Coffee processing industrial wastewater treatment using batch electrochemical coagulation with stainless steel and Fe electrodes and their combinations, and recovery and reuse of sludge

Sahana M., Srikantha H., Mahesh S. and Mahadeva Swamy M.

ABSTRACT

The efficiency of chemical oxygen demand (COD) and color removal from raw coffee processing wastewater (CPWW) using batch electrochemical coagulation (BECC) treatment process using stainless steel (SS) and iron (Fe) electrode combinations are investigated. Of the combinations: four SS, four Fe, Fe-Fe-SS-SS, Fe-SS-Fe-SS, SS-SS-Fe-Fe, and SS-Fe-SS-Fe; four SS electrodes operated at 23 V having 120 A/m^2 current density was found as a good operating condition to achieve ~87% COD removal from its initial COD of 1,984 mg/L and corresponding color removal of 97.1% (initial color 7,000 PCU). The second best electrode combination, SS-SS-Fe-Fe, had COD and color removals of 75% and 91%. When using polyaluminum chloride (PAC) as aid with different dosages of 20–100 mg/L, 50 mg/L PAC showed maximum COD and color removals of 80% and 92%. Comparison of proximate and ultimate analyses of various solid fuels with CPWW ECC sludge showed its usefulness as a soil supplement and as an adsorbent for reutilization. The solid residue obtained after BECC was characterized using energy dispersive X-ray spectroscopy and other analyses. Summarizing the results, it was concluded that BECC can be effectively used for maximum removal of organics from raw CPWW with clean water reclamations of up to ~90% using ECC as a novel treatment technique.

Key words | additives/coagulant aid, batch electrochemical coagulation, coffee processing wastewater, electrode combinations, point of zero charge (pH$_{PZC}$), proximate and ultimate analysis

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INTRODUCTION

The agri-based industrial activity is a global issue of concern because agri-based industries generate large quantities of wastewater and their disposal requires proper treatment. The various types of agri-based industries include textile industry, sugar industry, vegetable oil industry, tea industry, coffee industry, and leather goods industry. Of these, coffee processing industries are of great concern because of their polluting potential. Coffee is one of the most popular beverages in the world and second largest traded commodity after petroleum (Murthy & Naidu 2012). India ranks seventh in coffee production and is one of the few countries which produce both arabica and robusta varieties of coffee (United States Department of Agriculture 2017). The wastewater produced from wet coffee processing originates from coffee fruits rich in caffeine, sugars, phenolic compounds, fatty acids, lignin, cellulose, pectic substances and other macromolecules (Mussatto et al. 2011; Pujol et al. 2013) which are unsuitable for disposal into soil and waterways. Coffee processing is one of the major industries using large quantities of water during various stages in the production process with wastewater generation ranging from 40 to 45 L for every kilogram of coffee (Rodríguez et al. 2000). The major steps involved in coffee processing are primary, secondary and tertiary processes. Primary processing is carried out either by a dry process or wet process. In the secondary process, the parchment layer of dried beans is removed mechanically and graded based on the required size, shape, weight, and uniformity. In the tertiary process, coffee powder undergoes

various processes in sequence to develop varieties of products such as instant coffee and decaffeinated coffee (Padmapriya *et al.* 2015).

Coffee processing wastewaters (CPWWs [t/s l.c.]) are generally dark brown in color covering a large number of persistent pigments called melanoidins which are highly toxic, recalcitrant and non-biodegradable (Gengec *et al.* 2012). CPWW discharged into receiving streams produces obnoxious odor causing forced eutrophication. The highly colored nature of CPWW reduces Secchi depth and prevents sunlight penetration into deeper portions of water bodies, resulting in de-oxygenation as a negative external effect. Inappropriate land discharge of CPWW contributes significantly to soil pollution and acidification, inhibits seed germination and causes soil manganese deficiency, indirectly damaging agricultural crops. Generally, CPWWs are subjected to primary treatment, secondary treatment, and tertiary treatment for the removal of organics. Traditional biological treatment has major drawbacks such as production of uncontrollable biomass sludge with fluctuating settling properties, sludge bulking, sensitivity to shock loading, incapability to remove toxic substances (Khansorthong & Hunsom 2009) and poor filterability.

Electrochemical methods for treating wastewaters offer distinctive advantages over traditional treatment methods such as environmental compatibility, energy efficiency, versatility, safety, selectivity, ease of scale-up, amenability to automation, cost-effectiveness and excellent settling and good filterability (Yavuz & Koparal 2006; Mahesh *et al.* 2006b). Electrochemical coagulation (ECC) also allows continuous treatment, offering low hydraulic retention times (HRTs) (Mahesh *et al.* 2016). ECC, being a complex interdependent process, uses only DC current across two-dimensional/three-dimensional and particle electrodes to release charged metal ionic species in an electrolytic solution, which react with negatively charged colloidal and suspended particles to form flocs, which can be later removed by skimming (García-García *et al.* 2011). The electrochemical treatment process has found applications in various industrial wastewaters like oil mill effluent (Un *et al.* 2006), textile dyes (O'Neill *et al.* 1999), electroplating (Kobya *et al.* 2010), landfill leachate (Li *et al.* 2011), distilleries (Khandegar & Saroh 2014), pulp and paper mill (Mahesh *et al.* 2006a, 2006b), and poultry slaughterhouse (Kobya *et al.* 2006), proving its versatility and environmental compatibility.

