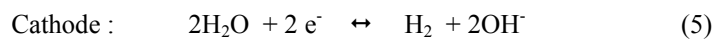
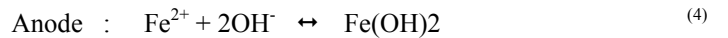
To understand the fundamental mechanisms of electro-chemical behavior of the system, it is important to describe the general electrolytic reactions. The basis of electro-coagulation is the in-situ formation of a coagulant species that can remove various pollutants from the water and wastewater being treated. The following are the three main mechanisms of electro-coagulation/flotation process: (1) electrolytic reactions at electrode surfaces, (2) formation of coagulants in the aqueous phase, (3) adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation. [8, 9]

When iron is used as anodes, upon oxidation in an electrolytic system, it produces iron hydroxide,  $\text{Fe(OH)}_n$

where  $n = 2$  or  $3$  [10]. The main reactions that occur at the electrodes are shown in equation (1) through (6):



When  $n=3$



Similarly, ferric ions generated by electro-chemical oxidation of iron electrode may form monomeric ions, and polymeric hydroxyl complexes, namely:  $\text{Fe(H}_2\text{O)}_6^{3+}$ ,  $\text{Fe(H}_2\text{O)}_5(\text{OH})_2^+$ ,  $\text{Fe(H}_2\text{O)}_4(\text{OH})_2^+$ ,  $\text{Fe}_2(\text{H}_2\text{O)}_8(\text{OH})_2^{4+}$  and  $\text{Fe}_2(\text{H}_2\text{O)}_6(\text{OH})_4^{4+}$  depending on the pH of the aqueous medium [11,12,13]

## 3. Experimental Work

### 3.1. Materials

The raw wastewater sample was obtained from the Jordan paper and Cardboard Factories Co. Ltd. (JPCFCL) located in the City of Zarka. The JPCFCL produces about 550 m<sup>3</sup> of wastewater per day, which is currently treated with the conventional method of coagulation and flocculation process. The wastewater sample was collected from the primary sedimentation tank effluent of the treatment plant and kept in the refrigerator at 4 °C. The characteristics of wastewater are given in Table 1.

Table 1  
Chemical and physical properties of JPCFCL's Wastewater

Parameter	Value
pH	7.56
Total dissolved solid TDS mg/l	8125
Total suspended solid TSS mg/l	3446
Total solid TS mg/l	11571
COD mg/l	2950
Electrical conductivity EC $\mu\text{s/cm}$	9,340

### 3.2. Procedure

The electro-coagulation (EC) setup is shown in figure 1. The electro-coagulation unit was constructed from Plexiglas having a dimension of 0.15m×0.25m×0.2 m. A low-cost iron plate with a total surface area of 0.02 m<sup>2</sup> was used for the sacrificial electrodes, arranged in monopolar configurations. Six iron plates were constructed in the electrochemical reactor three electrodes were connected as anodes and three as cathodes. The distance between plates was fixed at approximately 3 cm. The electrodes were connected to a DC power supply (GW. GPC-3030D) providing 0-30V (0-6A) with galvanostatic operational options for controlling the current density.

The total volume of wastewater sample in each experiment was approximately 5 dm<sup>3</sup>. The samples were mixed with constant stirring speed of 200 rpm. All samples for analysis were taken from the effluent located 5 cm above the bottom of the reactor. The samples were then analyzed after sedimentation. Initially, the effects of working parameters, such as initial pH, coagulants, current density and duration of treatment, were studied in an attempt to achieve the optimal treatment conditions to effectively treat the wastewater. The optimized parameters were then applied for the treatment of the remaining wastewater samples to validate the treatment efficiency. All experiments were repeated two times, and the experimental error within 3%.

### 3.3. Analytical method

COD measurements were determined according to the Standard Methods for Examination of Water and Wastewater. The total suspended solids (TSS) were obtained by centrifugation then drying at 105 °C [14]. The pH was measured with a pH meter 3151 WTW pH meter (WTW GMBH, Germany). Conductivity was determined by a conductivity meter (Lutron CD-4303). The pH and conductivity was calibrated using NaOH or H<sub>2</sub>SO<sub>4</sub> (Sigma).

