COD REMOVAL BY ELECTRO-COAGULATION

Akash Kumar Gupta[1], Anil Kumar[2], Ajeet Kumar Yadav[3], Mrinank Pandey[4]

[1,2,3]*Research Scholar, Dept. of Civil Engg., Suyash Institute Of Information Technology, Gorakhpur, U.P., India*
[4]*Assistant Professor, Dept. of Civil Engg., Institute Of Technology & Management, Gorakhpur, U.P., India*

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Abstract - *Textile industry is water based industry which discharges large quantities of waste water in each manufacturing cycle. Therefore a batch flow reactor will not offer feasible solution for wastewater in such large quantities. Thus an attempt was made to find feasibility of electro-coagulation for treatment of textile wastewater in continuous flow reactor. In the present study, plug flow reactor were tried to determine the applicability of EC for textile wastewater, to optimize the operating conditions of EC process simultaneously in terms of, COD reduction, electrode consumption and energy requirement for treatment. The continuous mode of the EC process has however been less investigated, except in a few studies, especially the conditions of flock removal and COD reduction. Electro-coagulation using iron electrode was investigated to have optimized combination of affecting parameters like applied voltage, detention time and energy supplied. Experiments were conducted using textile wastewater collected from Sanganer industrial area. Effect of applied voltage and detention time on COD removal efficiency was investigated for horizontal continuous plug flow reactor. An attempt was made to find out the specific energy consumed for unit COD removal. A study was made to predict the effectiveness of electro-coagulation technique in term of COD removal and economics of treatment. Change in conductivity, pH and colour of wastewater after treatment was also analyzed. The results show that electro-coagulation technique has good removal efficiency and economics of treatment. Electro-coagulation technique seems to be promising technique for treatment of textile wastewater.*

*Key Words***: Feasibility, Electro-Coagulation, COD removal, Flock, Plug Flow**

1. INTRODUCTION

Water is an essential requirement for all leaving creature for their survival. The availability of water of desired quality, its cost and the treatment of wastewater are growing areas of concern. Many industries like textile, refineries, chemical, plastic and food-processing plants produce wastewaters characterized by a perceptible content of organics (e.g. phenolic compounds) with strong color. For example, a typical textile dyeing process consists of desizing, scouring, bleaching, dyeing, finishing and drying operations. Except the last two stages, each operation is associated with rinsing step, requires large amount of water. In general, textile industries generate effluent at an average of 100–170 l kg−1 of cloth processed, which is characterized by strong color, high COD with wide variation in pH.

Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products. Conventional methods for dealing with textile wastewater consist of various combinations of biological, chemical and physical methods. Textile wastewater is well known with its high chemical oxygen demand, strong color, large amount of suspended solids, variable pH, salt content and high temperature. Therefore, the treatment systems combined with physical, biological and chemical methods become inefficient for the effective treatment of industrial textile wastewater due to the variation of wastewater characteristics and heavy COD load.

1.1 STUDY AREA-SANGANER

Sanganer is a town located on the outskirt of the Jaipur City, the capital of Rajasthan and comprises an area of around 635.5 sq. km. The historical nature of the city resulted in the mushrooming of the dyeing industries and that too in an unorganized manner. These 459 units which are involved in dyeing, printing and handmade paper production is causing havoc in terms of pollution load in the area, as most of them are operating from the residential area. The units are operating from as little as 100 sq. ft. to as large as 8000 m² space and discharges their chemical effluent directly into the Amanishah Nala that runs through the heart of these units and goes on to connect with river Dhund. Some part of this effluent slowly infiltrates into the land and finds its way to the ground water table, thereby making it unsafe for drinking and other domestic purposes. The effluent discharges from these units per day are as given below in Table 1.1 on the assumption that the 15% of the water evaporates (*RIICO, Last Final Draft Report*).

