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ORIGINAL PAPER

Electrochemical treatment of actual sugar industry wastewater using aluminum electrode

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Abstract In the present study, electrochemical (EC) treatment of sugar industry wastewater (SIWW) was investigated using aluminum electrode. Effect of various parameters such as pH, current density (CD), electrode gap and electrolysis time was evaluated for chemical oxygen demand (COD) and color reduction. Energy requirement and electrode loss were found to increase with an increase in pH. Kinetics studies showed that the COD reduction rate was second order with respect to organic materials (COD) and 0.591 order with respect to CD. Filtration of treated slurry was found to be best near the neutral pH, while settling was best at pH 10. Operating cost of the treatment has been calculated. Results demonstrate that EC can be applied to reduce pollution load of SIWW.

Keywords COD removal · Color removal · Current density · Filtration · Settling

Introduction

Sugar industry is one of the largest agro-based industries in the world. Among the various sugar-producing countries, India is the second largest producer and consumer of sugar per annum. In sugar industry, around 1.5–2 m^3 of water is consumed and about 1 m^3 of effluent is generated for every ton of cane processed (Asaithambi and Matheswaran 2011). Effluents are generated from various sections of plants such as from floor washing, condensate, leakage and spillage of cane juice in various parts. Wastewaters coming out from these sections have different characteristics; therefore, equalization is done so as to have common characteristics of the discharged effluent. In a typical sugar industry, the grit and suspended solids are removed by passing it through bar screening. After that, it is taken to equalization tank where compressed air is passed for uniform distribution of components present in it. Wastewater of equalization tank contains BOD 1,700–6,000 mg/dm^3, chemical oxygen demand (COD) 2,300–8,000 mg/dm^3 and suspended solids about 5,000 mg/dm^3 (EHS 2007). Apart from these, it contains pathogens and contaminated materials.

Release of effluent without proper treatment leads to serious environmental and health problems; therefore, proper treatment is necessary before its discharge into the water bodies. Physicochemical and biological (aerobic and or anaerobic) processes are most commonly applied in sugar industry. Anaerobic treatment has advantage of producing methane-rich gas, but limitation of this process is its ability to decompose part of organics; therefore, it is further treated by biological oxidation process. Another option to treat sugar industry wastewater (SIWW) is coagulation with alum in the presence of lime followed by biological oxidation. Both processes are collectively not able to produce treated effluent up to the discharge standards for release into surface water (COD < 100 mg/dm^3) and serves (COD < 300 mg/dm^3) prescribed by World Health Organization (WHO). Treated effluent is dark black in color, which resists oxygen diffusion and sunlight penetration causing death of aquatic life.

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Different methods and technologies such as coagulation (Tan et al. 2000; Chaudhari et al. 2007), aerobic and anaerobic treatments (LaPara et al. 2000), advanced oxidation process (Esplugas et al. 2002; Asaithambi et al. 2014), adsorption (Faust and Aly 1987) and electrolysis (Szpyrkowicz et al. 1995; Sridhar et al. 2014) have been reported to treat industrial wastewaters. These treatment processes require high capital and operating cost. Among various technologies, electrochemical (EC) treatment is one of the best economical alternative processes (Chen 2004; Ponselvan et al. 2009) when conventional treatment methods fail to reduce pollution among industrial effluents (Brillas et al. 1998). EC process is a recently developed technique which is being employed in the treatment of various wastewaters (Kim et al. 2002; Aoudj et al. 2010; Serge et al. 2010; Kamaraj et al. 2013; Maleki et al. 2014; Ndjomgoue-Yossa et al. 2014). It is a simple, efficient, safe, flexible and cost-effective treatment process (Bayramoglu et al. 2004, 2007; Guven et al. 2009). Less sludge generation, less chemicals requirement, little space requirement, shorter residence time and colorless treated effluent production are some advantages of this process (Ahlawat et al. 2008). Kushwaha (2013) has shown various treatment technologies to treat SIWW in his review article. Some works have been reported on treatment of simulated SIWW by EC process (Guven et al. 2009; Asaithambi and Matheswaran 2011); however, no work has been reported to treat original cane-based SIWW.

The present paper aimed to use aluminum electrodes for the removal of COD and color from the SIWW. Effects of pH, CD, electrode gap (EG) and treatment time (t_R) have been studied on the removal of COD and color. Kinetics of the treatment process has been studied, and settling and filterability characteristics of the EC-treated SIWW and operating cost has also been reported.

Materials and methods

Materials

Wastewater used for experiments was from Bhoramdev Sugar Industry Ltd., Kawardha, Chhattisgarh, India. The composition of effluent before and after treatment is presented in Table 1. Analytical grade chemicals made by Merck Limited, Mumbai, India, were used for analysis. The aluminum sheet was used as electrode which was purchased from local market.

Experimental method

The complete setup of experimental program is shown in Fig. 1 and dimension is given in Table 2. EC reactor (ECR) was made of Perspex glass in which four aluminum anode and cathode electrodes were arranged in parallel mono-polar mode and connected with DC power supply. Current flow through the cell and the voltage across the electrodes were measured with an ammeter and a voltmeter, respectively. A magnetic bar and speed regulator were also placed for mixing the effluent during the treatment. For treatment, 1.4 dm^3 of SIWW was taken in 1.5 dm^3 ECR, and after treatment time intervals, 10 ml sample was taken in test tube and sludge contained in it was allowed to settle. Supernatant liquid was analyzed for COD, color and other parameters. Temperature of the suspension in EC reactor was measured using a thermometer. Before each run, the electrodes were washed with 10 % HCl to remove grease and impurities on the electrode surfaces.

Table 1 Characteristics of SIWW before and after treatment at CD 178 A/dm^2, EG = 20 mm, pH 7

S. no	Characteristics	Before treatment	After treatments
1	Color	Dark brown	Pale yellow
2	pH	5.5	8.24
3	COD	3,682	699
5	Phosphate	5.9	2.1
6	Protein	43	16
7	Total solid	1,987	757
8	Suspended solid	540	247
9	Dissolved solid	1,447	510
10	Chloride	50	18
11	Hardness	900	422

All the values except pH and color is in mg/dm^3

Analytical procedure

COD of the sample was determined by the standard dichromate open reflux method (Clesceri et al. 1989). Chloride concentration was determined by the standard titrimetric Volhard method (Vogal 1958). Sulfate was determined by gravitational method. Phosphate was estimated by using standard methods (Clesceri et al. 1989). The protein content was determined by the Lowry method (Cartier et al. 1997). The color of the sample was measured in terms of the percentage decrease in absorbance at $\lambda = 420$ nm (Guimarac et al. 2005; Can et al. 2006). For colorimetric analysis, UV–visible spectrophotometer made by Thermo Electron Corporation, USA, was used.

