Pharmaceutical Waste Water Treatment By Electrocoagulation Process

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Abstract: The aim of this study is to optimize the organic matter reduction condition for the reclamation of pharmaceutical wastewater from an industry by the electro-coagulation process. The electrocoagulation was used to determine the effect of pH value range 4-7, electrode distance range 1-3 cm and current density 1.6-30 mA/cm^2. Under the optimal conditions of reaction time of 3.5 h, pulse duty cycle of 0.3, pulse frequency of 1.0 kHz, current density of 19.44 mA/cm^2, and electrode distance of 2.0 cm, gives the removal efficiencies of BOD and COD up to 70.0% and 69.6%, respectively. The experimental observations were in reasonable agreement with model value. The ultimate goal is to be able to substitute for the existing treatment facility that is composed of a series of complicated processes (e.g., flotation, sand filtration, carbon filtration, and diatomaceous filtration).

Keywords: Chemical process, electrocoagulation, BOD & COD removal, physical process, wastewater.

I. INTRODUCTION

Water is a basic necessity of life & water is a unique substance in our discovered universe. over two thirds of Earth's surface is covered by water Poorer water quality means water pollution

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures.

Among water pollutants, organic pollutants are important due to their high quantities and ranges in water resources, an elevated concentration, specific properties, and incomplete removal by conventional water treatment plants. Natural organic matter (NOM) is a complex mixture of different organic compounds originating from both natural and anthropogenic sources and is present in all water bodies. The presence of Natural organic matter not only affects some water quality parameters such as color, but also interferes with the performance of treatment processes such as coagulation, adsorption, and membranes. It also has negative effects on the distribution system. In addition, if chlorine is used in the disinfection process, Natural organic matter reacts with chlorine and may form disinfection by-products. There are many methods such as chemical coagulation and sedimentation, oxidation, adsorption, ion exchange, and filtration using various membranes to remove Natural organic matter from aqueous environments. Electro coagulation (EC) process is an environmentally-friendly method. This method has some advantages: no need for chemicals addition; requires simple equipment and less space for installation; simple operation; no need for pH adjustment; low retention time. Furthermore, it produces sludge with low water content in comparison with chemical coagulation,. In addition, this process has lower effluent total dissolved solids compared with chemical treatment methods, and can remove the smallest colloidal particles. This can be achieved by establishing an electrical current between the electrodes. Subsequently, the sacrificial anode corrodes due to the applied current while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. In the present study, the application of an EC treatment technique using combined iron and aluminum electrodes was studied at laboratory scale to remove Natural organic matter compounds.

Theory of Electro-coagulation

Electro-coagulation (EC) is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. EC process the coagulating ions are produced 'in situ' andit involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the 'sacrificial electrode',(ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The destabilization mechanisms of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and maybe summarized as follows:

- Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.

- Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic inter-particle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.

• Floc formation; the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium.The solid oxides, hydroxides and oxy-hydroxides provide active surfaces for the adsorption of the polluting species.Electro-coagulation has been successfully employed in re-moving metals, suspended particles, clay minerals, organic dyes, and oil and greases from a variety of industrial effluents.

In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions:

• Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze topolymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the an-ode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electro-flotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ.

• Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogenat the cathode. These bubbles attract the flocculated particles and, through natural buoyancy, float the flocculated pollutants to the surface.

In addition, the following physiochemical reactions may also take place in the EC cell:

• Cathodic reduction of impurities present in wastewater.

• Discharge and coagulation of colloidal particles.

• Electro-phoretic migration of the ions in solution.

•Electro-flotation of the coagulated particles by O_2 and H2bubbles produced at the electrodes.

• Reduction of metal ions at the cathode.

• Other electrochemical and chemical processes.

Characterization of the Pharmaceutical Waste Water Sample

The physical and chemical characteristics of the collected effluent from the pharmaceutical are shown in Table 3.1. The calculated biodegradability index (taken as BOD/COD ratio) is 0.245, caused by the high COD value. Such index indicates the presence of refractory substances, probably stable organic compounds, which can hardly undergo biological degradation. Reports have shown that at biodegradability index below 0.3 the sample is not adequate for biological treatment. Moreover, the high COD value (49,720 mg L^{-1}) implies that the natural coagulation of this effluent is not convenient (must be lower than 800mgL^{-1}), therefore it was proposed the EC as preliminary method.