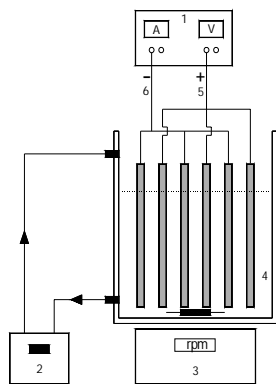


Figure 1. Experiment set up (1) power supply, (2) water circulator, (3) magnetic stirrer, (4) wastewater reservoir tank, (5) cathode, (6) anode

## 4. Results and Discussion

### 4.1 Effect of flocculants

The efficient removal of pollutants by the electro-coagulation technique requires an effective coagulants formation step in order to achieve better coagulation between the coagulants generated in the system and the pollutants. Thus, adding chemicals coagulant aids not only increase the coagulation process but also increase the conductivity [6, 15]. The effect of adding coagulant aids was explored using two salts, Fe and Ca. The salt coagulant aids were added at a dose ranging from 1–5 mg/L. The chosen dose of the selected salt was directly added into the wastewater sample. Subsequent analyses of the residual levels of TSS and COD was then measured.

The experimental results indicated that the two coagulant aids were effective at concentrations starting from 1mg/L for both TSS and COD removal. The two coagulant aids yielded similar TSS and COD removal levels for low concentration of pollutants. The Fe coagulant aid; however, provided slightly better removal of TSS and COD levels at all concentration of coagulant as shown in fig. 2(a) and 2(b). For example, the TSS removal by dose 2mg/l of Fe and Ca were 10% (344.6 mg/l) and 6% (206.7 mg/l), respectively. The COD removal by dose 2mg/l of Fe and Ca were 22% (649 mg/l) and 16% (472 mg/l), respectively. The percent removal of a pollutant was calculated using the following equations:

$$\text{CODred} = (\text{COD}_i - \text{COD}_f) / \text{COD}_i$$

$$\text{TSS red} = (\text{TSS}_i - \text{TSS}_f) / \text{TSS}_i$$

### 4.2 Effect of initial pH of wastewater

In the electro-coagulation process, the pH is an important parameter influencing the performance of the electro-chemical process [13, 16, 17]. The effect of the initial pH of the wastewater was studied in range of 4–9 using a fixed current density of 60 A/m<sup>2</sup> and circulating flow rate of 0.2 l/min. The contact time was varied between 10 and 90 minutes. Figure 3(a) shows the percent removal of TSS vs. contact time for various values of initial pH. Figure 3(b) shows the percent removal of COD vs. contact time for various values of initial pH. In the range of initial pH of 4–9, the TSS and COD percent removals ranged between 40 and 80%, (1378.4–2756.8 mg/L) and 37 to 84%, (1091.5–2360 mg/L) respectively.

The minimum percent removals of TSS and COD were achieved at acidic condition with initial pH = 4. The maximum percent removal of TSS and COD were achieved at alkaline condition with initial pH = 8. The maximum removal efficiencies of TSS and COD at pH = 8 were 80% (2756.8 mg/L), and 84% (2360mg/L), respectively. The maximum percent removal was reached at approximately 30 min for all pH conditions.

The percent removal of both TSS and COD at initial pH of 4 and 9 were lower than the % removal achieved at the acidic conditions with initial pH of 6 and 8. This behavior has been observed by many investigators and are thought to be attributed to an amphoteric behavior of  $\text{Fe}(\text{OH})_3$ . This behavior could also be due to the presence of polyhydroxyl iron (III) complexes at these pH condition which are reactive and can couple with the pollutants in wastewater leading to lower amount of pollutants in wastewater [11,18].

### 4.3 Effect of current density

As have been already observed by several authors [13, 16], the applied current density has influence on the efficiency of the electro-coagulation process. The effect of current density was explored in this study to confirm or refute the previous findings. The supply of current influences the amount of ferrous ions produced from the electrodes. At high current, the extent of anodic dissolution of iron increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, bubble generation rate increases and the bubble size decreases with increasing current density. These effects are both beneficial for high pollutant removal, but it wastes electrical energy in heating up the water [16, 19].

Experiments for this study were carried out with current density ranging from 20 to 80 A/m<sup>2</sup>, with a fixed circulating flow rate of wastewater of 0.2 l/min and an initial pH of 8. The experimental results are shown on figures 4(a) and 4(b). It can be concluded from figure 4(a) and 4(b) that the percent removal of TSS and COD increased as the current density increased from 20 to 80 A/m<sup>2</sup>. The rate of TSS and COD removal was very high up to contact time of 30 minutes for all current densities. The rate of removal then attained a constant level after 30 min. The maximum percent removal of TSS ranged from 71% (2446.6 mg/l) at current density of 20 A/m<sup>2</sup> to 82 % (2825.7mg/l) at current density of 80 A/m<sup>2</sup>. The maximum percent removal of COD ranged from 69% (2035.5 mg/l) at 20 A/m<sup>2</sup> to 84 % (2478mg/l) at 80 A/m<sup>2</sup>. The maximum percent removal for both TSS and COD was achieved at contact time of approximately 30 minutes for all current densities.

