Study of Electrocoagulation mechanism on dairy wastewater for COD and Turbidity removal

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Abstract: The removal of COD and turbidity from dairywastewaterwas experimentally investigated using direct current electrocoagulation (EC). In the EC of dairywastewater, the effects of initial pH, electrolysis time, voltage and different electrodes were examined. The batch experimental results revealed that the removal efficiencies of the overall turbidity, COD depend on the nature of the electrode material. The optimum operating range for each operating variable was experimentally determined. The greatest removal efficiency was obtained with the use of aluminium as anode and iron as cathode (Al–Fe system). With this latest system, optimal values of voltage, initial pH, boric acid concentration and electrolysis time were 5V, 6.0, 5 g/L and 10 min respectively. The batch experimental results revealed that COD and turbidity in aqueous phase was effectively removed. The overall COD and turbidity removal efficiencies reached 92.6% and 95.2%, respectively. The Mean energy consumption was 0.0003 kWh/kg of COD removed.

Keywords: Electrocoagulation, iron electrode, aluminium electrode, COD, turbidity.

I. INTRODUCTION

Milk may be defined as the whole, fresh, clean, lacteal secretion obtained by the healthy milk animals. It is generally defined by the three components as follows: (i) the fat or oil that is inside the emulsion droplets, (ii) the interfacial matter between the lipidic phase and the aqueous phase representing part (iii) of the emulsion. Each of these phases may be chemically complex. Milk consists also of three parts: (i) an oil-in-water emulsion in which the fat droplets are dispersed in the serum, (ii) a colloidal suspension of casein micelles, protein and lipoprotein particulates and the aqueous phase (iii) containing soluble proteins, mineral salts and vitamins.

Large quantity of wastewater originates due to their different operations. The organic substances in the wastes comes either in the form in which they were present in milk, or in a degraded from due to their processing. As such, the dairy wastewater, though biodegradable, are very strong in nature. Dairy waste effluents are concentrated in nature, and the main contributors of organic charge to these effluents are carbohydrates, proteins and fats originating from milk. The liquid waste from dairies originates from different sections like receiving station, bottling plant, cheese plant, casein plant, condensed milk plant, dried milk plant and ice cream plant. The dairy wastes are very often discharged intermittently. The nature and composition of waste depends on the type of products produced and size of the plant.

The other techniques used to treat the diary wastewaters are conventional aerobic purification and anaerobic processes. However, others techniques have also been used, e.g. coagulation flocculation, nanofiltration (NF), reverse osmosis (RO) and use of membrane bioreactors. Biological processes require big spaces and long time of treatment and generate great amount of sludge. The physicochemical processes suffer the disadvantage that reagent costs are high and the soluble COD removal is

low. Besides, chemical treatments could induce a secondary pollution due to the fact that chemical additives may contaminate the treated water. Among physico-chemical methods, electrocoagulation technique is one of the processes which offer high removal efficiencies in compact reactors, with simple equipments for control and relatively moderate operating cost.

Electrocoagulation (EC)/flotation process can be other alternative process for treating dairy waste effluents. This technology has been very successfully employed in removing oil/grease and SS from a variety of industrial effluents and is a combined coagulation and flotation process induced by the passage of electric current. It was tested successfully to treat drinking water, oil refinery wastewater[26], textile wastewater[14][17][19][21][28][30], municipal sewage[15][22], diary wastewater[1][6][23], tannery wastewater[2], pharmaceutical wastewater[8], waste metal cutting fluid[12], agro industry wastewater[18], slaughterhouse wastewater[9] by various investigators. It was also used to remove heavy metals like Phenol[27], Arsenic[3], Cyanide[10], Nickel, Copper, Zinc.

