Electrochemical treatment of biodigester effluent of maize based starch industry

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An electrochemical (EC) method for treating industrial wastewater involves compact facilities, easy operation and high efficiency. EC using iron electrode has been employed to effect the reduction of chemical oxygen demand (COD) and colour in biodigester effluent (BDE) of maize based starch industry. The operating parameters considered in this study are voltage (0-30 V), current density (CD) (49.5-247.5 A m⁻²) and *p*H (3.5-9.5). The maximum COD reduction of 89.2% is found at *p*H 6.5. Colour reduction at the same *p*H is 97% at current density 99A m⁻². These reductions are achieved at a cost of 26 mg/dm⁻³ of BDE of electrode loss with the energy consumption of 7.85 Wh/dm⁻³ of BDE. The 55% settling is obtained in 30 min. at *p*H 6.5. Filtration studies of treated effluent and sludge have also been reported in this study. The EDAX analysis demonstrates the presence of various micro nutrients. TGA analysis of the sludge has also been presented.

Keywords: Biodigester, Effluent, Chemical oxygen demand, Colour reduction, Energy consumption, Filterability, Settling.

Among various agricultural products maize is one of the major cereal grains across the world. Maize starch is used for the production of starch esters, starch phosphates, glucose, dextrose, sorbitol, ethyl alcohol etc. In India, about 8000 dm³ of fresh water is utilized to process a ton of maize and that generates 5500 m³ of highly concentrated organic wastewater¹. An integrated maize processing industry generates wastewater having chemical oxygen demand (COD) ranging between 40,000 to 50,000 mg dm⁻³ and pH in between 5 to 6. Initially, maize based starch industry waste water (MSIWW) is treated in anaerobic biodigester to recover energy in the form of methane rich gas since MSIWW contains easily biodegradable matter. The anaerobic biodigester works best at around pH 7. The composite raw effluent is mixed with biodigester effluent and it helps to maintain pHaround 7. It also reduces COD in the range of 20000-25000 mg dm⁻³ in biomethanation process. Nearly half of the BDE is used to mix with raw effluent and the remaining half is sent for further aerobic treatment. The aerobic process enables to reduce COD up to 60%, but still it is above stringent discharge limit of effluent for its release into surface water (COD< 100 mg dm⁻³) and sewers (COD< 300 mg dm⁻³) as prescribed by Central Pollution Control Board (CPCB), India¹. Aside from this, in the aerobic process submerged air bubbles or surface aerator is used for oxygen supply which has high operational

cost. This procedure is also unable to remove black colour of effluent, which hinders self purification of the surface water.

There are several treatment techniques available for organic wastewater to remove COD and colour such as adsorption^{2,3}, coagulation⁴, chemical oxidation⁵ and thermal treatment⁶⁻⁸ etc. But all these processes have some advantages and disadvantages. Only a few works are reported in the literature for maize based industry wastewater. The utilization of such methods is, however cost intensive for large-scale maize based industry wastewater. For these reasons, there have been increasing interest in the use of new methods such as electrochemical (EC) degradation^{9,10}. The EC process provides a simple, reliable and cost effective method for the treatment of wastewater without any use of chemicals, and very less generation of secondary pollutants. It also reduces the amount of sludge, which needs to be further disposed off. This technique utilizes a DC source between metal electrodes immersed in contaminated water¹¹.

In the present work, treatment of BDE from maize based starch industry has been established using EC process. So far, no work has been reported for BDE treatment using EC technology in the literature. The reduction of two tangible parameters (COD and color) was examined in the batch EC reactor by varying the process parameters such as current density (CD), initial $pH(pH_i)$, electrolysis time (t) and electrode gap (g). Settling and filtration studies were also understand undertaken to the settleability characteristics of the sludge produced during the EC process. Figure 1(a) shows the steps involved in the EC process of the present investigation. In the EC process, the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material. Iron as anode forms iron hydroxide, Fe $(OH)_n$, where n = 2 or 3 which remains in the aqueous stream as a gelatinous suspension and it helps to reduce the pollutants from the effluent either by complexation or electrostatic attraction and followed by coagulation.