However, at the highest tested current density of 80 A/m<sup>2</sup>, the degree of TSS reduction slightly decreased

with operating times longer than 30 min. This might be attributed to the fact that a large amount of iron ions was produced at this high current density leading to the resurgence of TSS in the treated wastewater. With respect to reduction in the COD levels, increasing the current density led to an increased removal of COD, up to contact time of 45 minutes. Thereafter, the COD levels slightly increased from 45 min onwards for all applied current densities. This behavior presumably could be due to the fact that large amounts of iron (II) ions were generated at long electrolysis times which can react with the dissolved oxygen in the wastewater. This leads to lowering the amount of oxygen in the treated wastewater [20, 21].

### 4.4 Effect of operating time and flocculants

The effect of operating time and the addition of the salt coagulant, Fe and Ca, on the removal efficiency of the COD and TSS was investigated in this experiment. The experimental operation conditions were a fixed current density of 60 A/m<sup>2</sup>, a circulating flow rate of wastewater of 0.2 l/min, and initial pH of wastewater of 8. The effect of adding 2 mg/l of Fe and Ca was considered. The percent removal of TSS and COD as a function of contact time are shown in figure 5. This figure shows that an increase in time from 0 to 30 minutes yielded an increase in the removal efficiencies of TSS and COD. The rate of TSS and COD removal was very high within 30 minutes and nearly steady after 30 minutes. The optimum operating time is 30 min since the highest removal efficiencies of TSS and COD were observed at this time. The TSS removal with Fe and Ca. are 95% (3276.7 mg/l) and 90% (3101.4 mg/l) respectively. The COD removal with Fe and Ca. are 96% (2832 mg/l) and 90% (2654.5 mg/l) respectively. The clear suggestion from these results is that, under these conditions the addition of  $\text{Fe}_2(\text{SO}_4)_3$  is better than  $\text{CaCO}_3$  in the electro-coagulation process and may be advantageous. Although it may lead to the ability to reduce the electro-coagulation time to attain the degree of reduced TSS and COD [22].

Finally, the energy consumptions is given in figure 6. The energy consumption per Kg of TSS and COD removed showed increasing trend with high rate for both pollutant at the first 15 min and then increasing very slow. The energy consumed to remove 1 kg of each pollutant (TSS and COD) during the electro-coagulation was calculated with the following equation:

$$E \equiv \frac{V \times J \times t}{60 \times v \times (C_o - C)} \quad (7)$$

Where E The energy consumed to remove 1 kg of each pollutants (KWh / Kg), V is the applied voltage (V), J the current amount (A), t the electrolysis time (min), Co the

initial concentrations ( $g/l$ ),  $C$  the concentration value of pollutants ( $g/l$ ) at time  $t$ , and  $v$  is the volume of the sample.

## 5. Conclusion and recommendations

The efficiency of the Electro-coagulation treatment methods for the treatment of wastewater from paper industries was considered in this study. Three treatment methods were considered. The wastewater was first treated using iron salts or carbonate chemical coagulants alone. Then wastewater was treated using electro-coagulation method alone. Finally the electro-coagulation with the addition of the chemical salts was studied.

The traditional method of chemical treatment using iron salts as a chemical coagulant showed that a TSS and COD removal of 20%, 15% was achieved, respectively. The use of Ca salt alone resulted in TSS and COD removal of 35% and 25 %, respectively.

A low-cost iron plates were used for the sacrificial electrodes in the electro-coagulation method. The effect of the operation conditions on the treatment efficiency was investigated. The optimum condition of treating such wastewater were as follows: a circulating flow rate of 0.2 l/min, 60A /m<sup>2</sup> current density, operating time of 30 min and pH=8. These optimum conditions of electro-coagulation technique alone yielded TSS and COD removal of 84% and 82%, respectively. Finally, combining the chemical salt coagulants with the electro-coagulation technique resulted in improved removal efficiency. The addition of the iron salt was found to be more appropriate to EC than the addition of Ca. The TSS removal with Fe and Ca were 95% and 90%, respectively, and the COD removal with Fe and Ca were 96% and 92%, respectively.

The findings of this study confirmed the findings of previous researches as described in background section of this paper. Based on these findings, it could be concluded that the best option for the treatment of the wastewater from paper industries is the electro-coagulation technique, at the optimal operating condition, with the addition of the iron salt.