Results and discussion

Mechanism of electrochemical treatment

Various types of EC reactions in the reactor depend on electrode materials used in the process. Aluminum and iron

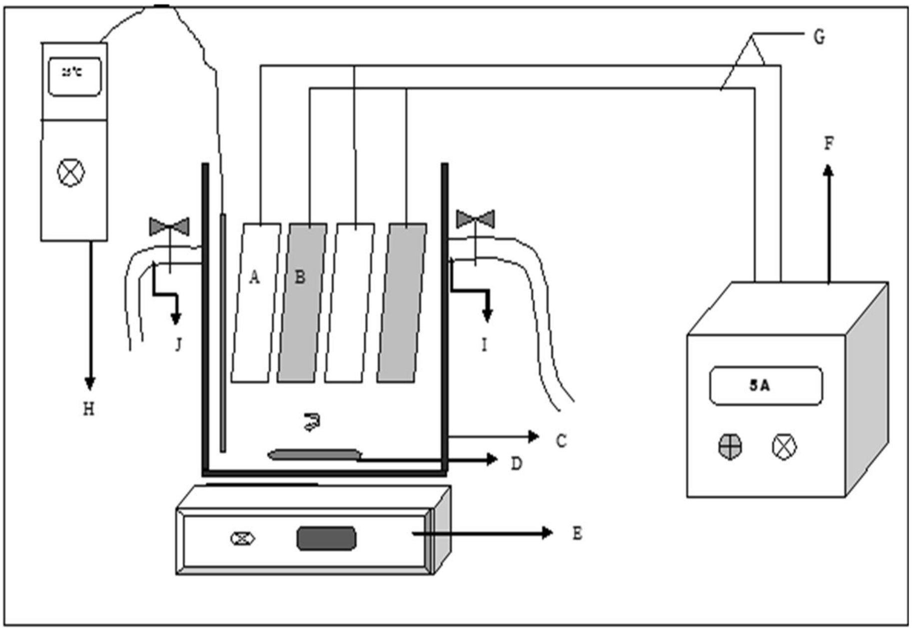

Fig. 1 Electrochemical experimental setup. (*A*) anode, (*B*) cathode, (*C*) electrochemical reactor, (*D*) magnetic bar, (*E*) magnetic stirrer, (*F*) DC supply, (*G*) wire, (*H*) digital thermometer, (*I*) water inlet and (*J*) water outlet

Table 2 Characteristics of EC (Al plate)

S. no		
Electrode		
1	Material(anode and cathode)	Aluminum
2	Shape	Rectangular may be square
3	Size	7.5 cm × 7.5 cm
4	Thickness	2 mm
5	Plate arrangement	Parallel
6	Effective electrode surface area	56.25 cm^2
Reactor characteristics		
1	Make	Perspex glass
2	Reactor type	Batch mode
3	Dimensions(cm)	10.7 × 10.7 × 13.7
4	Volume(dm^3)	1.5
5	Electrode gap	15–25 mm
6	Stirring mechanism	Magnetic bar
Power supply		
1	Voltage range	0–30(V)
2	Current	0–5(A)

electrodes have been used widely in EC systems. Treatment efficiency of aluminum seems to be superior compared with iron in most cases (Akanksha and Lokesh 2013). But, high cost of aluminum and its adverse effect on health limits its use. In the EC process, coagulants get generated in situ from aluminum electrode material. Charged ionic colloidal species in the wastewater are removed by their interaction with an ion having opposite charge. Steps occurring during EC treatment are as follows: (1) anode dissolution, (2) formation of OH^- ions and H_2 at the cathode, (3) electrolytic reactions at electrode surfaces, (4) adsorption of coagulant on colloidal pollutants and (5) removal by sedimentation or flotation (Nordsom and May 1989; Kushwaha et al. 2011). When aluminum electrodes are used, the following EC reactions occur (Singh et al. 2013a, b, c):

At the anode:

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

$$2H_2O \rightarrow 4H^+_{(aq)} + O_2 + 4e^- \tag{2}$$

At the cathode, depending on pH:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{3}$$

$$2H_{(aq)} + 2e^- \rightarrow H_{2(g)} \tag{4}$$

The $Al^{3+}_{(aq)}$ ions combine with water and hydroxyl ions to form corresponding hydroxides and/or polyhydroxides as follows (Holt et al. 2005). Monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ are generated as shown in Eqs. 5, 6 and 8. Amorphous and less soluble species such as $Al(OH)_3$ are generated as shown in Eq. 7.

$$Al^{3+} + H_2O \rightarrow Al\ (OH)^{2+} + H^+ \tag{5}$$

$$l(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \tag{6}$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \tag{7}$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \tag{8}$$

The concentration of the various Al forms present in the solution depends on pH (Vik et al. 1984). The removal of pollutants takes place by the following mechanism. (1) Aluminum cations and hydroxide complexes acting as coagulants are adsorbed on the SIWW and thus neutralizing the colloidal charges and resulting in destabilization of the colloids. (2) The amorphous and neutralized masses adsorb the pollutants during its settling and remove it through the phenomena of sweeping. (3) Hydrogen bubbles formed at the cathode absorb the flocculated species and induce their flotation, thus helping in the removal of lighter colloids by floatation. Bubbles formed also reduce cathode surface fouling which occurs due the deposition of colloids. The net rate of pollutant removal is due to combination of all the three mechanisms.

Effect of initial pH

Effect of pH_i on COD and color removal

The pH_i has been found to influence highly on treatment of various effluents in EC process. Therefore, its effects on COD and color reduction were examined at CD = 89 A/m^2 and EG = 20 mm for t_R = 120 min. The results are presented in Fig. 2a, b. It may be seen from the Fig. 2a that the COD reduction increased with increase in pH_i from 2 to 7, after that it decreased with increase in pH. At pH 2, 4, 6, 7, 8 and 10, COD reductions were 32, 42, 50, 60, 52 and 42 %, respectively. The color reductions followed the order of COD reductions and found to increase up to pH 7. The color reductions of 43, 49, 57 and 67 % were noted at pH 2, 4, 6 and 7, respectively, which decreased to 64 and 49 % at pH 8 and 10. The COD and color reduction data reflect pH 7 to optimum. Aluminum ions may be found in different forms and phases, depending on the pH and chemical characteristics of the solution (Aoudj et al. 2010; Serge et al. 2010). It has been reported, at pH value <4, aluminum ions released from electrodes are found in the form $Al(H_2O)_6^{3+}$, while at a pH range of 5–6, aluminum may be in the form $Al(OH)^{2+}$ and further increase in pH changes aluminum to $Al(OH)_3$. The changes in pH also modify the surface charge of colloidal particles present in the effluent and greatly influence its removal. It has also been reported that pH changes the chemical forms of aluminum and that it affects electrocoagulation efficiency to some extent (Drogui et al. 2008). SIWW contains colloidal suspensions and melanoidins. Both have a net negative charge which react with metal and metal hydroxide cations and form neutral heavy mass which settles down. The other mechanisms involved in the EC treatment have already been discussed.

