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Treatment of dairy waste water by electro coagulation using aluminum electrodes and settling, filtration studies

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Abstract: The removal of COD and oil from dairy wastewater was experimentally investigated using direct current (DC) electrocoagulation (EC). In the EC of dairy wastewater, the effects of initial pH, electrolysis time, initial concentration of COD, and current intensity were examined. The COD in the aqueous phase were effectively removed when aluminum plates were used as sacrificial electrodes. The optimum operating range for each operating variable was experimentally determined. The batch experimental results revealed that COD in aqueous phase was effectively removed. The overall COD removal efficiencies reached 87%. The optimum current intensity, pH and electrolysis time for 1070 mg/dm3 and were 3A, 9, 75 min, respectively. Mean energy consumption was 112.9 kWh/kg
Keywords: Electro coagulation, Dairy waste water, Aluminum Electrodes, COD, Dairy Effluent.

Introduction

The dairy industry, like most other agro-industries, generates strong wastewaters characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) content. Furthermore, the dairy industry is one of the largest sources of industrial effluents. A typical European dairy generates approximately 500 m3 of waste effluent daily [2]. Since dairy waste streams contain high concentrations of organic matter, these effluents may cause serious problems, in terms of organic load on the local municipal sewage treatment systems. Environmental problems can results from discharge of dairy wastewater (DW). Introduction of Most of the wastewater volume generated in the dairy industry results from cleaning of transport lines and equipment between production cycles, cleaning of tank trucks, washing of milk silos and equipment malfunctions or operational errors [4-6]. DW treated using physico-chemical and biological treatment methods [3-5]. However, since the reagent costs are high and the soluble

COD removal is poor in physical–chemical treatment processes, biological processes are usually preferred [7]. Among biological treatment processes, treatment in ponds, activated sludge plants and anaerobic treatment are commonly employed for DW [8]. In contrast the contrary, high energy requirements of aerobic treatment plants are a significant drawback of these processes. COD concentrations of dairy effluents (DE) significantly; moreover, dairy effluents are warm and strong. DE are ideal for anaerobic treatment. Furthermore, no requirement for aeration, low amount of excess sludge production and low area demand are additional advantages of anaerobic treatment processes, in comparison to aerobic processes. Wastewaters from the dairy industry are usually generated in an intermittent way, so the flow rates of these. Effluents change significantly. High seasonal variations are also encountered frequently and correlate with the volume of milk received for processing; which is typically high in summer and low in winter months. Moreover, since the dairy industry produces different products, such as milk, butter, yoghurt, ice-cream, various types of desserts and cheese, the characteristics of these effluents also vary greatly, depending on the type of system and the methods of operation used [9]. The effluent contains various things like inorganic nitrogen (proteins, urea, nucleic acids, or as ions such as NH4+, NO2- and NO3-). Phosphorus (orthophosphate and polyphosphate), sulphate, suspended solids (SS) and volatile suspended solids (VSS) , chlorides and metal elements (Na, K, Ca, Mg, Fe, Co, Ni and Mn etc). The typical composition of waste water of dairy plant is shown in Table 1.1.

Table 1.1: Treatment performance levels of various methods for dairy wastewaters

Initial COD (mg/L)	Method	COD removal efficiency (%)	Reference
9359 (AF)	Anaerobic filter reactor	91.8	[7]
4000	Aerobic purification	96.8	[12]
3200	Buoyant fitler bioreactor (BFBR)	90	[10]
10000	Nanofiltration and reverse osmosis membranes	95	[19]