Additionally data in Table 1 shows the presence of high quantities of nitrogen compounds and sulfate ions whose presence can cause rivers and lakes eutrophication. The concentration of Cl^- ions is also high.

Table 1: Typical Physical and Chemical Characteristics of pharmaceutical waste water.

PARAMETER	VALUE
pH	7.11
Conductivity (mS /cm)	8.0
Turbidity (NTU)	225
Total Dissolve Solid (TDS)mg/lit	22,500
Total Suspended Solid (TSS) mg/lit	10,250
Total Solid (TS) mg/lit	32,000
COD (mg/ L)	49,720
BOD5(mg/ L)	12,400
BOD5/COD (biodegradability)	0.245
Sulfate (mg/ L)	800.7

II. MATERIALS & METHODS

The EC apparatus used in this investigation consists of a alternative arrangement of iron and aluminum electrodes in series (dimensions: 10 cm × 10 cm × 0.20 cm of thickness), area approximately 100cm^2, with the electrodes distanced by 2.0 cm. Electrodes were connected to **a dc** power supplier Fig. 1 .Electro-coagulation apparatus diagram of 5 A and 12 V, operating with current density of 763Am^{-2}.A reactor made up of fiber of 5 Liter volume was used for the same electro-coagulation process. The investigation of the desirable electro-coagulation time was carried out on a batch-type system by using 4500 ml of original PWW samples (as collected from the industry) at pH of 4.0, 5.0, 6.0, 7.0 and 10.0. All pH adjustment realized in the present work was done by HCl and NaOH addition under stirring.

The effect of various parameters like pH, electrode distance and stabilization time is observed over the BOD, COD and turbidity reduction. Out of that the optimum operating conditions for the maximum BOD and COD reduction was observed.

Figure1: Schematic diagram of Electro coagulation setup

III. RESULT & DISCUSSION

Comparison of Al and Fe Electrodes

Electrode materials have significant effects on the treatment efficiency of EC process. High efficiency, easy to attain and non-toxic were the most important requirements for materials to be considered as electrodes.

Al and Fe were usually used as anodes in EC systems, because they could generate hydroxides, oxy hydroxides and polymeric hydroxides, which could successfully destabilize colloidal suspensions and emulsions, and form flocs. that could be removed by sedimentation, filtration or flotation. The removals of COD and BOD in EC process with Al and Fe electrodes were presented in Fig. 2.