Experimental Section Material

All chemicals used in this study were of analytical grade from Merck India Ltd. BDE used in this study was obtained from Raja Ram Maize Industry Pvt. Ltd., Rajnandgaon, Chhattisgarh, India. The characteristics of the wastewater used in this study are listed out in the Table 1.

Analytical process

The COD of the sample was determined by the close reflux method. Chlorides, sulphate and phosphate were determined by standard methods¹². Protein was estimated by Lowry method¹³ and the pH of the sample was determined by digital pH meter

(EI Make, India). The colour of the samples was estimated using UV-spectrophotometer (Thermo Electron Corporation make, England) at a particular wavelength ($\lambda = 460$ nm) in terms of platinum cobalt unit (PCU). Scanning electron microscopy (SEM) (LEO 435VP, England) characterization was carried out to observe the morphological image of scum and sludge. Thermal analysis of the sludge was conducted using a thermal analysis instrument (Perkin-Elmer Pyris Diamond).

Table 1 — Properties of maize industry wastewater (g =1.5 cm, CD = 99A m ⁻²)							
Contents*	Raw	Influent to BD	BDE	<i>p</i> H-6.5			
COD	42767	20583	1840	198			
Protein	4200	1420	215	124			
PO4 ⁺⁺	1075	650	320	30			
Organic N	417	504	794				
Inorganic N	275	291	536				
(Ammonical N)							
Total N	692	795	1330				
Reducing	2615	2174	769	157			
carbohydrate							
Cl	2300	1950	1875	1550			
SO_4^-	6750	6100	5796	4044			
pH	5.4	6.8	7.8	8.3			
Colour	black	light	Dark	Light			
		black	brown	yellowish brown			

*All values except pH is mg dm⁻³



Fig. 1 - (a) Flow chart showing the steps for EC study and (b) Experimental setup for EC process

Experimental setup and procedure

EC experiments were conducted in 1.5 dm³ perspex glass reactor (Fig. 1(b). Four iron electrode plates of dimension ($70 \times 72 \times 2$ mm; length×width×thickness) were used in the reactor. Total effective surface area of the each electrode was 5040 mm². A gap of 15 mm was maintained between the bottom of the electrodes and the bottom of the reactor for the movement of magnetic stirrer. A spacing of 15 mm was kept between two electrodes. During the experiment electrodes were connected in parallel. The electrode plates were cleaned manually by abrasion with sand paper, and treated with HCl solution (10%) followed by washing with distilled water prior to their use.

The anode and cathode leads were connected to the respective terminals of DC source fitted with an ammeter and voltmeter. All test runs were performed at ambient temperature $(30\pm2^{\circ}C)$. The current density was maintained as constant by means of precision digital direct current supply (0-5A, 0-30V). At the end of the experiments, the sample was filtered to remove the sludge and filtrate was used for colour and COD analysis. In each run 1.4 dm³ of BDE was taken in the electrochemical reactor. Experiments were conducted at various CD (49.5, 99, 148.5 and 198 A m⁻²) and voltages (0-30 V).

Results and Discussion

EC treatment involves a combination of various processes like electrolytic reactions at the electrode surface, formation of coagulants (hydroxides of anodic metal) in the aqueous phase, adsorption of soluble or colloidal pollutants onto the surface of coagulants and removal by electroflotation, and adhesion to bubbles. The stability and destabilization of the colloidal particles generally depend on the surface charge which is created by ionization of the functional groups present on polluting substances. The effluent contains carbohydrates, proteins, and melonoidin^{14,15}.