1.1 Treatment Technologies of Wastewater in Dairy Industry

Wastewaters from agro-industries are characterized by chemical oxygen demand (COD) due to their high level of organic contents [10]. The dairy industry generates a huge amount of wastewaters: approximately 0.2 m3 to 0.5 m3 of waste per m3 of processed milk [11]. In most cases, these effluents are not treated and are simply thrown into rivers where they contribute to eutrophication by phosphorus and nitrogen compounds [11-14]. Treating dairy effluents is thus of crucial importance not only for the environment, but also for the purpose of recycling water for use in industrial processes [15]. Now a days, many physico-chemical and biological methods are used to treat dairy effluents, with the particular aim of reducing the volume of the produced sludge. The physico-chemical processes suffer the disadvantage that reagent costs are high and the soluble COD removal is low [10]. Moreover, chemical treatments could induce a secondary pollution due to the fact that chemical additives may contaminate the treated water. Among methods, methanisation is by far the most interesting since it transforms the organic matter in milk to methane, a compound well known for its unquestionable combustion properties. Moreover, high removal rates of the COD are obtained [16] even though this process does not eliminate phosphorus and nitrogen compounds contained in the dairy effluents [17]. Implementation of a complementary physicochemical treatment would reduce phosphorus and nitrogen content. Electro coagulation is an electrolytic process that has been already experienced for the treatment of various liquid wastes. For this to be achieved, a convenient current is imposed on soluble anodes like aluminum, iron or their alloys in an electrochemical cell acting as the reactor for the experiment separated by decantation or filtration, depending upon their density . Although the principle of the treatment of an effluent is identical for both electrocoagulation and chemical coagulation, the Electro coagulation results in the dissolution of the electrode to yield metal ions (Fe2+, Fe3+ or Al3+) which are active coagulants precursors involved in the neutralization of the negative charges on the colloids of the effluent. These metal ions then react with the hydroxyl colloidal particles is specific in each of these processes [18]. During electro coagulation, the coagulants are obtained in situ by the dissolution of the anode, which is not the case for chemical coagulation in which the coagulants are obtained by dissolution of aluminum or iron salts [19]. 1.2EC Mechnism.

If aluminum electrodes are used, the generated Al 3+ (aq) ions will immediately undergo further spon-taneous reactions to produce corresponding hydroxides and/or polyhydroxides. The aluminium ions are the common ions generated the dissolution of aluminum. In contrast, OH − ions are produced at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of matrices (dyes and cations) by adsorption and coprecipitation. In the study of aluminum anodes, two mechanisms for the production of the metal hydroxides have been proposed From previous studies[20-22] (the treatment process can be described by Eqs. ((1) – (4)). The electrochemical reactions (1,2) are followed by the chemical one (3). Since pH increases near the cathode, a corrosion of aluminium takes place according to the Eq. (4). [30-32](The Al(OH)n(s) formed remains in the aqueous stream as a gelatinous suspension, which can remove the waste matter from wastewater either by complexation or by electrostatic attraction followed by coagulation.

$$Al \longrightarrow Al^{3+} + 3e$$
$$3H_2O + 3e \longrightarrow 3/2H_2 + 3OH$$
$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$
$$Al + 3H_2O + OH^- \longrightarrow Al(OH)_4 + 3/2H_2$$

2. Material and Methods

2.1 Electrochemical reactor

The lab-scale batch experimental setup used for the electrochemical degradation studies is schematically shown in Fig. 3.1. The dimensional characteristics of the experimental setup and the electrical assembly are shown in Table 3.1. Electrochemical treatment of both anionic and cationic species is possible by using an aluminum plate/ rod as the sacrificial electrode. The plates, if connected in series, have higher resistance. In a parallel arrangement, the electric current is divided between all the electrodes in relation to the resistance of the individual cell.[23-24] Therefore, the electrode plates were arranged in parallel. There were four electrodes connected in a bipolar mode in the electrochemical reactor, each one with dimensions of8 X 8.4 X.3.The electrode plates were cleaned manually by abrasion with sandpaper, and they were treated with 15% HCl for cleaning followed by washing with distilled water prior to their use[31]. The electrodes were spaced 15 mm apart (because <10 mm spacing between electrodes prevented movement of liquid adsorbate in the interstitial spaces of the electrodes thus, hindering/affecting removal efficiency). The anode and the cathode leads were connected to the respective terminals of DC power supply. The thicknesses of the plates were 3.00mm. and the Effective electrode surface was 69.2 cm2.