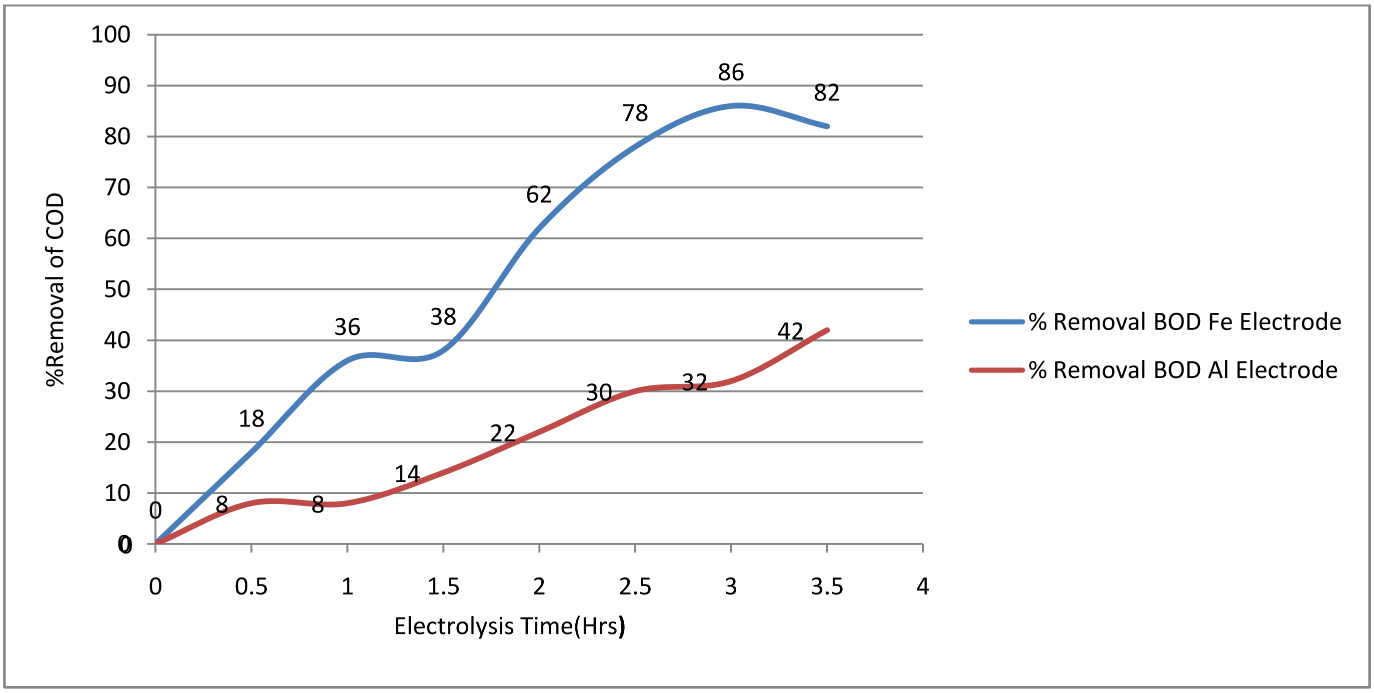

Figure 2: The removal efficiencies of BOD versus time with Al and Fe electrodes

It showed that the removal efficiencies of COD and BOD were significantly higher by using Fe electrode than by using Al electrode. With Fe electrode, the removal efficiency reached above 80% within 3.5 h, which was about twice as high as with Al electrode. It might be attributed to the synergetic effect of the following causes: on one hand, Fe hydroxides were faster formed and of a higher density than Al hydroxides, and settled quite fast after electrode-conducted EC; on the other hand, the dissolution current efficiency was far higher for Al than for Fe electrode. The electrochemical equivalent was 335.6 mg/Ah for Al, while the value was 1041 mg/Ah for Fe, which was about three times of Al. Consequently, more coagulants would be produced by Fe anodes when the same electric charge passed.

From Figure 2 it was found that the maximum reduction in the value of BOD and COD was obtained with Fe electrode. This does not mean that the Al electrode is less effective because there are many side effect of using Fe electrodes. First, on using Fe electrode there is a problem of corrosion, second the dissolution current efficiency of Fe electrode is less than Al.

Alternative series arrangement of Al and Fe electrodes

We use the alternative series arrangement of Fe and Al electrode (Al worked as sacrificial anode).The removal efficiency of COD and BOD with respect to time using alternative series arrangement of Al and Fe electrodes**.** Figure 3 shows that for an electrolysis time of 3.5 hr the BOD and COD reduction is 70 and 65.6 % respectively.