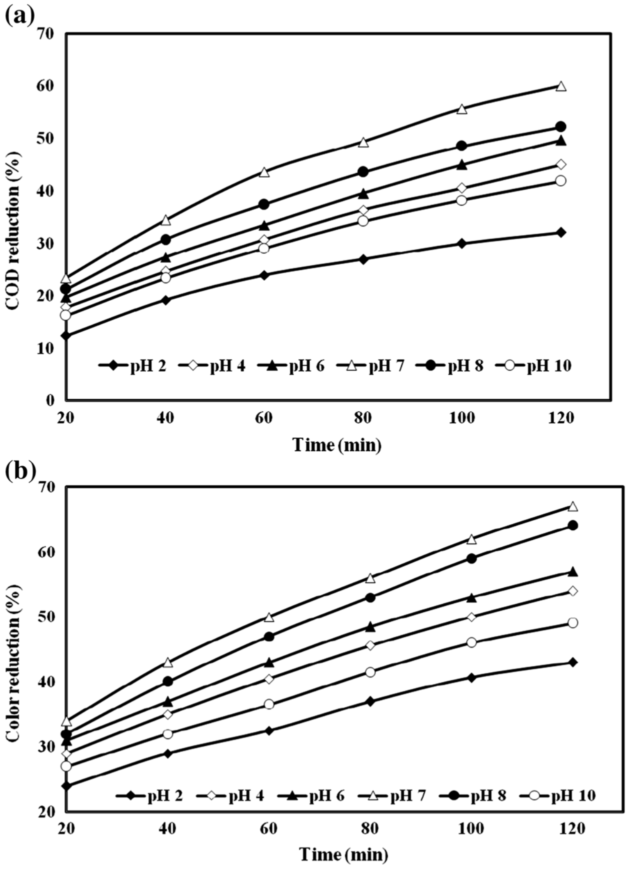

Fig. 2 Effect of pH on **a** COD removal and **b** color removal. CD 89 A/m^2, EG 20 mm

Effect of pH on energy consumption

Among the operating cost of electrochemical treatment (ECT), the cost of aluminum electrodes consumption and electrical energy consumption are the most important (Singh et al. 2013b). Energy consumption is defined as energy consumed per unit volume of treated effluent and SEC is defined as the amount of energy consumed per unit volume of effluent treated and per unit mass of COD removed expressed in kWh/(dm^3 kg COD removed).Energy consumption and specific energy consumption (SEC) were evaluated using Eqs. 9 and 10, respectively.

$$\text{Energy consumption}\,(\text{Wh}\,\text{dm}^{-3}) = \frac{\text{VIt}}{\text{Treated volume}\,(\text{dm}^3)} \tag{9}$$

$$\text{SEC}\left(\frac{\text{kWh}}{\text{dm}^3\ \text{kg COD removal}}\right) = \frac{\text{VIt}}{\text{Treated volume}\,(\text{dm}^3)\,\text{kg COD removed}} \tag{10}$$

where V is the voltage across the electrodes, I is the current, and t is the time in hour. To estimate the energy consumption and SEC, experiments were carried out at CD 89 A/m^2 and at various pH_i for a period of 120 min. The results are presented in Fig. 3a and 3b. Energy consumption values were found to be 16.20, 17.14, 20.75, 22.85, 32.10 and 33.70 kWh/m^3 for SIWW treated at pH 2, 4, 6, 7, 8 and 10, respectively. During the EC

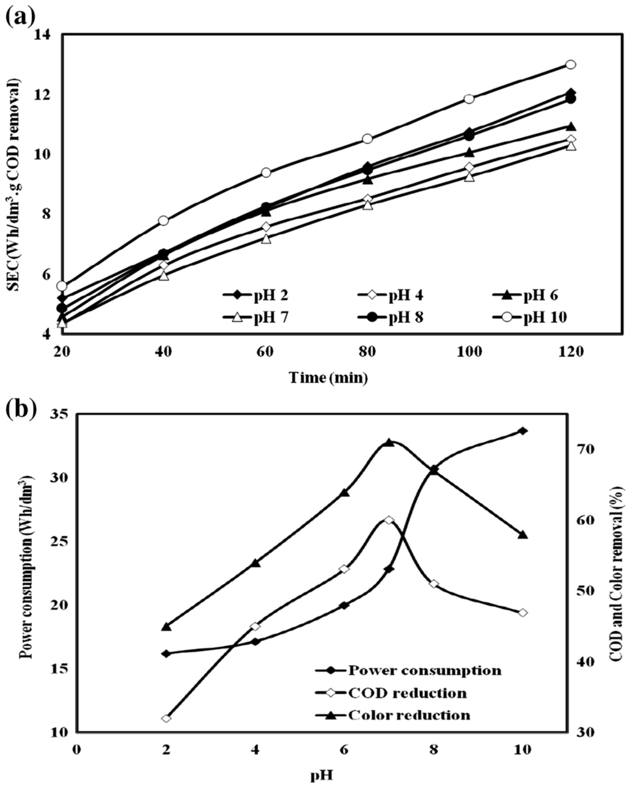

Fig. 3 Effect of pH on **a** specific energy consumption and **b** power consumption. CD 89 A/m^2, EG 20 mm

treatment, colloidal flocs adhere to the aluminum electrode surface which further work as an insulator causing an increase in voltage (Maleki et al. 2014). During experiment, voltage was found to increase with increase in pH, which causes high power consumption. The SEC of 12.08, 10.52, 10.95, 10.30, 11.85 and 13.01 kWh/(dm^3 kg COD removal) were obtained at pH 2, 4, 6, 7, 8 and 10, respectively. SEC was not in order of energy consumption. Besides having high energy consumption, SEC was less at pH 7, which is due to relatively high COD reductions at different pH.