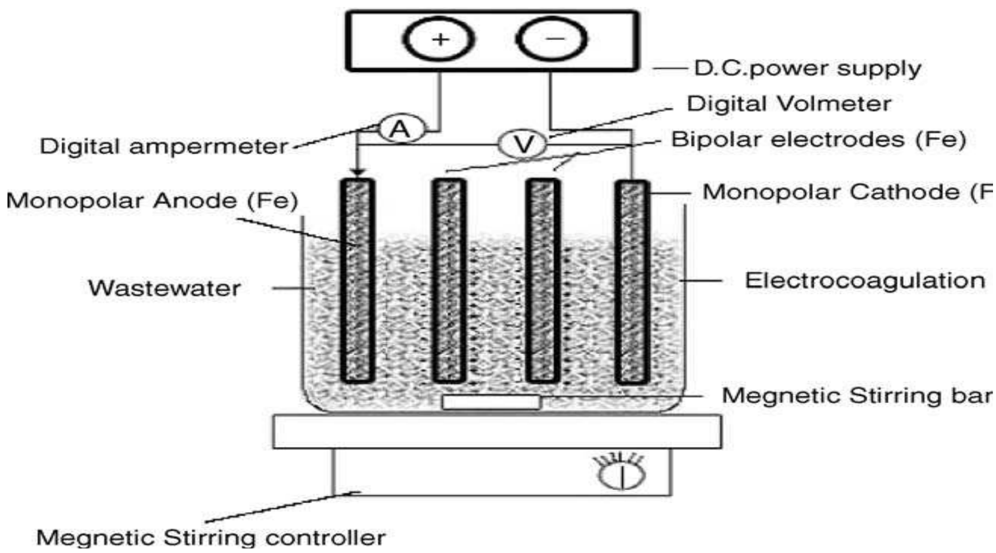

Fig. 2.1   Bench-scale EC reactor with bipolar electrodes in parallel connection

2.2 Wastewater samples and experimental procedure

Wastewater was obtained from a Sanchi dugdh sandh kumhari Raipur Chhattisgarh containing a mixture of exhaust solutions at a dairy factory in Chhattisgarh (India) producing approximately 10 m3 of wastewater per day. The com-position of the wastewater is shown in Table 2.1.

Table 2.1 Characteristics of wastewater used

Characteristics	Value
Chemical oxygen demand (COD) (mg/L)	1070
Oil and grease (mg/L)	500
TSS (mg/L)	1500
Conductivity (µS/cm)	800
pH	6.0–7.5

. The pHs were adjusted to a desirable value using HCl and NaOH solutions. The conductivity of the waste water was adjusted to the desired levels by adding an appropriate amount of NaCl. This adjustment has shown negligible effect on the initial pH of the wastewater. 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 were placed into the reactor. The reaction was timed starting when the dc power supply was switched on. Aluminum salts produce electrode passivation and it causes a 50% increase in treatment time and power requirements. Eliminat-ing the salt formation at the anode could reduce this effect. The cell was cleaned after each experiment to obtain same experi-mental conditions. For this reason, the electrodes were rinsed in the diluted HCl (1 + 1) solution after the each experiment. Samples were periodically taken from the reactor. The par-ticulates of colloidal aluminum oxyhydroxides gave white-brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation[25-27]. 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 (pore size 11m) and then the solution was analyzed. COD and oil–grease analysis were carried out according to the following procedure for examination of water and wastewater.The effluent contains several compounds. The determination of COD was carried out using spectroscopic method[28]. For this 0.3 ml COD solution A, 2.3 ml COD solution B and 3 ml effluent/treated sample was taken in a 10 ml digestion tube. The tubes (max 25) were heated at 148 o for 2h in a digester (spectroquant TR -420, MERCK made). After this tubes were cooled for half an hour. The absorbance's of digested sample were taken at 605 nm using spectrometer (Nicolet Evolution 100, Thermo Electron Corporation made) and corresponding COD was estimated. The settling characteristics were calculated on the basis on the kynch theory while filtration was tested using a gravimetric filtration. The filter paper was supported over a ceramic Buechner funnel of 75 mm internal diameter (filter area) 4.415 × 10-3 m^2. The volume of filtrate collected in the graduated vertical cylinder was recorded at regular time intervals. The cake retained at the top of filter paper was carefully removed, weighed, and dried at 105 °C until it attained a constant weight. The residue was expressed as mass of solids per volume in the slurry. A plot between $\Delta t/ \Delta V$ versus V used to calculate the specific cake resistance and filter media resistant.[29-30]