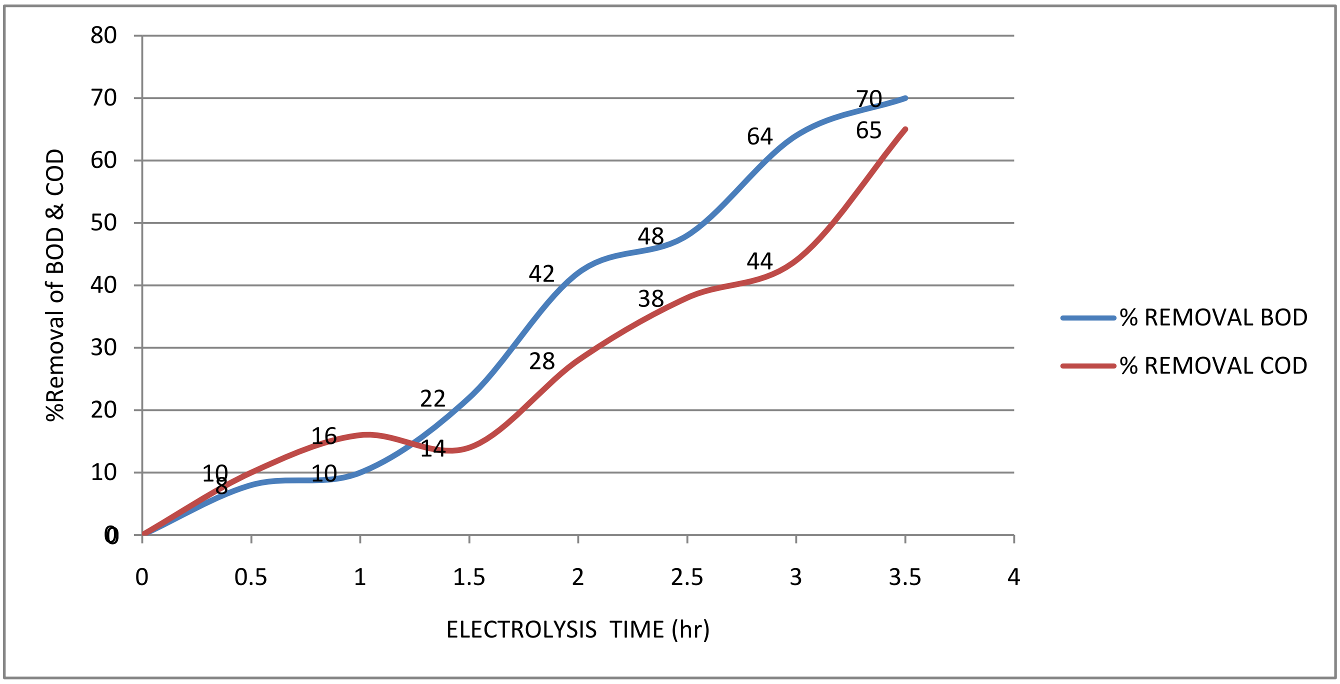

Figure 3: The removal efficiencies of COD and BOD versus time with alternative series arrangement