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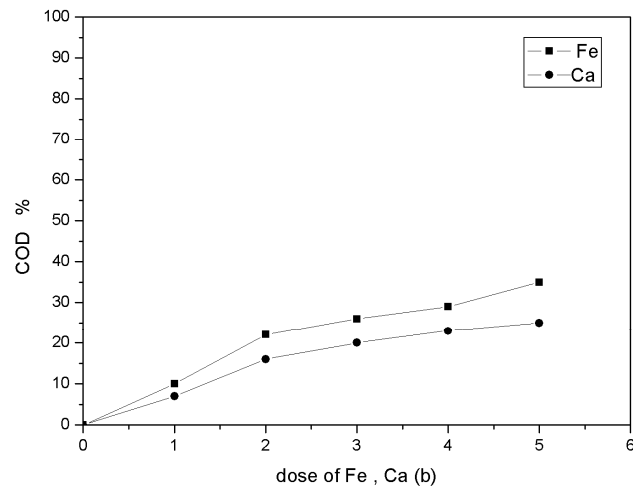
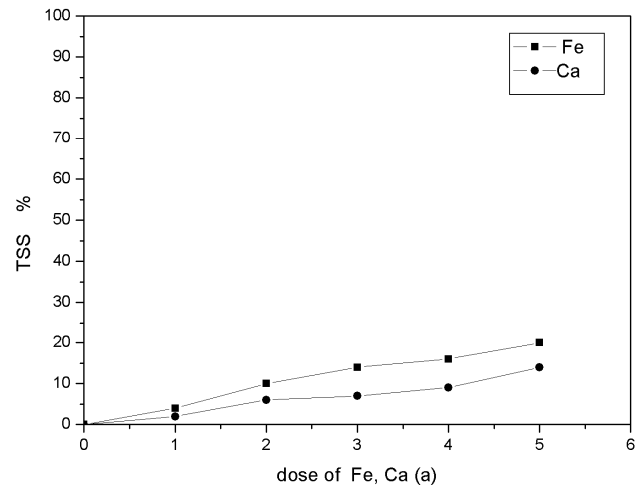


Fig.2. Removal percentages of TSS (a) and COD (b) by  $Fe_2(SO_4)_3$  (Fe) and  $CaCO_3$  (Ca)

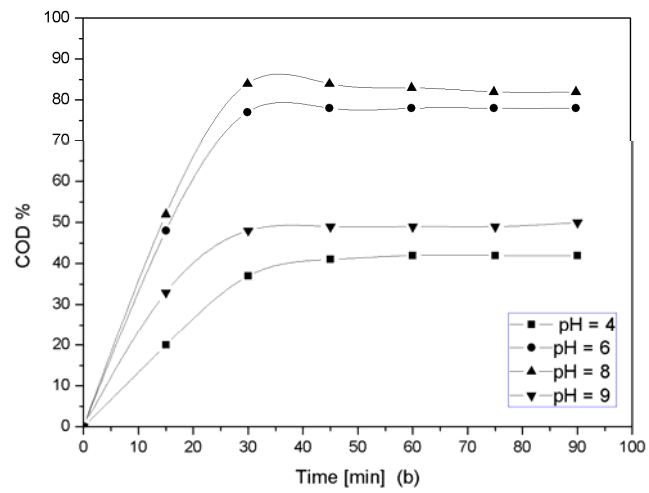
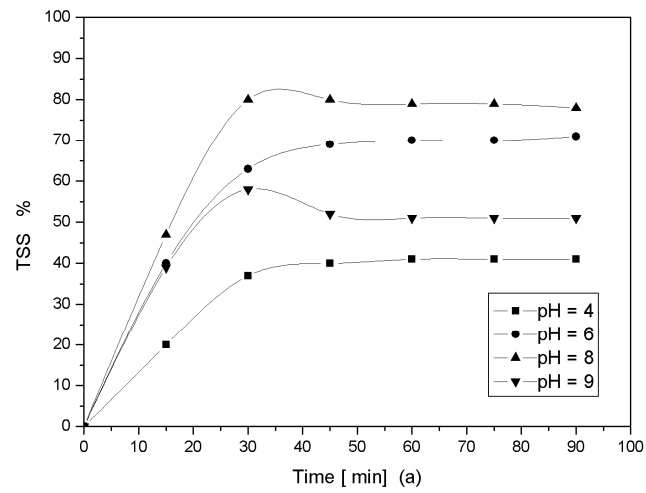