II. A BRIEF DESCRIPTION OF ELECTROCOAGULATION MECHANISM

A simple electrocoagulating reactor is made up of one anode and one cathode. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. If iron or aluminium electrodes are used, the generated Fe3⁺(aq) or Al3⁺ (aq) ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. The Fe(II) ions are the common ions generated the dissolution of iron. In contrast, OH– ions are produced at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of matrices by adsorption and coprecipitation. In the study of Aluminium as anode and Iron as cathode, the reactions takes place as follows [4]:

At the anode:

$$Al(s) \rightarrow Al(aq)^{3+} + 3e^{-}$$
 (1)

The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced through Eq. 2, whereas under acidic conditions Eq. 3 describes better hydrogen evolution at the cathode:

$$2H_2O(1) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
 (2)

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

The generated metal ions $(Al^{3+}$ (aq)) immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. The Al^{3+} and OH^- ions produced at the electrodes can react to form various mono-nuclear $(Al(OH)^{2+}, Al(OH)^{2+}, Al_2(OH)_2^{4+})$ and poly-nuclear $(Al_6(OH)_{15}^{3+}, Al_7(OH)_{17}^{4+}, Al_8(OH)_{20}^{4+}, Al_{13}(OH)_{34}^{5+}, Al_{13}O_4(OH)_{24}^{7+})$ species, which are finally transformed into aluminium hydroxide: $Al(OH)_3$. The large specific area of $Al(OH)_3$ then facilitates compound adsorption and traps the colloids

III. MATERIALS AND METHODS

3.1. Electrochemical reactor

The batch experimental setup is schematically shown in Fig. 1. The EC unit consists of two electrodes in an EC cell, a DC power supply. The iron cathode and aluminium anode of dimensions 5cm x 5cm x 5cm are separated by a space of 1 cm and dipped in the wastewater. The EC of dairy wastewater was carried out in the reactor (14cm x 9cm 15 cm) using magnetic stirrer to agitate the solutions. The working volume of reactor was 1L. The total area of electrodes plates submerged into the solution was 5 cm². A stirring intensity of 100 rpm was used in order to get a correct homogenization of the wastewater–flocs mixture. EC experiments were carried out at 298 K. The DC source was used to power supply the system with 0–30 V and 0–2 A.

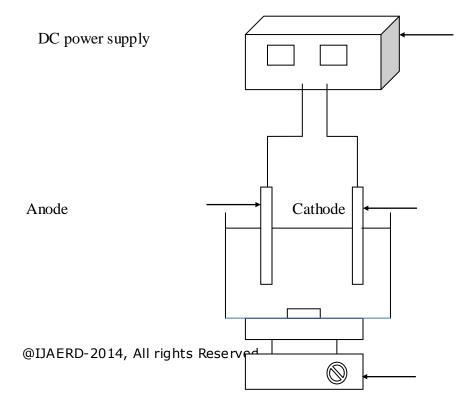
3.2. Wastewater samples and experimental procedure

The Dairy wastewater was obtained from the Dharwad Milk Union, KMF Dairy, India. The KMF Dairy produces about 500m3 of wastewater per day, which is currently treated with aerobic stages with activated sludge. The wastewater was collected from the treatment plant after screens and kept in refrigerator at 4 °C. The apparatus for EC is shown in Fig. 1. The composition of the wastewater is shown in Table 1. The pH was adjusted to a desirable value using HCl and NaOH solutions. The conductivity of the wastewater was adjusted to the desired levels by adding an appropriate amount of boric acid (H₃BO₃). This adjustment has shown negligible effect on the initial pH of the wastewater.

Table 1.Characteristics of Dairy wastewater

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Parameter	Value
pН	6.0
Conductivity	0.4ms/cm
Color	whitish
COD	1110mg/l
Turbidity	125 NTU



Stirrer

Fig 1 Experimental setup

The salt concentrations for increasing conductivity were 5g/L. pH and voltage values were 6.0,7.0,8.0 and 3V,5V,7V and 9V respectively. At the beginning of a run, the wastewater was fed into the reactor and the pH and conductivity were adjusted to a desired value. The electrodes Iron as cathode and Aluminium as anode were placed into the reactor. The reaction was timed starting when the DC power supply was switched on.