Effect of pH on electrode loss

Electrode losses (EL) were also calculated at different pH. Two anodes and two cathodes were used in experiments. Faraday's law relates current density (CD) (A/dm^2) and the amount of substances (M) dissolved (g of M/cm^3):

$$W = \frac{\mathrm{CD.t.M}}{\mathrm{nF}} \tag{11}$$

where W is the quantity of electrode material dissolved (g of M/cm^3), CD is the current density (A/cm^2), t is time in sec, M is relative molar mass of the electrode concerned, n is the number of electrons in oxidation/reduction reaction, and F is the Faraday's constant, 96,500 C/mol.

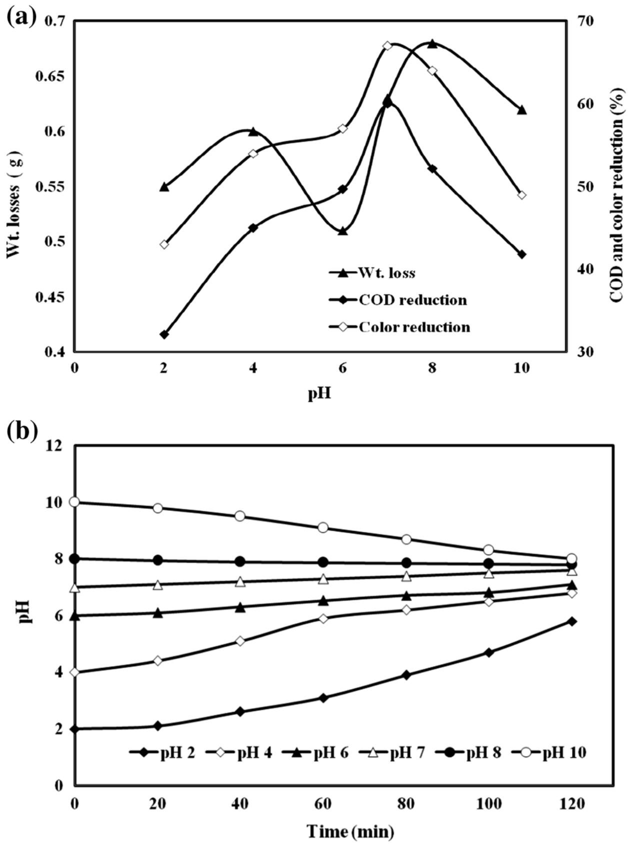

Fig. 4 Effect of pH on **a** electrode weight loss and **b** change in pH. pH$_i$ 7, CD 89 A/m^2

EL with pH values is shown in Fig. 4a. EL loss was increased considerably with increase in pH from pH 6–8. In the pH range of 2–6, EL was the highest at pH 4. The values of EL were estimated to be 0.55, 0.60, 0.51, 0.63, 0.68 and 0.62 g/dm^3 for SIWW for 2 h at pH 2, 4, 6, 7, 8 and 10, respectively. High EL at basic pH may be due to the presence of more OH$^-$ ions which leads to the formation of $Al(OH)_3$ and at acidic pH, H$^+$ attacks anode. Experimental data show that at pH 7, maximum 60 % COD reduction and 70 % color reduction were obtained with cost of 0.51 g/dm^3 EL and the lowest SEC = 10.30 kWh/(dm^3 kg COD removal), which shows EC operation at pH 7 is the best. The results obtained are at CD 89 A/m^2. As per Faraday's law represented in Eq. 11, amount of aluminum ions increases with CD. High CD increases the operation cost as there is increase in energy consumption and metal dissolution. In the process, 79 % COD reduction achieved when CD increased to 178 A/m^2.

Effect of process time on pH

pH has been found to have considerable effect on the efficiency of the EC process, and its value varied with time. Change in pH depends on the type of electrode material and initial pH of solution. To study the effect of reaction time on pH change, experiments were performed at CD = 89 A/m^2 and EG = 20 mm. pH of solution was noted at 20-min intervals. Results are presented in Fig. 4b. It was noted that when sample was acidic in nature, the pH increased. For initial pH (pH_i) of 2, 4, 6 and 7, final pH was 5.8, 6.8, 7.1 and 7.6, respectively. For alkaline pH_i of 8 and 10, final pH decreased to 7.8 and 8.0, respectively. For all the experiments, the rate of change in pH was found to be fast in the first 40 min of reaction and became slow later on. This is due to formation of negative- and positive-charged species which varied with pH of solution. When pH_i is significantly alkaline ($pH_i > 9$), it decreases probably due to the formation of aluminate ion $[Al(OH)_4^-]$, which is an alkalinity consumer (Bayramoglu et al. 2004); however, most of the aluminum ions are in the form $Al(OH)_3$ at basic pH.

Effect of electrode gaps

The space between two electrodes also affects the electrolysis reaction. It is one of the controlling parameters which can affect the size of the reactor, the EC and overall cost of treatment as well. Effect of EG on treatment of SIWW was carried out at fixed operational condition ($pH_i = 7$, CD = 89 A/m^2, and $t_R = 120$ min) and altering gap (10, 15, 20 and 25 mm) between electrodes. The results are presented in Fig. 5. The results show moderate increase in COD removal efficiency (from 38 to 60 %) with increase in EG from 10 to 20 mm. Further increase in EG to value 25 mm reduced the COD reduction to 55 %. Color reductions followed the same order. At EG of 10, 15, 20 and 25 mm, 44.6, 54, 61 and 67 % color reductions were obtained, respectively. Decreasing the EG could decrease the flotation process by limiting the generated bubbles in a narrow space which results in higher removal efficiencies. But, there should be proper space for circulation of effluent in ECR. Both the effects contribute to net removal of COD. As EG increases, the resistance also increases, thus, power consumption also increases. Therefore, increase in IR drop by increase in EG between anode and cathode is not recommended in EC process (Vik et al. 1984). The relation between EG and resistance is expressed by the equation:

$$R = \frac{EG}{KA} \tag{12}$$

where K is the cell-specific conductance and A is electrode surface area. Increase in value of EG after certain limit decreases the aluminum oxidation rate and thus decreases COD and color removal efficiency. Based on the results, 20 mm of spacing was selected as the optimal value of distance between electrodes for the experiments.