Result and Discussion

3.1 Effect of PH on COD Reduction of Dairy waste water.

Since the pH of solution play, important role in influencing the electro chemical processes, the effect of pH0 in the range of 3 to 11 was investigated. The mechanism of destabilization of dispersed particle during electro-chemical treatment using aluminum electrode in similar to that of chemical coagulation using AlCl3. During electro coagulation neutral pH and slightly alkaline pH was found to better for COD reduction. Treated effluent having COD of 930, 802, 159, 140 and 357 mg/dm3 were obtained at pH0 3, pH0 5, pH0 7, pH0 9, and pH0 11 respectively for 75 min of electro coagulation. Considerable COD reduction was obtained at pH0 7, 9, and 11 during initial period of electro coagulation. The COD of the effluent during this period was 412, 302 and 582 respectively (Fig. 3.1). During electro coagulation, the dissolution of aluminum take place and it influence by pH. At pH0 9 with 3 A current electrode loss of 1.92 g took placed with maximum COD reduction of 86.91% and sludge formation of 4.42 g/dm3. A minimum COD reduction of 5.04% occurred at pH0 3 with 3 A current and electrode loss of 1.48 gm and sludge formation of 2.32 g/dm3 (Table 4.3) . In the table it may be also seen that 4.42 gm/dm3 of sludge retained at pH0 9 and 3 A; while lowest amount of sludge obtained was at pH 3 with COD reduction of 5.04%.

3.2 Effect of current

Reduction of organic load (COD) of DW was also studied at different current intensity (0.5 A to 3A). The results are presented in Fig. 3.2. From the figure it may be seen that with increase in current intensity COD of treated effluent decreased. The COD of DE was reduced to 720 , 540, 403 and 302 mg/dm3 in 15 minutes at current intensity 0 .5 , 1, 2 and 3A respectively, which were further reduced to 523, 392, 210,and 140 mg/dm3 in 75 minutes of electro coagulation. The electrode loss as well as power consumption was found to increase with increase in current intensity from 0.5 to 3 A. 1.05, 1.20, 1.52, 1.92 gm aluminum loss took placed at 0.5, 1, 2, and 3 ampere current respectively. At these current the COD reductions were 51.58, 63.32, 77.15 and 86.11 respectively. These data are presented in Table 3.1. The increase in electrode loss and corresponding increase in COD reduction is due to charge neutralization of negative ions contain in effluent, which neutralize when it combines with aluminum cations and polymeric hydroxide cations and forms heavy mass which settled down. The other reason is formation on Al(OH)3 and metal polymer hydroxide at alkaline pH which promote the sweep coagulation[21].

Table 3.1 : Power consummation during Electro Coagulation , distance between electrode 1.5 C. M., Initial COD 1070 g/dm3, Treatment time 75 minutes

pH	Current (A)	Average Voltage(V)	Power(W=V*I), (W)	Electrode loss (g)	Wt.of Sludge retained(g/l)	% COD Reduction
9	0.5	5	2.5	1.05	-	51.12
9	1	10	10	1.20	-	63.36
9	2	20	40	1.52	-	77.15
9	3	30	90	1.92	4.42	86.91
3	3	17	51	1.48	2.32	5.04
5	3	14	42	1.57	2.43	25.04
7	3	26	78	1.62	3.61	85.14
11	3	29	87	2.12	-	62.80