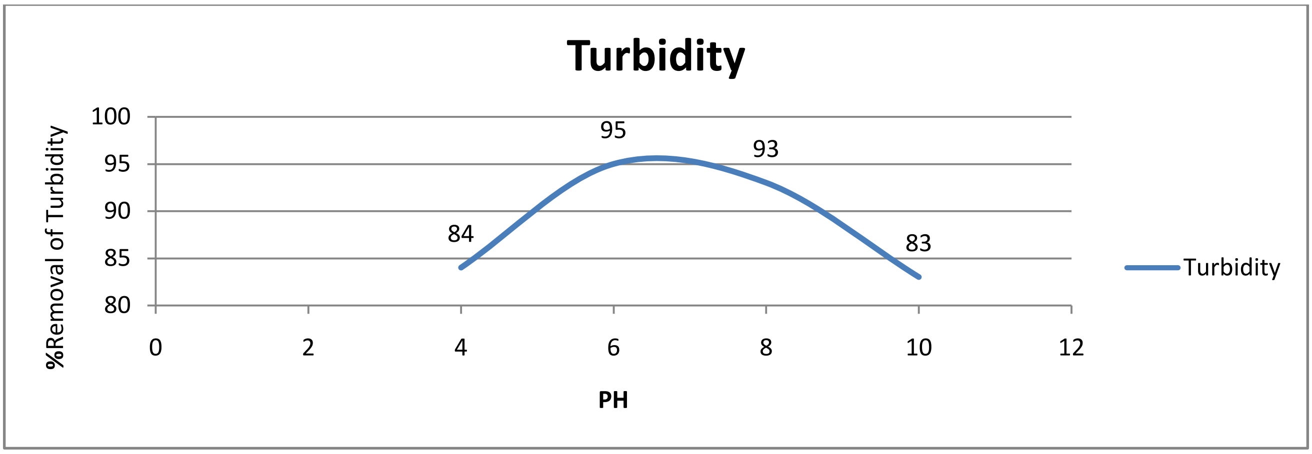

Figure 4: Turbidity removal of EC treated water at several pH

Effect of the pH on Turbidity

The effect of the initial pH on the EC treatment using iron and aluminum electrodes (as cathode and anode) was investigated at constant 763Am^{-2} current density and 30 min of electrolysis. According to this data, the COD removal percentage oscillates between 78% and 82%, showing relative standard deviations ranging from 2% to 6%; the test confirmed the absence of the initial pH influence on these COD results. However, the turbidity removal percentage ranges between 85% and 95%, with a relative standard deviation ranging from 3% to 5%,

Effect of the pH on COD Removal

The COD removal of EC treated water at several pH, applied by 30 min and 1600 Am-2is shown in fig.5. There are no differences in those extraction efficiency percentages at initial pH 5.0–7.0 (region corresponding to the highest turbidity removal). The pH 6.0 was taken as optimum initial pH, which is employed for all subsequent EC experiments.

At pH 6.0 the main Fe n^+ species formed in solution is Fe $(OH)_2^+$, which can neutralize organic substances and suspended materials (usually presenting negative charge density) leading them to aggregation process. At higher pH (alkaline medium), instead of Fe $(OH)_2^+$ (prevalent species at pH5) other species prevail, such as $Fe(OH)_3$ (prevalent species at pH 8),a hydrophobic compound which can form polymeric entities leading the contaminants to aggregate.