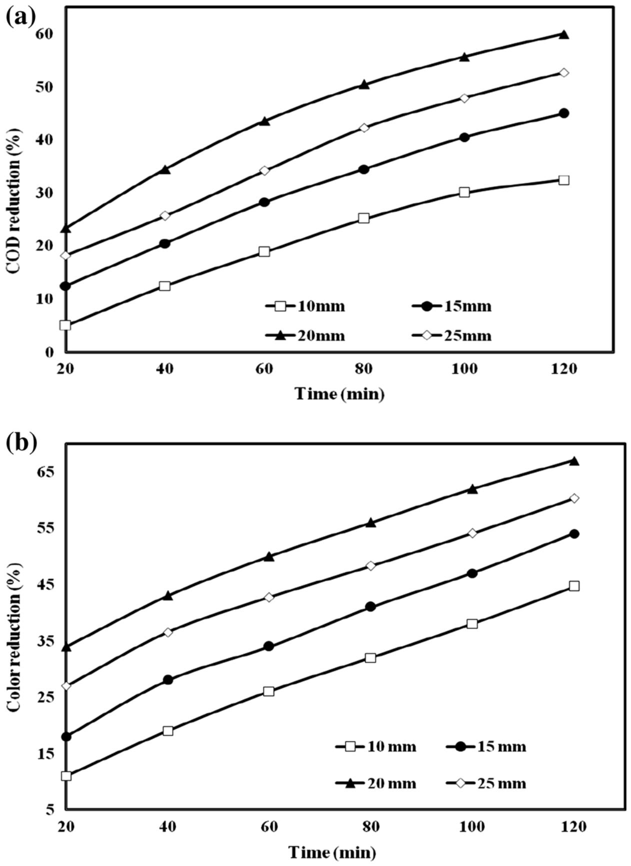

Fig. 5 Effect of electrode gap on **a** COD removal and **b** color removal. pH_i 7, CD 89 A/m^2

Effect of current density

Effect of current density on COD and color reduction

Current density is one of the important parameters which significantly influence the ECT (Mahesh et al. 2006; Asaithambi and Matheswaran 2011). To examine the effect of CD, experiments were performed in the CD range of 44.5–222.5 A/m^2 (1-5 A) at constant EG 20 mm and pH_i 7. The results as COD and color reduction are presented in Fig. 6a, b. Figure shows COD removal efficiencies of 52, 60, 69, 79 and 74 % and color removal efficiencies of 64, 67, 73.5, 82 and 78 % at CD 44.4, 89, 178 and 222.5 A/m^2, respectively. The results ascertain increase in the removal efficiency with applied CD. The rate of anodic dissolution of aluminum increases at higher CDs, resulting in a greater amount of coagulant and precipitant production. Consequently, this resulted in a higher removal efficiency of organics. Apart from this, increase in smaller-sized bubbles at high CD results in a higher removal efficiency of organics via H_2 flotation, in addition to the effect of coagulation (Song et al. 2008). The excess formation of aluminum and its hydroxide cations at CD = 222.5 A/m^2

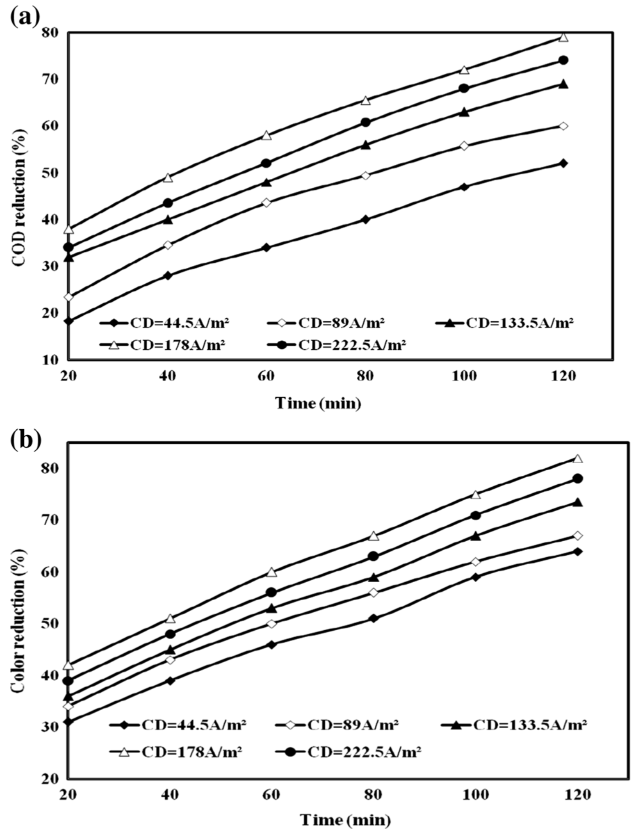

Fig. 6 Effect of CD on **a** COD removal and **b** color removal. pH_i 7, EG 20 mm

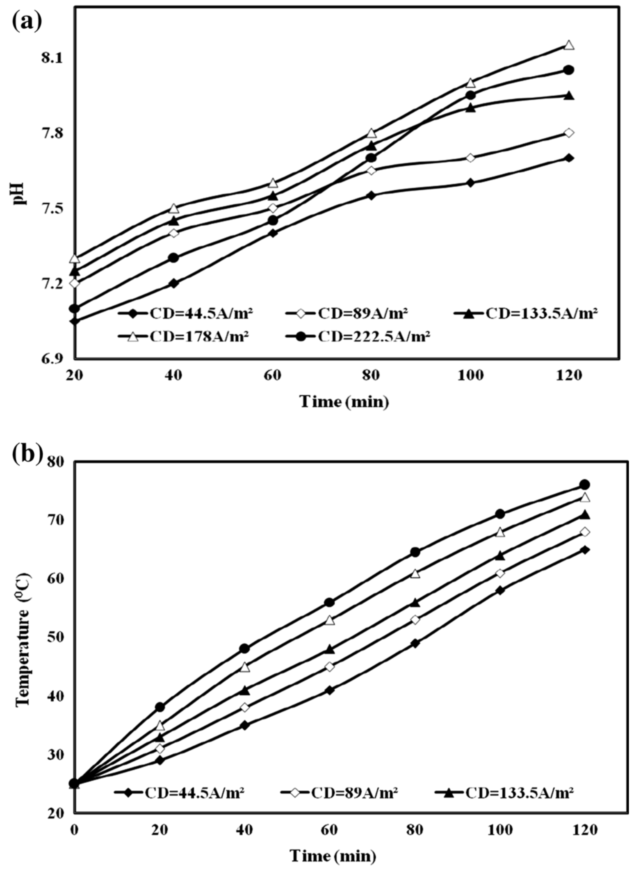

Fig. 7 Effect of CD on **a** pH changes and **b** temperature changes. pH_i 7, EG 20 mm

results in colloid restabilization, which causes less COD reduction (74 %) as compare to 79 % COD reduction at 178 A/m^2.