Table 1.1: Composition of Effluent Discharged

Effluent Discharge Of Different Units	Lt. Per Day
Tie & Dye Units	34,08,580
Handmade Paper Units	1,67,100
Printing Units	5,26,140
Screen Art & Washing Units	28,760
Total	**41,30,580**

1.2 ELECTROCOAGULATION

Electro-coagulation is an alternative technology for wastewater treatment in addition to its other conventional applications. The main advantages of electro coagulation over other conventional techniques, such as chemical coagulation and adsorption, are "in situ" delivery of reactive agents, no generation of secondary pollution, and compact equipment (M. Malakootian et, al 1011). The earlier studies have reported the potential of electro-coagulation to treat a variety of industrial and domestic wastewater (S. Muhammad et, al 2011). Electro-coagulation process has been successfully employed for color, heavy metals and COD removal of industrial wastewaters (Mohammad M. Emamjomeh et, al 2009). Electro-coagulation process has some advantages such as no need to chemical materials, no sludge production, need to small space and low investment costs (A.Savaˏs Koparal et.al 2009).

1.3 PRINCIPLE

In the electro-coagulation process when electrical current flows between two electrodes, metal ions and metal hydroxides having coagulating property, are generated in situ by electrolytic oxidation of the anode (S. Muhammad et, al 2011). Electro-coagulation is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralized and several particles combine into larger and separable agglomerates.

Electro-coagulation process involves applying electric current to sacrificial electrodes (mostly iron and aluminum) inside a reactor tank where the current generates a coagulating agent and gas bubbles. This process has three stages: (i) coagulants formation due to anode electrical oxidation, (ii) destabilizing pollutants and suspended substances and emulsion breaking (iii) combining instable particles to form flocs (A.Savaˏs Koparal et, al 2009). Destabilization mechanisms in this process include electrical double layer compression, adsorption and charge neutralization, enmeshment in a precipitate and interparticle. When iron or aluminum are used as electrode, trivalent iron or aluminum are produced which will react with hydroxyl ions and produce metal hydroxide and polyhydroxide ions. Electrocoagulation reactors could be operated by up or counter current flow or monopolar and dipolar connection.

2. ELECTROCHEMISTRY PROBLEM FORMULATION:

An EC reactor is an electrolytic cell comprising metal electrode with wastewater acting as electrolyte. Metal ions are generated at anode by electrical oxidation with general reaction being:-

$$M_{(s)} \rightarrow M^{n+} + ne^- \qquad (1)$$

The metal ions rapidly hydrolyse to form metal hydroxides which are active coagulant ligands as they diffuse into the bulk solution. Nascent metal ions are also produced by dissolution of metal hydroxides. These nascent metal ions are very efficient coagulant for anionic pollutants dissolved in water (P. Holt). Simultaneously, cathodic reduction takes place to satisfy charge conservation producing hydrogen under neutral or alkaline conditions via:

$$2H_2O_{(l)} + 2e^- \rightarrow 2(OH^-) + H_{2(g)} \qquad (2)$$
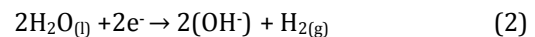
as well as under acidic conditions via:

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad (3)$$

Hydrogen gas released at cathode helps in floating out of flocculated particles from water (P. Holt).

Ideally all the anodic current is consumed by Eq.(1), where Faraday's Law can be used to predict the dissolution rate as:

$$m = ItM/zF \qquad (4)$$

where m = mass of metal dissolved (g), I = current (A), t = time (s), M = molecular weight of the electrode metal (g mol^{-1}), z = oxidation state of the dissolved metal, and F = Faraday constant (96485 C mol^{-1}). The actual dissolution rate, however, may deviate significantly from this relationship due to a range of nonfaradaic processes. Current efficiency (ϕ) is an experimentally determined correction factor that accounts for anomalous dissolution of the electrodes. Introducing ϕ and rearranging Eq(4) gives:

$$Y_{Me} = ajM/zF$$

where Y_{Me} = actual space-time yield of metal (g m^{-3} h^{-1}), a = specific electrode area (m^{2}m^{-3}), and j = current density (A m^{-2}) (Andrew Gadd).