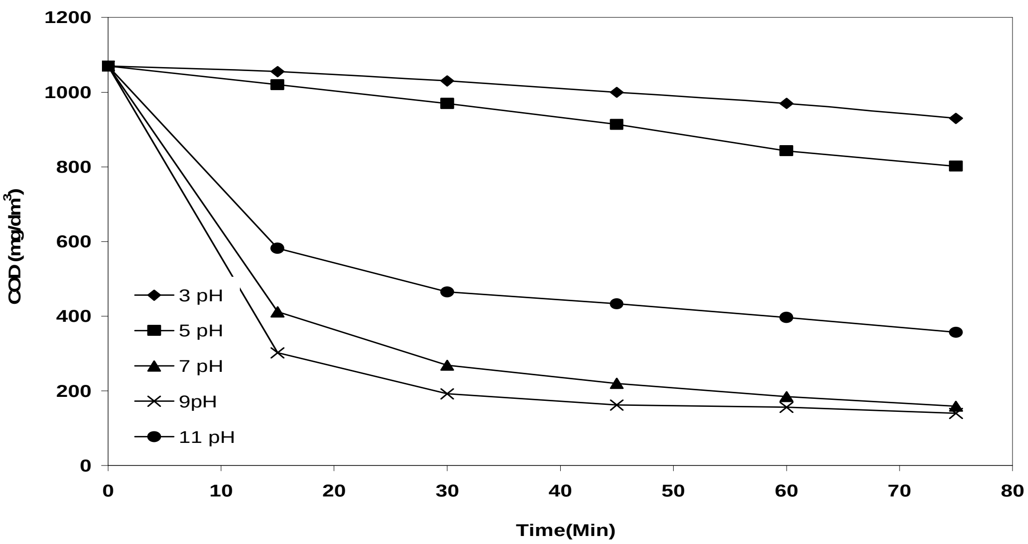

Fig. 3.1 Effect of pH0 on COD reduction of dairy wastewater by electro coagulation using aluminum electrode. COD0 = 1070 mg

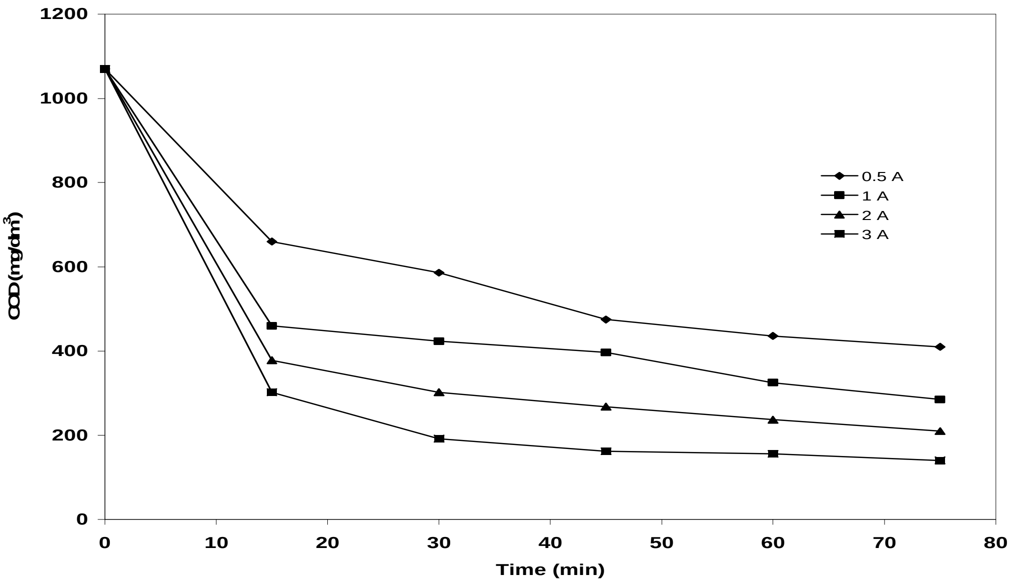

Fig. 3.2 Effect of current on COD reduction of dairy wastewater by electro coagulation using aluminum electrode. COD0 = 1070 mg/dm^3

3.3 Settling studies

Since it is necessary to remove the sludge form treated effluent it is necessary to go through the sedimentation process. For this Jar settling process was studied and the results are presented in Fig 3.3 The settling rate were in order of pH09> pH0 7> pH0 3> pH0 5. The solid liquid interface (H/H0) of the 0.25, 0.38, 0.5, 0.92, were obtained at pH0 3,5,7 and 9 respectively. Since highest interface of solid liquid was at pH0 9 and COD reduction is maximum (86.11 %) at this pH, EC at pH0 9 is favorable. From the figure it is also concluded that neutral and moderate basic pH is in favor of settling of sludge. Similar to settling studies performed in chemical coagulation treatment process, three stages of settling i.e. zone settling, transition settling and compressive settling was found in EC treatment[28-30].