Iron salts produce electrode passivation and it causes a 50% increase in treatment time and power requirements. Eliminating the salt formation at the anode could reduce this effect. The cell was cleaned after each experiment to obtain same experimental conditions. For this reason, the electrodes were rinsed in the diluted 15-20% HCl solution and detergent wash after the each experiment. Samples were periodically taken from the reactor. The particulates of colloidal ferric oxyhydroxides gave yellow-brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Thus, during electrolysis, the clear solution was obtained. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Therefore, filtration was not markedly effect COD and oil—grease removal. Sludge generating during treatment was separated from the solution by filtration using Whatman filter paper and then the solution was analyzed. COD analysis was carried out according to the standard methods for examination of water and wastewater and turbidity was analysed using Nephelometricturbidimeter.

IV. RESULTS AND DISCUSSION

4.1. Effect of initial pH

pH is an important parameter influencing the performance of the EC process. To examine its effect, the sample was adjusted to a desired pH for each experiment by using sodium hydroxide or hydrochloric acid. Fig 2 shows the removal efficiency of COD and turbidity as a function of the initial pH.pH of the medium increased during the process. The maximum removals of COD were observed at pH 6.0. Best removal results for 10 min electrolysis duration were observed at a pH of 6.0 and at 5V.But from the observation it is noticed that the turbidity removal was independent of pH. The maximum removal efficiencies of COD and turbidity as a function of pH at pH 6.0 were 92.6% and 97.6% respectively. It is interesting to note that the COD removal decreased when pH was greater than 6.0. The drop of parameters removal, when the initial pH tends toward acid or basic values, is in accordance with the amphoteric character of aluminium hydroxide Al(OH)₃ that precipitates at pH 6–7 and whose solubility increases when the solution becomes either more acidic or alkaline

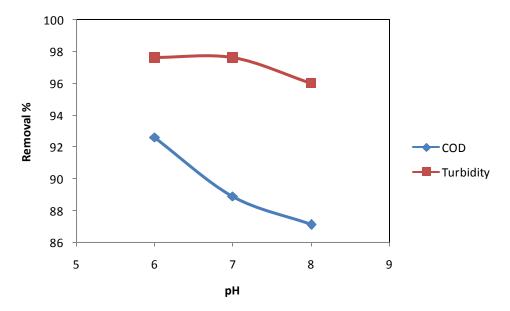


Fig 2 Effect of initial pH on the removal efficiency of COD and Turbidity when V=5V, $H_3BO_3=5g/L$, duration of electrolysis=10min, $C_{0,COD}$:1110mg/L

4.2. Effect of voltage on EC

It is well-known that current not only determines the coagulant dosage rate but also the bubble production rate, size and the flocs growth, which can influence the treatment efficiency and operating cost of the EC [12]. EC process was carried out using different voltages 3, 5, 7 and 9V. To determine the effect of voltage on EC process, pH was held constant. It was observed that the COD removal was independent of voltage. Though there was increase in voltage, the COD removal efficiency does not increased. The observations were made that the turbidity removal was dependent on voltage. As the voltage increased the turbidity removal also increased. The optimum removal efficiency was 97.6% at 9V (Fig 3).

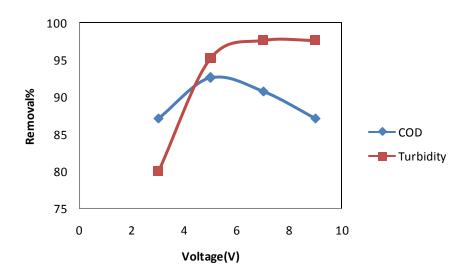


Fig 3 Effect of voltage on the removal efficiency of COD and Turbidity when pH=6.0, $H_3BO_3 = 5g/L$, duration of electrolysis= 10min, C_0 , COD: 1110mg/L

4.3. Effect of operating time on EC

Effect of operating time on the removal of COD and turbidity was shown in Fig. 4, indicated that an increase in the time of electrolysis from 0 to 10 min yielded an increase in the removal efficiencies of COD and turbidity. The optimum operating time for this study was chosen as 10 min since the highest removal efficiencies of COD and turbidity were observed at this time. It was observed that COD remains unchanged after an electrolysis time of 10 minutes. The reason for selecting 10 minutes as electrolysis time was, beyond 10 minutes, the COD remained unchanged. The experimental results showed that the abatement of the various pollution variables occurs in two phases as follows: The first phase of decreasing pollution features, or the "reactive stage" during which the COD and the turbidity removal yields increase with the current density. The second is called "stationary phase", reached after 2 min of treatment: in this period, further increase in iron concentration has less effect on the treatment.