There are a variety of ways in which species can interact in solution (P. Holt):

- Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization.

- The cation or hydroxyl ion (OH$^-$) forms a precipitate with the pollutant.

- The metallic cation interacts with OH$^-$ to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation).

- The hydroxides form larger lattice-like structures and sweeps through the water (sweep coagulation).

- Oxidation of pollutants to less toxic species.

- Removal by electroflotation and adhesion to bubbles.

These interactions in a batch cell are schematically shown in Fig. (1).
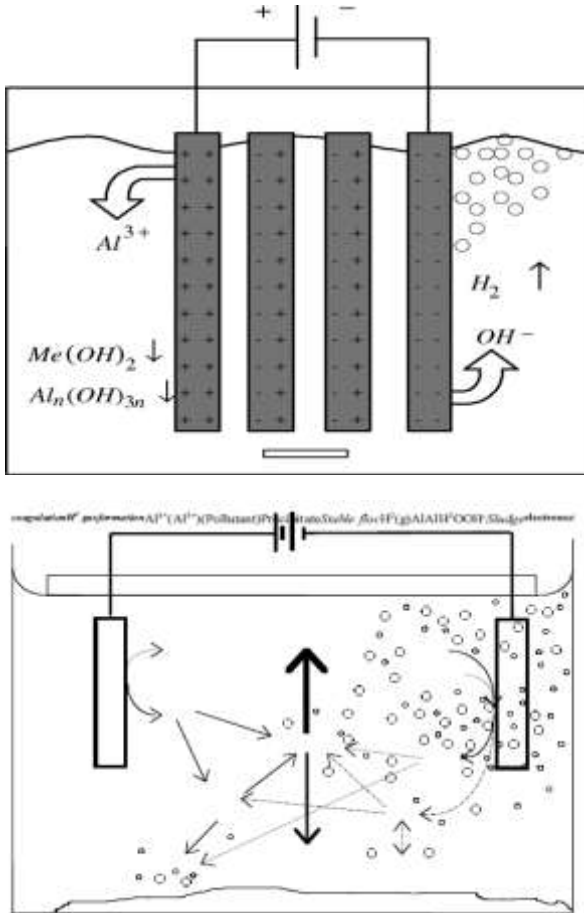
Fig.1: Sketch of some basic processes and various interactions.

2.1 APPLICATIONS OF ELECTROCOAGULATION

The electro-coagulation process can be successfully used to:

- Efficient in removing metals and oil from wastewater streams.

- Pretreatment before membrane technologies like reverse osmosis is not required with this technology.

- Helps in preconditioning of boiler makeup water by removing silica, hardness, TSS, etc.

- Recondition boiler blow down by removing dissolved solids eliminating the need for boiler chemical treatment.

- De-water sewage sludge and stabilize heavy metals in sewage, lowering freight and allowing sludge to be land applied

- Removes chlorine and bacteria before wastewater streams thus making it apt for reuse.

2.2 ADVANTAGES OF ELECTROCOAGULATION

Electro Coagulation technology offers many advantages over other processes like-

- Equipment used in EC is simple &easy to operate with sufficient operational latitude to handle the most operational problems encountered during operation.

- Treatment of wastewater gives palatable, clear, colorless and odorless water.

- EC is a low sludge producing technique. Moreover sludge formed is readily settable and de-water.

- Flocs produced in EC tend to much larger, contain less bound water, is acid resistant and more stable therefore can be separated faster by filtration.

- In comparison with chemical treatment, effluents formed in EC are of lower TDS content. If this effluent is reused, the low TDS level contributes to a lower water recovery cost.

- The electrical field used in EC process sets smallest colloidal particles in to faster motion, thereby facilitating their coagulation and removal.

- EC process stabilizes a buffer system composed of H2 gas and H+ ion, and hence tends to neutralize pH of influent wastewater during treatment (Chen,G.2004).