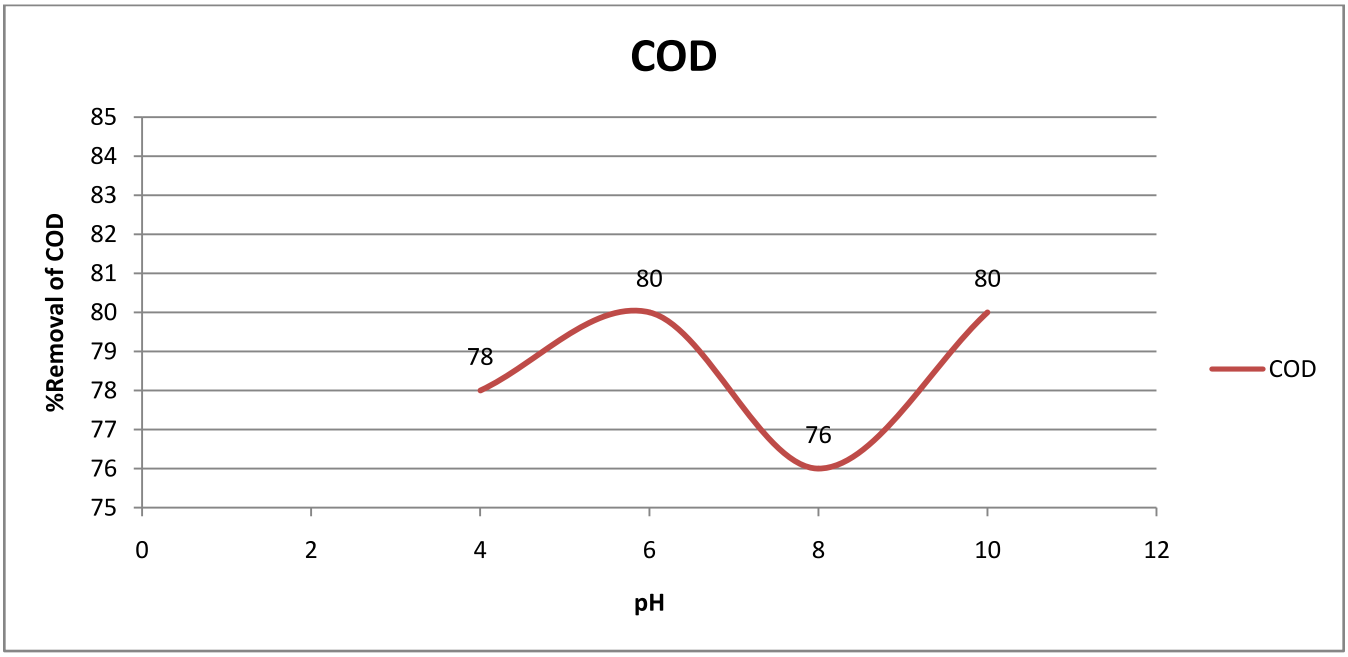

Figure 5: COD removal of EC treated water at several pH, applied by 30 min and 1600 Am^{-2}.

At a pH higher than 10,the $Fe(OH)_4^-$species is the main product; this species is not an effective coagulant agent.

This effect is important once the experimental pH increases during the EC application (Fig.5.4) mainly due to the

hydroxide ions produced in the cathode, from water reduction (forming H_2 and OH^-). After 60 min the pH exceeded 10 reaching approximately 10.5 after 100 min. Despite this, it is considered that iron derivatives sustain their coagulant efficiency until pH 11.

Effect of the electrode distance

Electrode distance played a significant role in the EC process. As showed in Fig. 6, the removal efficiencies of COD and BOD ascended at first and then fell down with the increase of the electrode distance. The removal rates of COD and BOD reached 68.0% and 72.0% separately at the optimum electrode distance of 2.0 cm. Short electrode distances inhibited the ion diffusion between electrodes, and reduced the coagulation efficiency. On the contrary, ion generation rate slowed down with the increase of the electrode distance, and it was prone to generate larger and looser flocs that could enhance the coagulation effect. However, the electrode reaction rate dropped at electrode distance above 2.0 cm. In addition, there was a linear relationship between electrode voltage gradient and electrode distance, and the electric resistance and voltage increased with the increase of the electrode distance, which caused higher energy consumption. Therefore, the electrode distance of the EC process should be kept at about 1.5–2.5 cm for efficiency, energy consumption and resource considerations.

Effect of current density on BOD and COD

Current density directly affected the treatment efficiency in the electrochemical process. It could not only determine the production rates of flocs, but also change the size and pace of bubbles produced, thus affecting the growth of flocs. The COD and BOD removals versus the current densities were presented in Fig. 7 Obviously, the removal efficiencies of COD and BOD improved gradually with the increase of current density. Higher current density would generate significant amount of flocs, which in turn would trap organic matters and thus enhance COD and BOD removal efficiencies. Moreover, bubble generation rates increased and the bubble sizes decreased with current density. Those effects were beneficial for pollutant removal. In addition, higher current density could provide some oxidation action.