When potential is applied across the iron plates, dissolution of iron takes place and thus forms the iron hydroxides as per the following mechanisms:

Mechanism-I At Anode:

$$4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^{-}$$

 $4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3 + 8H^+(aq)$
...(1)

At Cathode:

$$8H^+(aq) + 8e^- \rightarrow 4H_2(g)$$

 $4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3 + 4H_2(aq)$
...(2)

Mechanism –II
At anode:
$$\frac{Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}}{Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)}$$
...(3)

$$2H_{2}O(l) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq)$$

$$4Fe(s) + 2H_{2}O(l) \rightarrow Fe(OH)_{2}(s) + H_{2}(g) \qquad ...(4)$$

Depending upon the *p*H range, the electrogenerated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species. The species such as $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe(OH)^{4-}$, $Fe(H_2O)^{2+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$ finally transforms into $Fe(OH)_3^{16}$. Ionic species were removed from the effluent by allowing them to react with the opposite charged ions or flocs of the metallic hydroxides which were generated within the effluent. The $Fe(OH)_n$ ions which remain in the aqueous solution as a gelatinous suspension removes the pollutants from the effluent either by complexation or electrostatic attraction.

Effect of pH

The performance of the EC process depends on the pH of the solution¹¹. The metal ions generation takes place at the anode; hydrogen gas gets released at the cathode. The hydrogen gas helps in floatation of the flocculated particles on the surface of the aqueous phase. The pH of BDE was varied in the range of 3.5-9.5. The pH was adjusted to the desired pH by adding NaOH (1 M) or H_2SO_4 (1 N). The effect of pH on COD and colour reduction was studied at a current density of 99 A m⁻² in each run and the results are shown in Figs. 2(a) and 2(b). The working mechanism of EC treatment using iron electrodes is similar to that of chemical coagulation using FeCl₃ as a coagulant. The COD and colour reduction at different pH depend on types of metal hydroxide formed and behaviour of organics contained in the wastewater.

It was found that the reduction of COD from BDE was higher at pH 6.5 as compared to the other pH.

The rapid reduction of COD was observed during the initial 40 min and thereafter the reduction rate decreases. In the 40 min of EC process, the percentage COD reduction achieved were (pH 9.5) 58% < (pH 3.5) 61% < (pH 4.5) 63% < (pH 5.5) 65% < (pH 8.5) 66% < (pH 7.5) 67.9% < (pH 6.5) 71%. Further increase in electrolysis time up to 100 min percentage COD reduction increases to 77 % (pH 9.5)< 83.15 (pH 3.5) < 83.69 (pH 4.5) < 84.78 (pH 5.5) < 82.33% (pH 8.5) < 83.5 (pH 7.5) < 89.2% (pH 6.5) mg dm⁻³.

This data shows that COD reduction efficiency strongly depends on the initial pH (pH_i) of the process. The formation of Fe²⁺ metal ions, hydroxo cation species and iron hydroxides varies with pH. At acidic pH, Fe(III) ions coexist in the form of Fe³⁺, Fe(OH)²⁺, Fe(OH)²⁺ and the dimer Fe₂(OH)²⁺, which attributes to higher COD reduction. Percentage COD reduction starts decreasing after pH 6.5.

A significant reduction in the colour was obtained at pH 6.5. At this pH, percentage reduction in colour was 82.44 in the initial 40 min of the process, the colour reduction further increased to 97% in 100 min, from initial colour of 2900 PCU. Percentage colour reduction at pH 3.5, 4.5, 5.5, 7.5, 8.5 and 9.5 were 92.11, 93.72, 95.1, 94.28, 91.11 and 85.89 for 100 min of EC operation. Colour reduction is an important parameter for oxygen diffusion and sunlight penetration. The reduced values obtained at pH 6.5 are within the limit prescribed by the Central Pollution Control Board (CPCB), India.