- EC avoids use of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemicals added at high concentration as in case of chemical coagulation of wastewater.

- The H_2 gas bubbles produced during treatment can carry pollutant to the top of solution where it can be easily concentrated, collected and removed.

- Solar panel could be used as an alternative of electricity therefore EC process can be conveniently used in rural areas where electricity is not available.

3. LITERATURE REVIEW

Dyeing has been practiced from as early as 3000 B.C. in China, although no conclusive proof of this is available. The earliest records of Indian religious and social practices belong to the period of about 2500 B.C., and they contain references to colored silk and gold brocades from which it can be concluded that dyeing was then already an established practice (*Trotman, 1964*)

Perkin, an Englishman, working under a German professor, Hoffman, accidentally discovered the first synthetic dye in 1856, and thus the geographical focus of dye production laid in Germany (BASF, Bayer, Hoechst), England (Zeneca), and Switzerland (CIBA-GEIGY and Sandoz) for many years. Though this has been shifted to the countries like China, India, Taiwan, Thailand and Indonesia during the 1990s due to the radical transformation in their policies, reduction in import & excise duty and consolidation of small-scale sector; setting up these countries in the industrialization age.

Table 3.1: Effluent characteristics from the textile industry

Process	Composition	Nature
Sizing	starch, waxes, carboxymethyl cellulose, polyvinyl alcohol	High in BOD and COD
Desizing	starch, glucose, carboxymethyl cellulose, polyvinyl alcohol, fats and waxes	high BOD, COD, suspended solids, dissolved solids
Scouring	caustic soda, waxes, grease, soda ash, sodium silicate, fibres, surfactants, sodium phosphate	dark colored, high pH, high COD, dissolved solids
Bleaching	hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids, surfactants, sodium silicate, sodium phosphate	pH 10.5-12.5, COD- 2500 mg/l, High suspended solids
Mercerizing	caustic soda	pH- 10.5-12, COD- > 2700, high dissolved solids
Dyeing	various dyes, mordants, reducing agents, acetic acid, soap	strongly colored, COD- 3000-4000, low suspended solids, heavy metals
Printing	pastes, starch, gums, oil, mordants, acids, soaps	highly-colored, high COD, oily appearance, suspended solids
Finishing	inorganic salts, toxic compounds	slightly alkaline, low BOD

4. EXPERIMENTAL SETUP

It mainly consisted of two plastic reactors of 2000 ml volume each, to hold the sample for electrocoagulation process. Two pair of rectangular iron electrodes each with dimension of (7x5x0.5) cm & active surface area of 82 cm^2 was used as anode and cathode. Electrodes in a pair were arranged at a spacing of 3 cm and connected with an external DC power source in parallel mode. Testronix, 230 V DC regulated power supply unit was used to feed electric energy in setup for electrocoagulation process. The ammeter and voltmeter to read values of current and voltages were inbuilt in the used power supply unit. A lamellar settler made up of perfex sheet was connected with reactor for settling of flocks which were coming out with treated water from reactors.

During the EC process, flocks were formed which floats at the surface of sample. COD was measured before the process started and after an interval of consecutive 10 minutes till the pseudo steady state is achieved. It is the state in which no or very little reduction is observed in the COD of effluent. The equipment required to measure COD was UV/VIS spectrophotometer manufactured by Schimadzu model 6800 at 600 nm, while pH was analyzed with the help of pH meter.

Figure 2 The Experimental Setup Used in Study

(1 = wastewater reservoir, 2 = peristaltic pump, 3 & 4 = reactor, 5 = lamellar settler, 6 treated water container, 7 = Closed reflux apparatus, 8 = DC power supply, 9 = treated samples)

4.1 INSTRUMENTS USED

1. DC power supply

The instrument used for supply of dc linear power is manufactured by Testronix (230 V DC regulated power supply).

2. Closed reflux apparatus

The closed reflux apparatus manufactured by WTW, Germany, model "Thermoreactor CR 3000" was used for the digestion of the pollutants.