3.4 Filtration studies

To find the filtration characteristics the treated effluent, it waste also taken for filtration at atmospheric pressure gravity filtration processes described earlier for filtration of alum treated DW. The results are presented in Fig. 3.4 The cake resistance were found in order of 0.66 x 109 m/kg at pH0 9 < 0.75 x 109 m/kg at pH0 7 < 0 0.78 x 109 m/kg at pH0 5 < 0.84 x 109 m/kg at pH03 and filter media resistance were 1.8 /m at pH0 3 < 2/m at pH05 <2.205/m at pH07 < 2.34 at pH0 9 . The above data are presented in Table 3.2. The above values indicate cake resistance is low at high PH while the filter media resistance is low at low

pH. Low values of (0.4 to 0.6 times) in EC treatment in comparison to chemical coagulation (CC) treatment shows porous sludge formation in EC treatment. The values of Rm ¬ ia about 1.2-1.5 times to that obtained in chemical coagulation. The values of and Rm is less in comparison to reported by various investigators [29-30] for treatment of municipal effluent, distillery effluent and textile effluent.

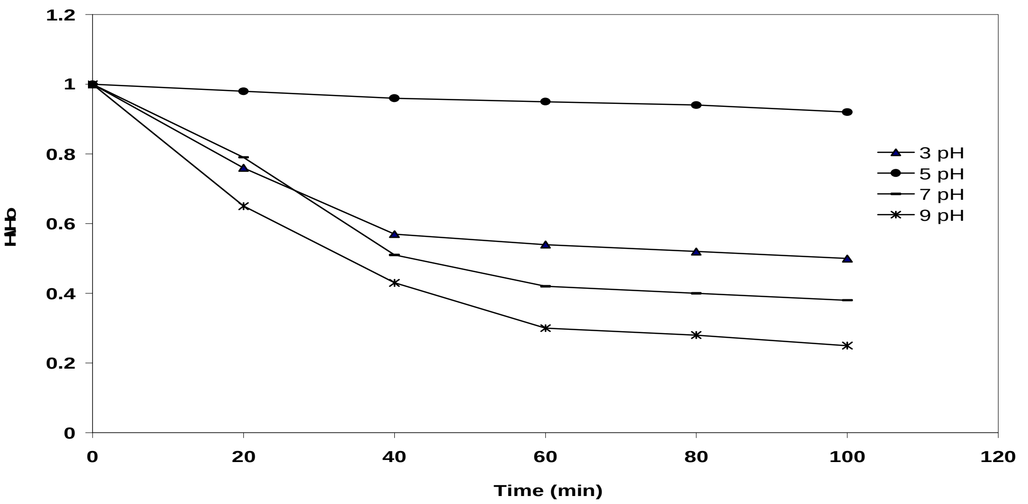

Fig. 3.3 Settling studies at different pH for electro coagulation treatment of dairy wastewater