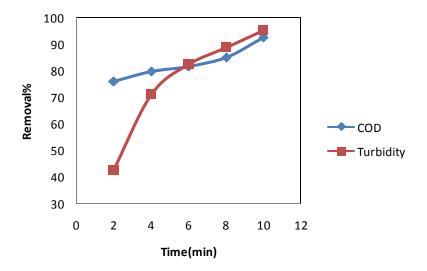


Fig 4 Effect of electrolysis duration on the removal efficiency of COD and Turbidity when $pH=6.0, V=5V, H_3BO_3=5g/L$, $C_{0,COD}:1110mg/L$

4.4 Effect of electrode materials

The nature of the electrode material is a key issue in electrochemical treatment and the appropriate selection of electrode material is very important. The most common electrode materials used for electrocoagulation technique are aluminium and iron because they are cheap, readily available and proven effective since their dissolution in aerated media generate trivalent species. The different electrode systems used apart from aluminium as anode and iron as cathode in this study are Iron as anode and Graphite as cathode, Zinc as anode and Iron as cathode were also investigated for comparison purpose. With the optimum condition initial pH 6.0, voltage 5 V and after 10 min of electrolysis process, the removal efficiency of COD and turbidity is reported in fig 5.

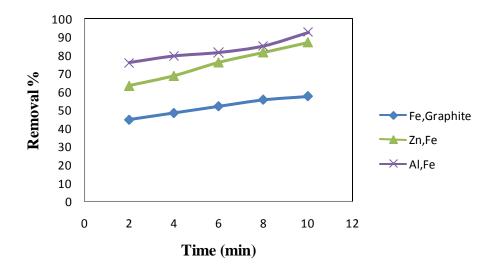


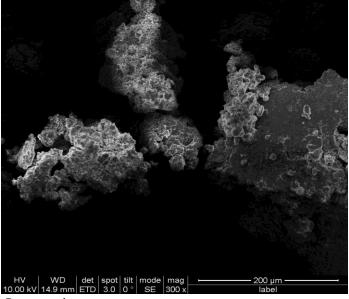
Fig 5 Effect of different electrode systems on the removal efficiency of COD and Turbidity when V=5V, $H_3BO_3=5g/L$, duration of electrolysis=10min, $C_{0,COD}$:1110mg/L

4.5. Sludge characterization

The treated sample was filtered to recover floated particles (scum) and settled solids (sludge) formed during EC treatment. The obtained product that we called sludge was washed with distilled water and then oven dried at 103 ± 2 °C until its weight was stabilized. The dried sludge was stored in desiccators to its analysis.

4.5.1 Scanning electron micrographs (SEM)

The SEM image indicates the presence of mostly amorphous and flake-shaped aggregates of solid particular structure. Pores of varying sizes which can be seen on the surface (Fig 6) could explain the high capacity of sludge to adsorb organic or mineral pollutant matter. This information confirms that once the suspended and colloidal matter is destabilized, it can be separated from the wastewater and that the iron ions generated by the electrolysis forms complexes with the pollutants which are adsorbed onto hydroxide formed during EC process.



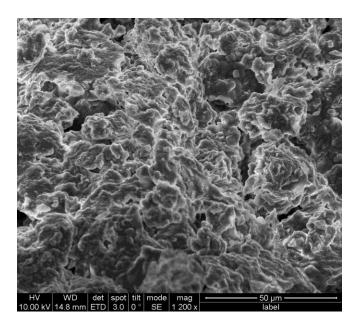


Fig 6 SEM images of the sludge produced in the electrochemical process (Fe-Al system). The photographs were recorded at the indicated magnification.

V. CONCLUSIONS

The EC process was successfully applied to the Dairy wastewater. The removal efficiencies of COD and turbidity for were found to be dependent on initial pH, applied voltage and operating time. Optimum operating conditions were obtained as pH 6.0, voltage 5V and operating time of 10 min, respectively. The electrocoagulation setup described in this study is simple in design and operation and can be used as a convenient tool in the removal of food related industrial wastewaters.

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