3. UV/VIS spectrophotometer

The UV/VIS spectrophotometer is used to measure COD and has a range of 200-900 nm. It is manufactured by Schimadzu of model 6800.

4. pH Meter

A pH meter manufactured by Lutron of model PH-201 was used for the determination of pH.

5. Conductivity meter

A conductivity meter manufactured by Lutron of model CD-4302 was used for analyzing conductivity. The range of this instrument is from 2-20 mS.

4.2 EXPERIMENTAL PROCEDURE

All the experiments were conducted in continuous plug flow mode to check out the feasibility of electrocoagulation process. Experiments were conducted at different applied voltages and detention time in order to find out the optimal combination of applied voltage and detention time to yield maximum COD removal efficiency. Flow rate was varied to achieve designated detention time for given experimental run. The volume of the wastewater used for the entire procedure was depending upon the detention time and the time in which pseudo steady state is achieved.

Experiments were conducted to obtain the COD removal profile for pseudo steady state, detention time and applied voltage. All the results were carried out in percentage of COD removal due to the difference in the initial COD value. The range of voltage varied from 10-15 V. Experiments was continued long past the pseudo steady state condition, where COD of consecutive samples were almost same. The experiments were carried out for 20, 30 and 40 minutes detention time and applied voltage of 10, 12.5 & 15 volts. Sampling was done after every 10 minutes for COD removal. The initial and final values of COD were obtained and recorded. Then percentage of COD removal was calculated depending on the given equation:

$$Y_{COD} (\%) = (COD_I - COD_E/ COD_I) \times 100 \qquad (1)$$

Where, Y_{COD} (%) = COD removal efficiency in percentage

COD_I = COD of raw sample of dye in gm/l.

COD_E = COD of sample after every 10 min in gm/l.

The experiments were continued till the COD_E for three consecutive samples were almost same. This state was taken as pseudo-steady state. The three values after pseudo-steady state were averaged and were used for subsequent data analysis. Each experiment was conducted for three times. Average values of COD removal efficiency were taken for further analysis

5. RESULTS AND DISCUSSION

Experiments were conducted as discussed in previous chapter and their results have been discussed in this chapter.

The feasibility of electro-coagulation for textile wastewater in continuous plug flow reactor was examined for detention time of 20, 30 and 40 minutes. To determine the effect of applied voltage on efficiency of this process, above set of experiments were conducted at 10, 12.5 & 15 volts. During these experiments, total electric work for unit COD removal and sacrificial weight of anode were also recorded. For conducting these experiments, same set of electrodes of size 7 X 7 X 0.5 cm. were used. The results of above sets of experiments have been presented and discussed in the following sections.

5.1 COD REMOVAL PROFILE

The experiments were carried out to understand the effect of Electro coagulation process under continuous flow regime. The samples were collected at regular time interval and their COD was determined. In this study, the primary aim is to comprehend the effect of detention time and applied voltage on COD_E i.e. COD removal profile were obtained for different detention time and applied voltage. The influent samples were collected from industries of Sanganer industrial area (mentioned in Chapter 3), but it was found that the COD of the sample was varying in a narrow range. Thus, results of performance of EC process for various detention time and applied voltage have been reported as COD removal efficiency and are calculated as-

$$Y_{COD} (\%) = (COD_I - COD_E/ COD_I) \times 100 \qquad (1)$$

Where, Y_{COD} (%) = COD removal efficiencies in percentage

COD_I = Influent COD

COD_E = Effluent COD

The experiments were continued till the COD_E for three consecutive samples were almost same. This state was taken as pseudo-steady state. The three values after pseudo-steady

state were averaged and were used for subsequent data analysis.