The electrode weight loss at different *p*H too was analyzed and presented in Fig. 2(c). An electrode weight loss of 24, 36, 46, 26, 28, 130, and 250 mg was calculated during treatment of 1 dm³ of BDE in 100 min of EC operation, obtained at *p*H 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5 respectively. The highest Fe dissolution of 250 mg dm⁻³ was obtained at *p*H 9.5, where COD and colour reduction were 76.79 and 85.89% respectively. The minimum weight loss of anode occurred at *p*H 3.5 during which 83.15% COD reduction and 92.11% colour reduction were



Fig. 2 — Effect of pH_i on (a) COD reduction (b) colour reduction (COD_i=1840 mg dm⁻³, Colour = 2900 PCU) (c) Anode consumption with COD and colour removal and (d)Energy consumption with COD and colour removal.

recorded. At *p*H 6.5, with a weight loss of 26 mg dm⁻³ of wastewater, COD and the colour reductions were 89.2 and 97% respectively. The effluent treated with iron electrode as anode, appears greenish first and then changes to yellowish brown and turbid. This green and yellowish brown colour might have resulted due to Fe^{2+} and Fe^{3+} ions generated during the EC process. Fe^{2+} is the most common ion generated during electrolysis of iron electrode. It has a relatively high solubility at acidic or neutral conditions and can be oxidized easily into Fe^{3+} by the dissolved oxygen in water.

The effect of *p*H on power consumption (P) was also calculated and presented in Fig. 2(d). It was found in the order of 7.85 (*p*H 6.5) < 8.57 (*p*H 5.5 and 7.5) < 9.14 (*p*H 8.5) < 9.38 (*p*H 9.5) < 10 (*p*H 3.5) < 10.47 (*p*H 4.5) (Wh/dm⁻³ of BDE). Energy consumption was lower at *p*H 6.5 with a significant COD and colour reduction. A COD reduction of 89.2% was achieved at *p*H 6.5 while colour reduction was 97%.

Effect of current density

The current density is generally defined as the current applied divided by the projected area of the electrodes. It influences the treatment efficiency in the EC process^{17,18}. An increase in current density the COD removal efficiency increases because when the current density increases more amounts of Fe^{3+} ions gets released and more ferrous hydroxide cations are formed. Which attaches with negative ions of BDE, thereby causing organic matter to convert in heavy flocks and ultimately Faraday's law describes the relationship between *j* and the amount of anode material that dissolves in the solution. It is given as:

$$m = \frac{Mjt}{ZF} \qquad \dots(5)$$

where *m* is the theoretical amount of ion produced per unit surface area by current density *j* passed for a duration of time *t*. *Z* is the number of electrons involved in the oxidation/reduction reaction; for Fe, Z=2. *M* is the atomic weight of anode material, for Fe, M=55.85 g/mol; and F is the Faraday's constant (96,486 C/mol). Generally it is known that COD removal increases with increasing iron dosages in chemical coagulation up to a certain limit. In EC, therefore, COD removal is expected to be governed by the amount of hydrous oxides formed in the solution. According to Faraday's law, *m* is directly proportional to *j*. Therefore, COD removal by EC is

governed by the formation of metal-hydrous ferric oxide complexes. It may be inferred from Fig. 3(a) that COD removal efficiency gets enhanced at higher *j* value. At higher *j*, elevated dissolution of electrode material (Faraday's law) with greater rate of formation of iron hydroxides results in higher COD removal efficiency via co-precipitation and sweep coagulation^{19,20}. The coagulated particles mass settles down due to its gravity. With the increase in applied current density the coagulant amount increases. The bubble production rate, size and the growth of flocs also increases with the increase in current density. These result in faster reduction of pollutants. Thus, the applied current density was varied (49.5-247.5 A m⁻²) to examine its effect on COD and colour reduction for a four plate configuration.

Figures 3 (a) and 3(b) depicts the result of current density on COD and colour reduction with respect to time, during the 100 min of the batch run at a *p*H value of 6.5. It is clear that at all the five current densities, the COD reduction increases with time. However, the optimum reduction in COD was observed when the current density was 99 A m⁻². At this current density, the COD value gets reduced to 198 mg dm⁻³ from 1840 mg dm⁻³, while colour is reduced to 87 PCU from 2900 PCU when the reaction time was 100 min.