Effect of current density on pH changes

Since pH is one of the influencing parameters in EC treatment, therefore, its variation with change in CD at pH_i 7 and EG 20 mm was also observed, which is shown in Fig. 7a. The pH_i 6 was found to reach pH 7.7, 7.8, 7.95, 8.05 and 8.15, respectively, at CD 44.5, 89, 133.5, 178 and 222.5 A/m^2 in t_R 120 min. This may be due to formation of negative ions (anion) at high CD.

Effect of current density on temperature change

Change in CD also affects other parameters including temperature. Therefore, change in temperature at different CD with treatment time (t_R) was also noted for ECT at EG 20 mm and pH 7. The results are presented in Fig. 7b. It was found that temperature reached to 65, 68, 71, 74 and 76 °C from room temperature 27 °C when EC process was performed at CD 44.5, 89, 133.5, 178 and 222.5 A/m^2 for $t_R = 120$ min, respectively. Temperature affects floc formation, reaction rates and conductivity. It has been reported that current efficiency of aluminum initially increases with increase in temperature up to 60 °C. Further increase in temperature results in decrease in current efficiency. When the temperature is too high, there is shrinkage of large pores of the $Al(OH)_3$ gel, which cause the formation of dense flocs that are more likely to deposit on the electrode surface (Chen 2004). Increasing temperature also enhances the solubility of aluminum. However, it seems that increasing temperature can have positive and negative effects on the removal efficiency. It is possible that the effect of temperature on removal efficiency depends on the removal mechanism of pollutants.

Kinetics study

COD reduction data generated from ECT were used to evaluate kinetics data. In EC process, when current is applied to the electrode, Al^{3+} cations form and it comes in the wastewater. These Al^{3+} cations further change into aluminum hydroxide cations. Cations neutralize the colloidal particles of wastewater which have negative charge. The neutralized mass settles down and it further removes organics which come on its way by sweep coagulation. The H_2 formed on cathode also removes organics of wastewater by its floatation. Thus, removal of organics of SIWW takes place by forming solid residues by various mechanisms. The supernatant is obtained at the top and solid residue settles down. The organic removal process can be expressed as:

$$\text{SIWW (organics)} \xrightarrow{\text{Metalcations+MetalHydraxides}} \text{Soluble organics (supernatant)} \uparrow + \text{Solid residues} \downarrow \tag{13}$$

SIWW contains various organics which can be lumped as COD. The Eq. 13 can be written as

$$\text{COD} \xrightarrow{\text{Metalcations+MetalHydraxides}} \text{Soluble organics} \uparrow + \text{Solid residues} \downarrow \tag{14}$$

In the ECT process, CD plays a major role. With increases in CD up to certain limit, COD reduction also increases. Thereafter, COD removal decreases. Similarly, COD reduction rate decreases with time, and after a certain electrolysis time, the COD removal becomes almost constant. Therefore, the rate equation, i.e., COD removal rate can be represented by a global power law equation:

$$\frac{-d(\mathrm{COD})}{\mathrm{d}t} = k^n\ \mathrm{COD}^n\ \mathrm{CD}^{\mathrm{m}} \tag{15}$$

For constant CD, Eq. (15) can be reduced to

$$\frac{-d\mathrm{COD}}{\mathrm{d}t} = k\ \mathrm{COD}^{\mathrm{n}} \tag{16}$$

where

$$k = k^n\ CD^m \tag{17}$$

Equation 16 was solved numerically using Euler's integration method and fitted well for second order with respect to COD. The experimental values are shown by point and numerical calculated values by line (Fig. 8). The values of k were evaluated as 2.20×10^{-6}, 3.0×10^{-6}, 3.70×10^{-6}, 5.25×10^{-6} and 4.30×10^{-6} $\mathrm{dm^3/(mg\ min)}$ at CD 44.5, 89, 133.5, 178 and 202.5 $\mathrm{A/m^2}$, respectively. Order with respect to CD in range 44.5–178 $\mathrm{A/m^2}$ is evaluated to be 0.591. Guven et al. (2009) reported 1.2 orders with respect to COD for ECT of simulated beet sugar factory wastewater. They have not reported order with respect to CD.

Liquid–solid separation

Settling

Settling is one of the economical processes used to separate solid and liquid of slurry or suspension. In settling study, whole process can be generally divided into five regimes: (1) clear, (2) discrete, (3) flocculent, (4) hindered and (5) compressed regimes. Using the batch sedimentation data, a continuous thickener may be designed (Font 1990; Font et al. 1999; Richardson et al. 2003). Thus, batch sedimentation tests are immensely important. Figure 9 presents solid–liquid interface in the form of dimensionless height (H/H_i) as a function of settling time at different system $\mathrm{pH_i}$. Initially, a steady state decrease in the solid/liquid interface was seen, which is called regime of zone settling. Thereafter, transition settling occurred. In the third stage, steady state compression settling took place. Overall, in the present study, the settling rate was found in the order of pH 10 > pH 2 > pH 8 > pH 7 > pH 4. Results indicate settling at basic and acidic conditions are better as compared to at neutral pH.

Filterability

Filtration is another unit operation used to separate solids contained in slurry. In the EC process, small colloidal particles form, which agglomerate and form as large-sized particles. For filtration of such agglomerate, the particle filtration method is one of the options. Filtration of such a slurry can be done in industrial scale by using either a plate and frame filter or a rotary vacuum filter. Gravity filtration can also be used for generating experimental data. Equation (18) proposed by MaCabe et al. (2001) can be used for the constant pressure filtration using a filter paper on a Büchner funnel.

$$\frac{\Delta t}{\Delta V} = \frac{\mu \alpha C}{A^2 \Delta P}.V + \frac{\mu}{A \Delta P}.R_{\mathrm{m}} \tag{18}$$

where Δt is the time interval of filtration, ΔV is the filtrate volume collected up to that time interval, C is the solids concentration in the slurry, V is the total liquid filtrate volume collected up to the time interval t, μ is the viscosity of the liquid filtrate, ΔP is the pressure drop across the filter $= \rho g h$, A is the filtration area, R_{m} is the resistance of the filter medium, and α is the specific resistance to filtration.