Fig.3. Removal percentages of TSS (a) and COD (b) as a function of time and pH

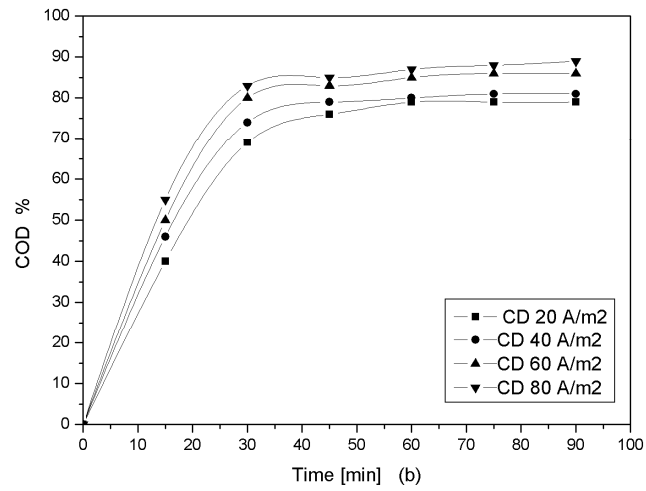
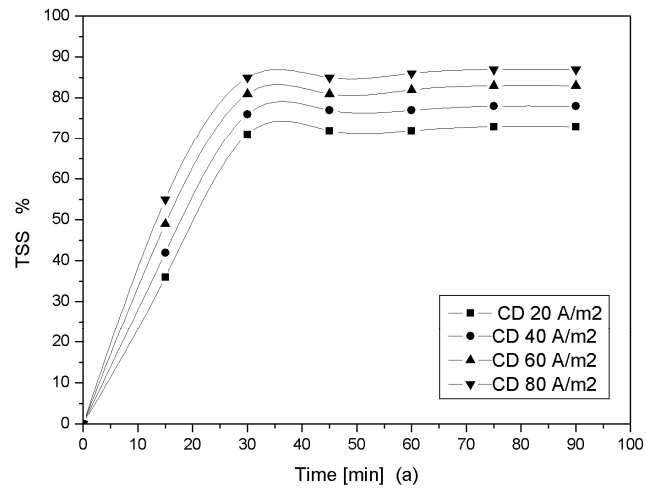


Fig.4. Removal percentages of TSS (a) and COD (b) as a function of time and current density



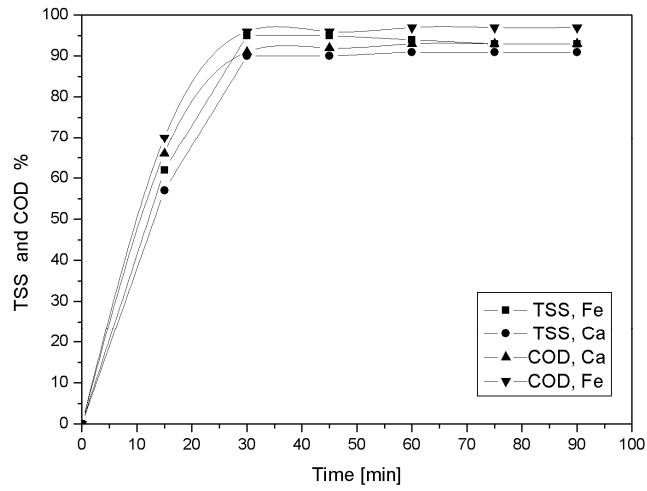


Fig.5. Removal percentages of TSS and COD as a function of time and current density

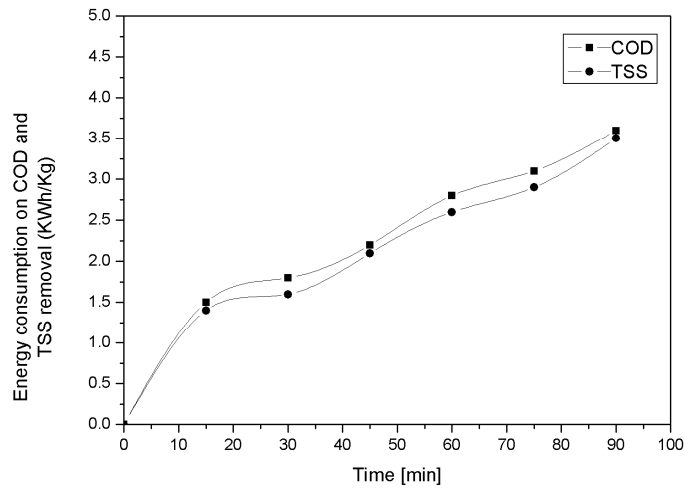


Fig.6 .Effect of electro coagulation time on energy consumption