Effect of electrolysis time

It can be deduced from Figs. 2 and 3, that operation time affects the COD and colour reductions. At all pH, the COD and colour get reduced faster in the initial 40 min of the EC process, after that the rate of reduction decreases. This is due to less amount of reactant (COD) available to co-ordinate with Fe species as time proceeds. In 40 min of EC process 71% COD and 82.44% colour reduction takes place, which increases to 89.2% COD and 97% colour reduction during 100 min at pH 6.5. Also at other pH and CD, COD and colour reduction seems to be faster in the initial period and then decreases with time. The electrolysis time also plays a very significant role for the treatment of effluent. Amount of ions produced is the function of electrolysis time, i.e. amount of ions production increases with respect to electrolysis time. Therefore, increase in t, causes an increase in concentration of iron ions and their hydroxide flocs. Consequently, when t is increased the COD and colour removal efficiency also increases.

The pH also changes with time and has a considerable effect on the treatment process. In



Fig. 3 — Effects of CD on (a) COD (b) colour reduction. (pH= 6.5) and (c) Change in initial pH of BDE-MSIWW during EC process

addition, pH changes during the process are dependent on the anode material and the initial pHvalue of the treated solution. To explore the effect of the operating time on the pH values, the variation in pH_i (3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5) of solution were observed at CD of 99 Am⁻² for four plate configurations. Fig. 3(c) shows a relationship between operating time and pH values. As shown in Fig. 3(c), the pH value changes as the time of EC process is extended. It was found that the pH of the solution increases as operation time gets extended at pH 3.5, 4.5, 5.5, 6.5 and 8.5. Final pH was found to decrease slightly during EC operation at pH_i 9.5. It was also observed that the pH increases linearly initially during the EC process at pH 3.5 and 5.5. The final pH of treated BDE changes to 7.2, 7.6, 7.9, 8.3, 8.4, 9.0 and 8.9 for pHi 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5 respectively. The increase of pH in acidic condition is attributed to hydrogen evolution at cathodes. This characteristic of pHchanges during the electrochemical process is quite meaningful in its application to treat maize based industrial wastewater. The pH_i also affects the heat evolution during electrolysis.

Sludge settling

Liquid-solid suspension obtained from the EC process was mixed, and the resultant slurry was used for the settling study. For the study the slurry was taken in a 0.5 dm³ graduated glass cylinder and height of interface with time was noted. The dimensionless height of the solid/liquid interface (H/H₀) versus time for different pH_i values, varying from 3.5-9.5 are presented in Fig. 4 (a). Initially slow sludge settling was observed for a very short period of time. It was due to the Brownian motion of the particles. Later a steady state decrease in height of the solid / liquid interface was observed, exhibiting the regime of zone settling. Thereafter, the transition settling period comes into play. Finally the compression settling

takes place, which has a steady state and a much smaller rate of decrease in height of the solid /liquid interface occurs. The settling characteristic of treated BDE at pH 3.5 to 6.5 was found to be good, while at other pH it was poor, 73% and 59% settling occurs at pH 3.5 and 6.5 respectively, in 40 min. The settling rate after 100 minutes operation exists in the order of *p*H 3.5 > *p*H 4.5 > *p*H 5.5 > *p*H 6.5 > *p*H 8.5 > *p*H 7.5 > pH 9.5.