After recording the experimental data volume of the filtrate as a function of time, a plot of $\Delta t/\Delta V$ versus V gives a straight line, which is shown in Fig. 10. The values of R_{m} and α were evaluated from the slope and the intercept of plot and are presented in Table 3. The values of α were found to be 7.8, 3.0, 1.9, 2.1, 2.2 and 3.7×10^{13} at pH 2, 4, 6, 7, 8 and 10, respectively. The data show that filterability at pH 6 is the best which is followed by that at pH 7. The value of R_{m} has importance at initial stage of filtration only, which is the highest at pH 2 and the lowest at pH 7. Specific cake resistance values have been reported by Barnes et al. (1981). These values are $4\text{–}12 \times 10^{13}$ m/kg

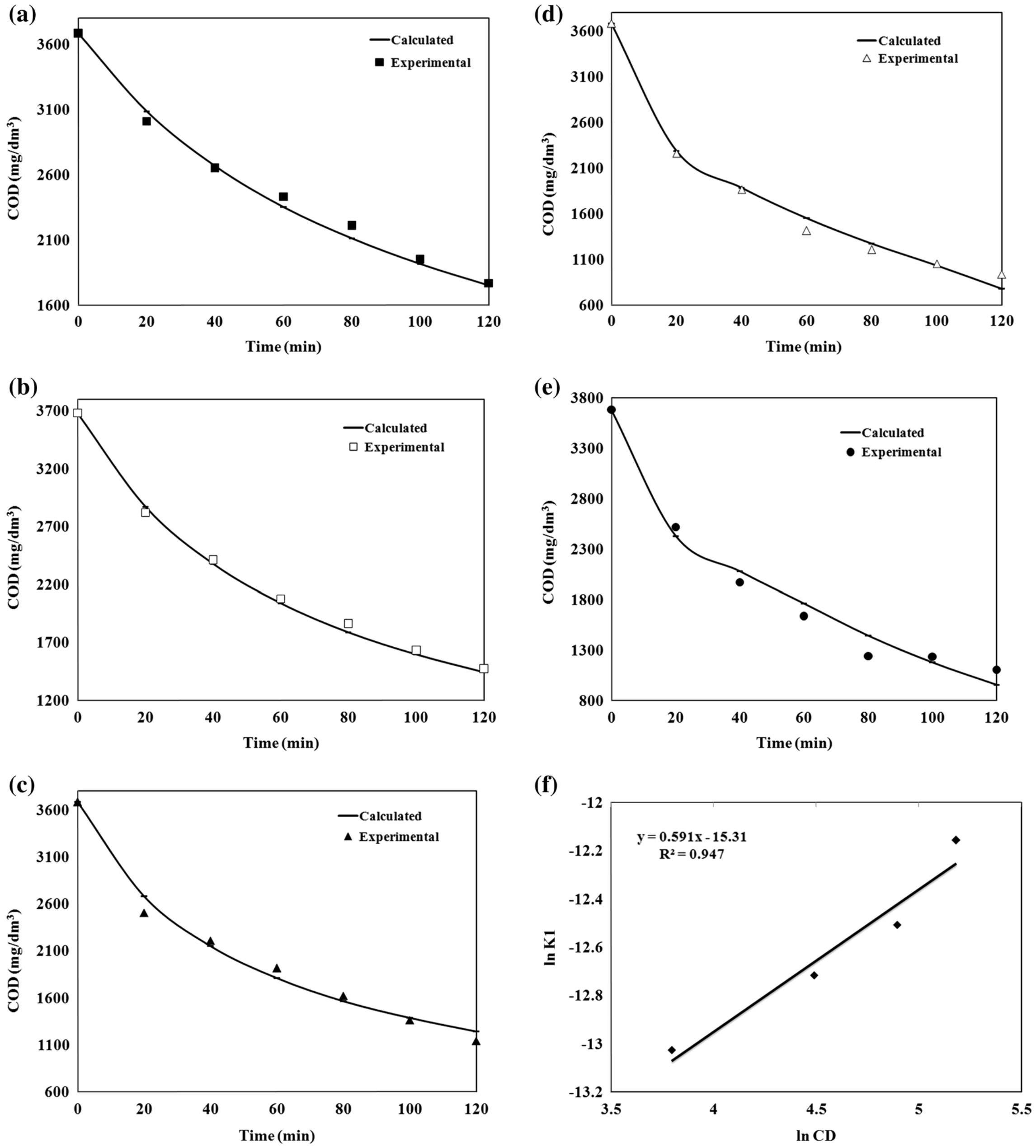

Fig. 8 Kinetics plot for EC treatment. COD reduction at **a** 44.5 A/m^2, **b** 99 A/m^2, **c** 143.5 A/m^2, **d** 198 A/m^2, **e** 242.5 A/m^2 and **f** plot for ln k_1 and current density

for activated sludge and 3–30 m/kg for digested sludge. Our values are in the range of 2–8 × m/kg 10^{13}. The filtration studies have also been presented by other investigators for treatment of pulp and paper mill effluent (Mahesh et al. 2006) and distillery effluent (Chaudhari et al. 2007).

Analysis of filtrate and residues

The properties of filtrate and residues are presented in Tables 1, 4, respectively. From Table 1, it can be seen that large amount of COD (3,682–699 mg/dm^3) was reduced after the EC process. COD is responsible for organic load in the effluent. Color also reduced from dark brown to pale yellow. Color is responsible to hinder the oxygen diffusion and sunlight penetration and thus, obstruct the photosynthesis process. Protein, chloride, phosphate, hardness and total solids also reduced to satisfactory level. The treated effluent still contains 699 mg/dm^3 COD which does not meet the discharge effluent standard, but it can be good feed for further treatment by membrane separation process to reach zero discharge. In our laboratory, the EC-treated

SIWW was further treated by coagulation. By this, COD value reduced to 200 mg/dm^3 and color practically nil.

Solid residues obtained on filter paper was dried at 110 °C and analyzed for various parameters. The properties are presented in Table 4. The highest mass of residues was obtained at pH 6 (5.83 kg/m^3) and the lowest at pH 2 (2.46 kg/m^3). The residues were flaky, hard, and difficult to grind and had different color. EC-treated organic residues possessing good heating values have already been reported (Mahesh et al. 2006).