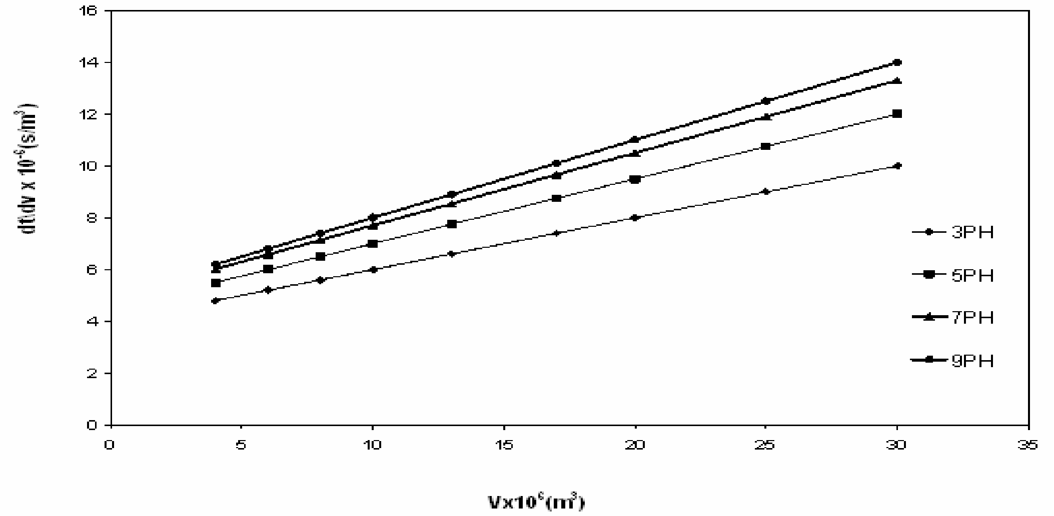

Fig 3.4. Filtration studies during electro coagulation of dairy wastewater using aluminum electrode. COD0 = 1070 mg/dm^3

Table 3.2: Filterability of slurry: Effect of initial pH

Initial PH	K_c * 10^{-12} (s/m6)	β*10^{-6} (s/m3)	C (Kg\m3)	μ*10^{-3} (Kg\ms)	α* 10^{-9} (m\Kg)	R_m *10^{-9} (m^{-1})
3PH	0.2	4	4.65	1	.84	1.8
5PH	0.25	4.5	6.27	1	0.78	2.0
7PH	0.28	5	7.22	1	0.75	2.205
9PH	0.3	5.3	8.84	1	0.66	2.34

Power consumption

To find out the power required per unit COD removal, the data were evaluated and presented in Fig. 3.5. The power consumption per unit COD removal were 103 kWh/kg at pH0 7 < 112.9 kWh/kg at pH0 9 < 143.24 kWh/kg at pH0 11 < 180 kWh/kg at pH05< 375 kWh/kg at pH0 3. Thus, power consumption in COD removal point of view, EC at pH0 7 and pH0 9 is better as compared to EC at other pH0.[30]

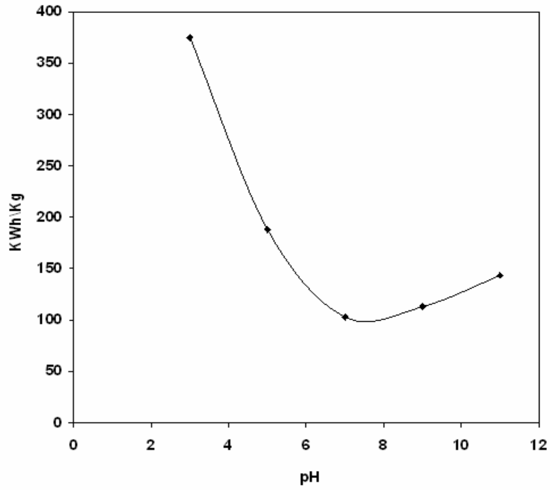

Fig. 3.5 Power consumption per unit COD removal by electro coagulation at different pH.
COD0 = 1070 mg/dm3

4.Conclusion

Electro Coagulation is a feasible process for the treatment of the dairy waste water, characterized by the high oil and greases content, fluctuated COD, BOD and SS Concentrations. The Treatment of Dairy Waste water using aluminum electrodes was affected by the initial pH, the current density, COD. The Result shows that that COD effectively removed at 9 pH. When the initial concentration of COD was 1070 mg/dm3. For the 75 min of electro coagulation time. With increase in current intensity, COD of treated effluent decreased. It is reduced to 140 mg/dm3 at the current intensity of 3A. the result also indicate that the removal efficiency of the COD is 87% at current intensity 3A and pH 9. The settling of EC treated DE solid liquid interface (H/H0) was best observed 0.92 at 9 pH. The filtration studies of EC treated sludge show the cake resistance were 0.66 x 109 m/kg at pH0 9 and filter media resistance 2.34 /m at pH0 9. At the optimum condition of COD reduction power consumption in EC for per unit COD removal were 112.9 kWh/kg at pH0 9 The EC treated DE have COD 140 mg/dm3can be used in the industries for cooling purpose as well as irrigation purpose.

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