Filtration study

To study the filtration characteristic of the slurry obtained after the EC process, the filtration



experiment was performed on Whatman 42 filter paper. The filter paper was supported on a ceramic Buckner funnel. Filtration resistances for the filter media as well as for the filter cake are obtained using the following equation²¹:

$$\frac{dt}{dV} = K_p V + \beta \qquad \dots (6)$$

$$k_p = \frac{c\alpha\mu}{A^2(-\Delta p)} \qquad \dots (7)$$

and

$$\beta = \frac{\mu Rm}{A(-\Delta p)} \qquad \dots (8)$$

where 't' is the time taken for filtration (s), 'V' volume of filtrate collected in t time (m³), k_p is the slope of the plot of Eq. (6) (s m⁻⁶), β is the intercept for the plot of Eq. (6) (s m⁻³), c is the concentration of sludge (kg m⁻³), α is the specific cake resistance (m kg⁻¹), μ viscosity of the filtrate (Pa s), A is the area of the filter media (m^2) , Δp is the pressure drop across the filter (Pa) and $R_{\rm m}$ the filter medium resistance (m^{-1}) .

Fig. 4 (b) shows the plot between (dt/dV) and volume at different values of pH ranging from 3.5 to 9.5. The value of filter media resistance was calculated as 24.5×10^9 , 21.64×10^9 , 46.01×10^9 , 40.0×10^9 , 41.02×10^9 , 39.24×10^9 , 36.87×10^9 m⁻¹ and cake resistances 104.52×10^{12} , 84.19×10^{12} , 249×10^{12} , 189×10^{12} , 120.78×10^{12} , 142.46×10^{12} and 129.2×10^{12} m kg⁻¹ at pH 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5 respectively. Filtrate analysis and filterability data of treated wastewater are presented in Table 2 and Table 3. The filter medium resistance plays an important role during the early stage of filtration. The values of specific cake resistance for

$\begin{array}{llllllllllllllllllllllllllllllllllll$		Colour	Specific gravity*	COD mg dm ⁻³	Colour (PCU)	
3.5	7.2	Light brown	1.092	310	228.8	
4.5	7.6	Light brown	1.111	300	182	
5.5	7.9	Light yellowish brown	1.109	280	142	
6.5	8.3	Light yellowish brown	1.107	198	87	
7.5	8.4	Light yellowish brown	1.110	305	165.9	
8.5	9.0	Light brown	1.120	325	257	
9.5	8.9	Light brown	1.121	427	409	

EC at diff. m 11 C .1 C14 1. . . . 1.0.

*V Specific gravity of water at $20^{\circ}C = 1.084$ Determined at ambient temperature (20°C) different sludge have been reported by Barnes *et al.*²². These values are $30-300 \times 10^{12}$ m kg⁻¹ for the digested sludge and $40-120 \times 10^{12}$ m kg⁻¹ for activated sludge. The specific cake resistance values calculated are found closer to the reported value of digested sludge.

Analysis of residues

The residue obtained from EC treatment at 99 A m⁻² is presented in Table 4. At *p*H 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5, the residue obtained after treatment are 8.12, 8.49, 8.58, 9.05, 8.21, 8.08 and 7.92 g dm⁻³ respectively. The colour of the residues was light brown and dark brown. The residues obtained at *p*H 3.5, 4.5 and 5.5 had fair grinding property, while at *p*H 6.5, 7.5, 8.5 and 9.5 residues were easily grindable.

SEM analysis of reactor sludge shows its granular nature (Fig. 5). EDAX analysis shows the presence of C, O, K, P, Cr, Fe, Ni and Cl. The Fe generated from SS plate, comes down in the sludge, due to this it FeK in sludge is 23.82 wt%. Carbon also gets deposited in the sludge and the CK value is 32.27 wt%. FeK in scum was 22.19 wt% and CK 23.30 wt% .After incineration the ash obtained can be used as a micronutrient for blending it either with organic manure or mixed with raw materials to manufacture bricks. The scum contains C, O, K, Fe in higher proportions along with small amounts of Na, S, Cl, Cr and Ni. The scum can also be used as a micronutrient after incineration. SEM analysis shows the amorphous nature of the scum.