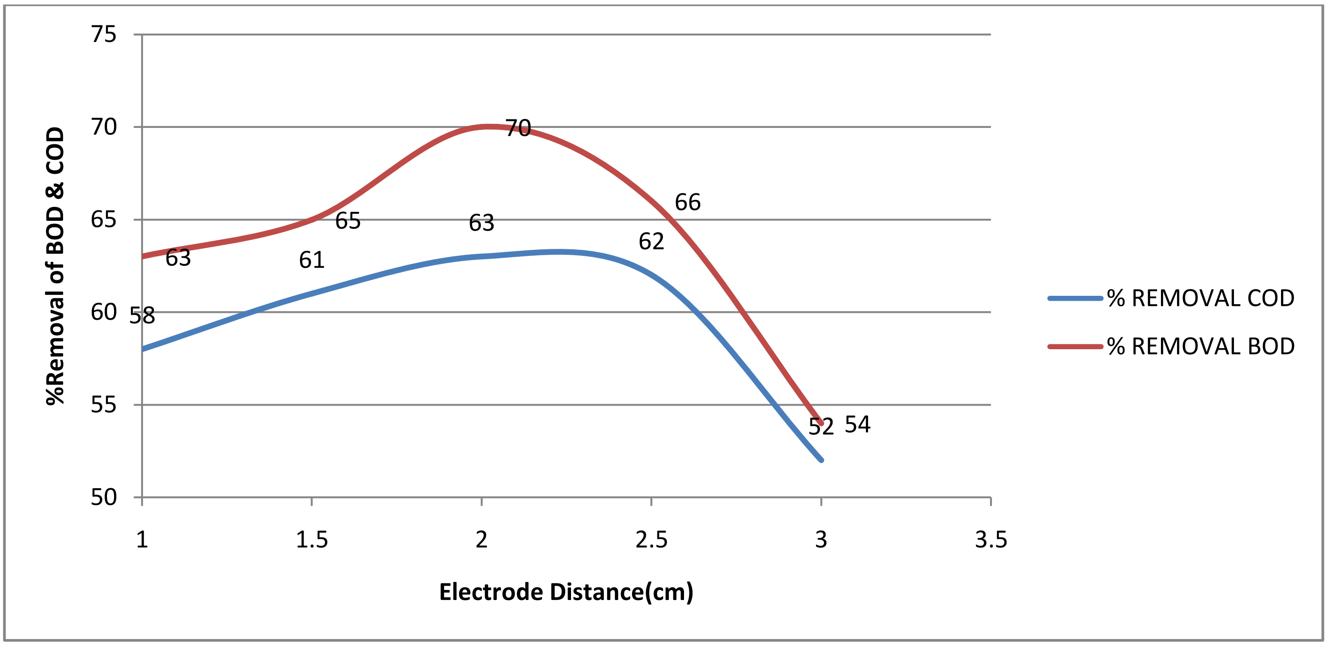

Figure 6: Effect of electrode distance on COD and BOD removal

The removal efficiency of COD rose from 68% to 82% when the current density ascended from 11.1 mA/cm^2 to 19.4 mA/cm^2 (current from 2 A to 3.5 A), followed by a similar variation of BOD removal. The removal efficiencies of COD and BOD reached the maximum percentages of 87.3% and 96.3% separately at current density of 27.8 mA/cm^2 (current of 5 A). However, the cell voltage went up with current density, resulting in the increases of energy and electrode material consumption. Therefore, the optimum current density of 19.4 mA/cm^2 (current of 3.5 A, voltage of 11.2 V) should be selected considering efficiency and cost of the process.