5.2 EFFECT OF VOLTAGE ON SACRIFICIAL WEIGHT OF ANODE

Experiments were carried out to analyze the effect of voltage and detention time on sacrificial weight of anode. In this study, experiments were carried out for detention time 20, 30 and 40 minutes, and for applied voltage of 10, 12.5 and 15V. The anode loss for unit COD removal was calculated and has been tabulated in Table

It is clearly evident from the figure that highest COD removal was observed at 40 minutes detention time and for applied voltage of 15 V. Thereafter, second highest COD removal was observed at 30 minutes detention time and the consumption of anode is double as comparison to 20 minutes detention time. As the detention time increases anode loss will also increases but it is not necessary that COD will also increases, so the further treatment may disturb the economy of process.

Detention Time (Minutes)	Voltage Applied	COD Removed (mg/l)	COD*total Volume (mg)	Anode Loss (mg)	Anode loss for Unit COD removal
20	10	661.136	28428.85	3635.8	0.127891
20	12.5	773.024	33240.03	3133.2	0.09426
20	15	810.32	34843.76	3959.8	0.113644
30	10	672.1283	20120.16	4944.6	0.245754
30	12.5	859.884	25740.63	4649.4	0.180625
30	15	766.35	22940.69	8141.4	0.354889
40	10	762.1102	17909.59	5720	0.319382
40	12.5	842.2128	19792	8956	0.452506
40	15	774.9101	18210.39	10813.8	0.593826

6. CONCLUSION

The study involves the experimentation of wastewater collected the textile industries of Sanganer, Rajasthan.

The feasibility of electro-coagulation for textile wastewater in continuous plug flow reactor was examined for detention time of 20, 30 and 40 minutes for (7x5x0.5) cm size of electrode. To determine the effect of applied voltage on efficiency of this process, above set of experiments were conducted at 10, 12.5 & 15 volts for all the three detention time. During these experiments, total electric work for unit COD removal and sacrificial weight of anode were also recorded. The data were analyzed and the major conclusions

and recommendations for future work are listed in this chapter.

1. Maximum efficiency of 87.52% was achieved at 30 min detention time with applied voltage 12.5 V. Maximum % of cod reduction is achieved with in first 20 to 30 min of the reaction.

2. It was observed that increase in detention time had resulted in an increase in removal efficiencies, when other affecting parameters were kept constant. For constant applied voltage of 10 V cod removal efficiency was increased from 59% to 74%. Similar results were also obtained in 30 min detention time.

3. For constant detention time of 20 min. maximum cod reduction was achieved at 15V, for 30 min detention time maximum cod reduction was achieved at 12.5V and for 30 min DT maximum cod reduction was achieved at 12.5V, so as the DT was increased the voltage to yield maximum cod removal efficiency decreases.

4. Minimum sacrificial wt. of the anode for unit COD removal was at 12.5V and maximum at 20V. While the system was most efficient at 12.5Vand 30 min DT with cod reduction 87.52 % and sacrificial wt. of anode was 0.180624967 mg per unit cod removed.

5. Minimum specific energy consumption was at 40 min for 10V. Specific energy required for sizable COD removal rate was 0.021 to 0.034 joule/mg and further supply of electric work may weakens the economy of electro coagulation process.

6. It was observed that the pH after EC treatment process would increases for acidic wastewater but decreases for alkaline wastewater. This neutralization effect is one of the advantages of this process.

7. During the course of each experimental run, it was observed that the conductivity of the solution increased with time.

8. It was observed that the effluent treated with iron electrode as anode, appeared greenish first and then turned yellow and turbid.

6.1 FUTURE RECOMMENDATIONS

1) The treatment of textile waste water should be performed in the laboratory in order to identify the effect of other parameters like current density, use of different electrode materials etc on the efficiency of process.

2) Treatment of textile wastewater having different physiochemical properties like pH, initial COD, turbidity, TDS, conductivity etc should be

experimented to revel their effect on COD removal efficiency.

3) Color removal by electrocoagulation should be analyzed and quantified.

4) Combination of electrocoagulation and adsorption should be tested to remove COD and color from wastewater.

5) Fungal and bacterial treatment or ozonation process may be used, for checking the biodegradability of EC treated waste water and sludge produced in this process.

6) Pilot scale studies are to be done.

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