Table 3 — Filterability of the treated wastewater							
Initial <i>p</i> H	$k_c \times 10^{-12}$ s m ⁻⁶	$\frac{\beta\times10^{\text{-6}}}{\text{s m}^{\text{-3}}}$	C g dm ⁻³	$\mu \times 10^3$ Pa.S	$\begin{array}{c} \alpha \times 10^{\text{-12}} \\ m \text{ kg}^{\text{-1}} \end{array}$	$\begin{array}{c} Rm \times 10^{-9} \\ m^{-1} \end{array}$	
3.5	0.0161	16.51	8.50	1.026	104.52	24.05	
4.5	0.0533	14.57	9.22	1.014	84.19	21.46	
5.5	0.1463	33.194	8.11	1.078	249	46.01	
6.5	0.1252	29.719	8.91	1.110	189	40.04	
7.5	.071	28.08	8.52	1.031	120.78	41.02	
8.5	.082	27.18	8.31	1.035	142.46	39.24	
9.5	.08	26.18	8.72	1.061	129.2	36.87	

DTG, DTA, and TG curve of the scum and precipitated sludge were obtained at pH 6.5. TG curve shows that up to 300°C temperature, dehydration and volatilization (reduction of volatiles) of the sample takes place and a reduction of 20 µg wt% and 17.2 µg wt% is recorded for scum and sludge respectively. From 300 to 600°C, in the span of 300°C, the precipitate is oxidized, losing about 8.4 wt% of scum and 4.6 wt% of the sludge. After 600°C the oxidation is slow and the final decrease in weight of the scum and sludge is recorded as 6.5 wt % and 3.5 wt% respectively. The ash in scum and sludge remains



Fig. 5 — SEM study of (a) scum and (b) sludge sample.

Table 4 — Analysis of the residue obtained after EC							
Initial <i>p</i> H	3.5	4.5	5.5	6.5	7.5	8.5	9.5
Final <i>p</i> H	7.2	7.6	7.9	8.3	8.4	9.0	8.9
Wt. of residue (g/dm ³)	8.12	8.49	8.58	9.05	8.21	8.08	7.92
Colour	Light brown	Light brown	Light brown	Light brown	Light brown	Dark brown	Dark brown
Nature	Flaky, difficult to grind	Lumpy mass , difficult to grind	Flaky difficult to grind	Flaky easy to grind	Flaky easy to grind	Flaky easy to grind	Flaky easy to grind
% Convertible COD	83.15	83.69	84.78	89.2	83.42	82.33	76.79

65.1% and 74.7%. The DTG curve shows the peak rate of weight loss of 87 μ g min⁻¹ at 140°C for sludge and 120 μ g min⁻¹ at 113°C for scum. The oxidation of top scum is exothermic, with a heat evolution of 230 MJ kg⁻¹ at 400°C. This study shows the inorganic nature of the sludge.

Conclusion

The present study demonstrates the applicability of EC process for COD and colour reduction from BDE. COD of BDE is reduced from initial value of 1840 mg dm⁻³ to 310, 300, 280, 198.7, 305, 325.1 and 422.4 mg dm⁻³ at pH 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5, respectively. Similarly at pH 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5, the colour reduction is found to be 228, 182.1, 142.1, 87, 165.8, 257.8 and 409.1 PCU from initial colour of 2900 PCU. The above results are obtained at optimum CD of 99 A m⁻². The settling characteristics of the treated BDE are found to be good at pH 3.5 (73%) and 6.5 (59%) during the initial 40 min. The settling rate is observed in the order of *p*H 3.5 > *p*H 4.5 > *p*H 5.5 > *p*H 6.5 > *p*H 8.5 > *p*H 7.5 > pH 9.5. At pH 6.5 the value of filter media resistance is found to be $40.04 \times 10^9 \text{ m}^{-1}$ and that of cake resistance is 189×10^{12} m kg⁻¹. The finding shows that EC treatment using iron electrode reduces the level of the COD and colour to a level where it can be directly released into the sewer.

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