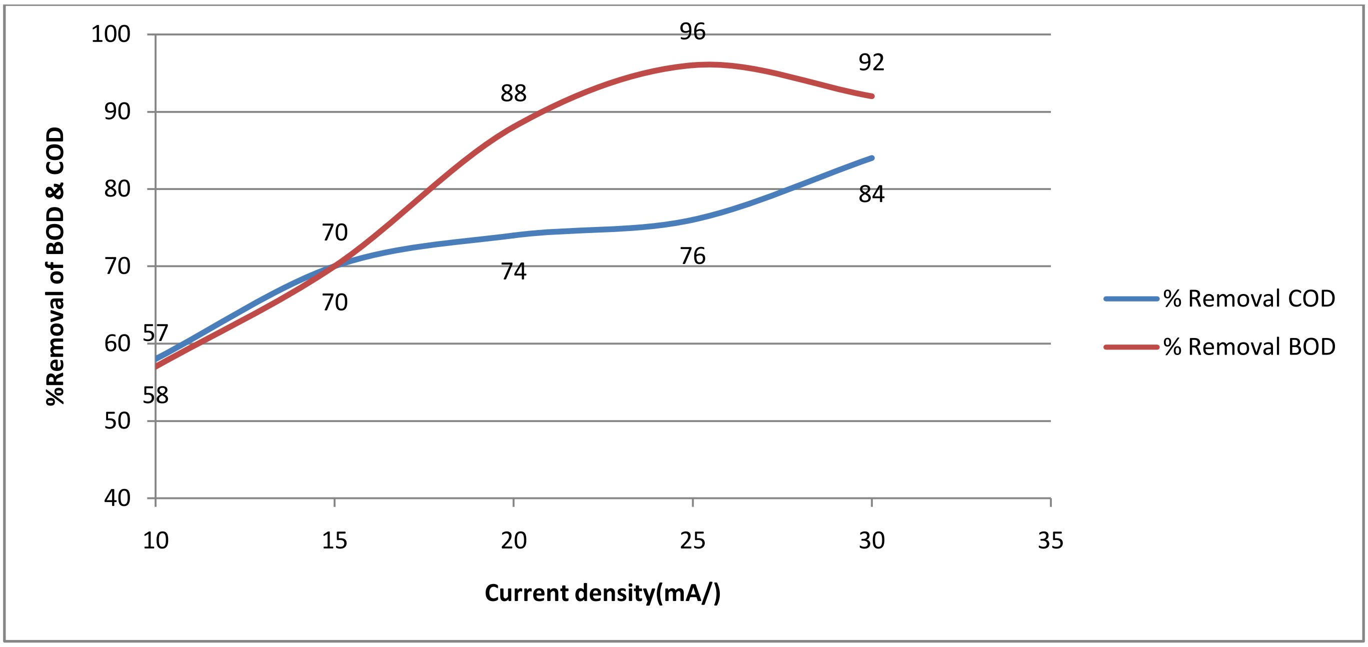

Figure 7: Effect of current density on COD and BOD removals

Overall results of EC

This Experiment showed that with Fe electrode the removal efficiencies of pollutants were significantly higher than that with Al electrode. By using alternative arrangement of Fe and Al electrode and simulated wastewater, the effects of pH, current density, electrode distance and electrolysis time on the removal efficiencies of BOD and COD were investigated. Under the optimal conditions of reaction time of 3.5 h, pulse duty cycle of 0.3, pulse frequency of 1.0 kHz, current density of 19.44 mA/cm^2, and electrode distance of 2.0 cm, the removal efficiencies of BOD and COD reached 70% and 69.5%,

Table 2: Overall result of electro-coagulation process for treatment of Pharmaceutical Waste Water

S.N.	EXPERIMENTAL RESULTS		
	CHARACTERISTICS	Effluent	Electro-coagulation
1.	pH	7.11	7.5
2.	Color	Yellowish brown	Lighter than initial
3.	Odor	Medicinal	Less
4.	Temp (°C)	40	34
5.	Turbidity(NTU)	225	99
6.	BOD_5(mg/lit)	12,400	3700
7.	COD (mg/lit)	49,720	13650
8.	BOD_5/COD	0.245	0.271
9.	Total Solid (mg/lit)	32,000	2750
10.	TDS (mg/lit)	22,500	1700
11.	TSS (mg/lit)	10,250	980
12.	Hardness (mg/lit)	261	110

IV. CONCLUSION

The analysis of results demonstrates that total suspended solids, organic matter may be removed from Pharmaceutical wastewater by the electro coagulation process. The technology demonstrated to be efficient allowing turbidity, organic matter and total suspended solids removal efficiencies. The results showed that treatment efficiencies based on treatment time, applied current and strength of Pharmaceutical waste water.

From the experimental results it was observed that the Electro coagulation reactor may be used for the treatment of Pharmaceutical waste water containing variable strengths of organic load and turbidity.

1. This Experiment showed that with Fe electrode the removal efficiencies of pollutants were significantly higher than that with Al electrode. By using alternative arrangement of Fe and Al electrode
2. The results shows that removed efficiency of BOD and COD reached 70% and 69.5%,

   in 3.5 Hr by using Fe Electrodes.

3. Turbidity removal percentage ranges between 85 to 95% at 24 hr in 6 pH.
4. The optimum electrode distance was 2 cm and optimum current 2Am to 3.5 Am best optimum in 6 pH
5. The best removal of BOD & COD has been reached from 87% at current dencity 27.8 mA/cm2 (5Am)

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NOMENCLATURE

BOD Biological Oxygen Demand
COD Chemical Oxygen Demand
EC Electrocoagulation
EF Electro-Fenton Process
NTU Nephelometric Turbidity Unit