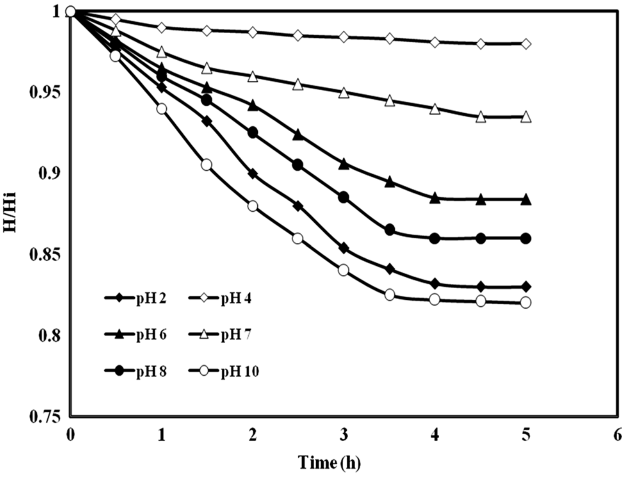

Fig. 9 Settling characteristics of treated SIWW. EG 20 mm, CD 89 A/m^2

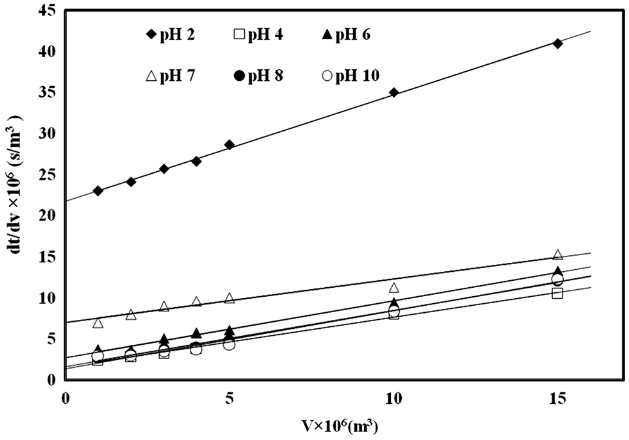

Fig. 10 Filterability of the electro coagulated slurry at different pH. EG 20 mm, CD 89 A/m^2

Cost analysis of EC Treatment of SIWW

Electricity and electrodes are considered to be the two major cost-involving components when applying ECT to wastewaters. The cost of energy for SIWW treatment and the cost of aluminum electrode material consumed were obtained from the experimental results and the sum was taken as the operating cost. To treat SIWW at pH = 7 and CD = 178 A/m^2, energy consumption was 58 Wh/dm^3 and electrode loss was 0.82 g/dm^3.

i. Cost of energy

Power consumption per m^3 of SIWW treated = 58 kWh

At an energy price in the Indian market = INR 4/kWh

Cost of energy per m^3 SIWW treated = INR 232

ii. Cost of aluminum

Aluminum required per m^3 of SIWW = 820 g

Cost of 3 mm aluminum sheet on bulk purchase = INR 210/kg

Cost of aluminum per m^3 of SIWW treated = 0.82 kg × INR 210/kg = INR 172/m^3

Operating cost = Cost of energy + Cost of electrode = 232 + 172 = INR 404 (USD = 6.22) per m^3 of SIWW treated.

Conclusion

The EC process with aluminum electrode proved to be an effective method for treatment of SIWW. The COD reductions of 32, 42, 45, 60, 52 and 42 % and color reductions of 43, 54, 57, 67, 64 and 49 % were obtained at constant CD 89 A/m^2 and pH 2, 4, 6, 7, 8 and 10,

Table 3 Filterability of the treated SIWW. CD 89 A/m^2, EG 20 mm

S. no	Initial pH	Kp × 10^{-12} s/m^6	β × 10^{-6} s/m^3	C kg/m^3	α × 10^{-13} m/kg	R_m × 10^{-11}
1	2	2.0	21.73	2.46	7.8	7.78
2	4	0.706	1.05	3.46	3.0	0.37
3	6	0.5	2.28	5.83	1.9	0.81
4	7	0.45	7.33	4.87	2.1	0.26
5	8	0.37	2.62	3.12	2.2	0.93
6	10	0.63	1.41	2.96	3.7	0.53

Table 4 Analysis of residue obtained after EC (Al plate) at different pH, CD 89 A/m^2

S. no	Parameter/pH	2	4	6	7	8	10
1	Weight of residue (kg/m^3)	2.46	3.46	5.83	4.87	3.12	2.96
2	Color	Light gray	Light gray	Gray	Gray	Gray	Dark gray
3	Nature	Flakey and easy to grind	Flakey and tough to grind	Flakey and tough to grind	Flakey and tough to grind	Flakey and tough to grind	Flakey and tough to grind
4	Size (mm)	1–4	2–6	2–6	1–5	1–5	1–6
6	Percentage convertible COD	38	42	60	52	45	35

respectively. COD and color reduction were found to increase with increase in CD. COD reductions of 52, 60, 69, 79 and 74 and color reductions of 64, 67, 73.5, 78 and 82 were obtained at pH 7 and CD 44.5, 89, 133.5, 178 and 222.5 A/m^2, respectively. Energy consumption increased with pH and was 16.2, 17.14, 20, 22.85, 32 and 33.7 Wh, respectively, for treatment of 1 dm^3 effluent at pH 2, 4, 6, 7, 8 and 10. At this pH, electrode losses were 0.55, 0.60, 0.51, 0.63, 0.68 and 0.62 gm per dm^3 SIWW treatment. Kinetics studies evaluated COD reduction rate to be of second order with respect to organics material (COD) and 0.591 order with respect to CD. Overall, $\text{pH} = 7$, $\text{EG} = 20$ mm and $\text{CD} = 178$ A/m^2 were the optimum operating conditions that resulted in COD reduction of 79 % and color reduction of 78 %. Energy consumption and electrode loss was also less at pH 7 as compared to treatment at other pH. Filterability of treated effluent was the best at pH 6. Further treatment of electrochemically treated SIWW by coagulation reduced COD of SIWW to <200 mg/dm^3 and color to practically nil.

List of symbols

A	Filtration area (m^2)
C	Solid concentration in the slurry (kg/m^3)
CD	Current density (A/m^2)
COD	Chemical oxygen demand
EG	Electrode gap
F	Faraday's constant, 96,500 C/mol
I	Current (A)
k	Reaction rate constant [dm^3/(mg min)]
M	Amount of substances dissolved (g of M/cm^3)
SEC	Specific energy consumption [kWh/(dm^3 kg COD removal)]
t	Time (s, min, h)
V	Voltage across the electrodes
V	Total liquid filtrate volume collected up to the time interval t (m^3)
ΔP	Pressure drop across the filter $= \rho g h$ (Pa)
Δt	Time interval of filtration (s)
ΔV	Filtrate volume collected up to that time interval (m^3)
α	Specific resistance to filtration, also called as SCR
μ	Viscosity of the liquid filtrate (Pa s)
R_m	Resistance of the filter medium (m^{-1})

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