The general reactions that occur during the ECC process are shown through Equations (1)–(4) with M being the electrode material and n the number of electrons. The metal ions generated near the anode face (in a bipolar arrangement) react with the hydroxyl ions generated near the cathode face to form metal hydroxides in the presence of sufficient alkalinity in the wastewater.

At anode/anode face:

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

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{2}$$

At cathode/cathode face:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \tag{3}$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{4}$$

This work was carried out to with the purpose of treating raw wastewater from CPWWs by applying a two-dimensional (2D) ECC process in a bipolar arrangement using iron (Fe) or stainless steel (SS) electrodes, and their combinations with the aim of removing chemical oxygen demand (COD), color, and total dissolved solids (TDS). The effect of anode materials, current intensity, and addition of additives/coagulant aid was investigated followed by sludge analysis. The operating parameters were electrode material, cell voltage/current density, electrode spacing, and electrolysis time (ET) for removal of COD, color, and TDS. Morphological characteristics and constituents in the ECC-generated sludge were observed using energy dispersive X-ray spectroscopy (EDS), and the point of zero charge (pH_{PZC}) of the sludge was also determined.

MATERIALS AND METHODS

Chemicals

The chemicals required for parameter estimation such as hydrochloric acid, sulfuric acid, ethyl alcohol, sodium hydroxide, potassium dichromate, mercuric sulfate, ammonium ferrous sulfate hexahydrate, silver nitrate, potassium chromate, and silver sulfate were of AR grade of high purity purchased from Himedia Laboratories, Mumbai, India.

Two-dimensional batch experiments

CPWW samples in their raw state were collected from a local Indian coffee manufacturing industry. The electrode materials, SS (304 grade) and Fe, were cut into thin sheets

of 1 mm thickness and rectangular shape sized enough to obtain the desired specific electrode area to volume (SA/V) of $20\ m^2/m^3$. The electrodes were cleaned with 15% hydrochloric acid, rinsed using distilled water and dried prior to use in the batch electrochemical coagulation (BECC) experiments. The electrochemical reactor (ECR) was designed to perform both as a batch reactor and a continuous flow stirred tank reactor having an effective working volume of 1 L. The ECR was fitted with two pairs of anode and cathode plates arranged in bipolar mode and connected to the respective terminals of a DC power supply unit using copper lead wires with the aid of crocodile clips. The schematic experimental setup of the 2D ECR and other accessories are shown in Figure 1 with inset pictures showing treatment. The reactor content was stirred continuously during treatment with an inductive magnetic stirrer (Remi 2MLH) using a magnetic bead to ensure homogeneous mixing for effective mass transfer. All ECC test runs were carried out at room temperature, 24–28 °C. The BECC experiments were divided into three parts using (i) four SS or four Fe electrodes on separate runs, (ii) electrode combinations Fe-Fe-SS-SS, Fe-SS-Fe-SS, SS-SS-Fe-Fe, and SS-Fe-SS-Fe, (iii) addition of additives/coagulant aid (poly-aluminum chloride (PAC)) at different dosages for the best electrode combinations.

The electrodes were weighed before and after each experiment to record the electrode dissolution (ED) pattern using a digital weighing balance. All BECC experiments were carried out applying cell voltages 13, 18, 23, and 28 V with corresponding current densities (CDs) of 40, 80, 120 and $160\ A/m^2$ keeping the electrode gaps constant at 10 mm for 90 min ET and stirring speed of 350 rpm. During ECC treatment sample aliquots were drawn at regular time intervals, filtered using Whatman 42 grade-1 filter paper and analyzed for pH, color, COD, TDS, and other quality parameters as per standard methods (APHA 2005). The retrieved water samples were analyzed for pH using an inoLab WTW pH-meter equipped with a combined glass electrode (Metrohm), COD by closed reflux–titrimetric method (DRB200, Hach, USA), color using platinum-cobalt (PCU) scale and TDS by gravimetric analysis. After each experiment the supernatant scum and settled sludge were separated, oven dried for 24 h, weighed and stored for analysis later for proximate and ultimate analysis using standard procedure (IS: 1350 (Part 1), Bureau of Indian Standards 1984). The dry sludge was used to find out the pH_{PZC} using solid addition method with NaCl. EDS analysis using an energy dispersive X-ray analyzer (Quanta, Model 200 FEG, USA) was used to find the chemical compounds and elemental quantification present in post-ECC solid residues.
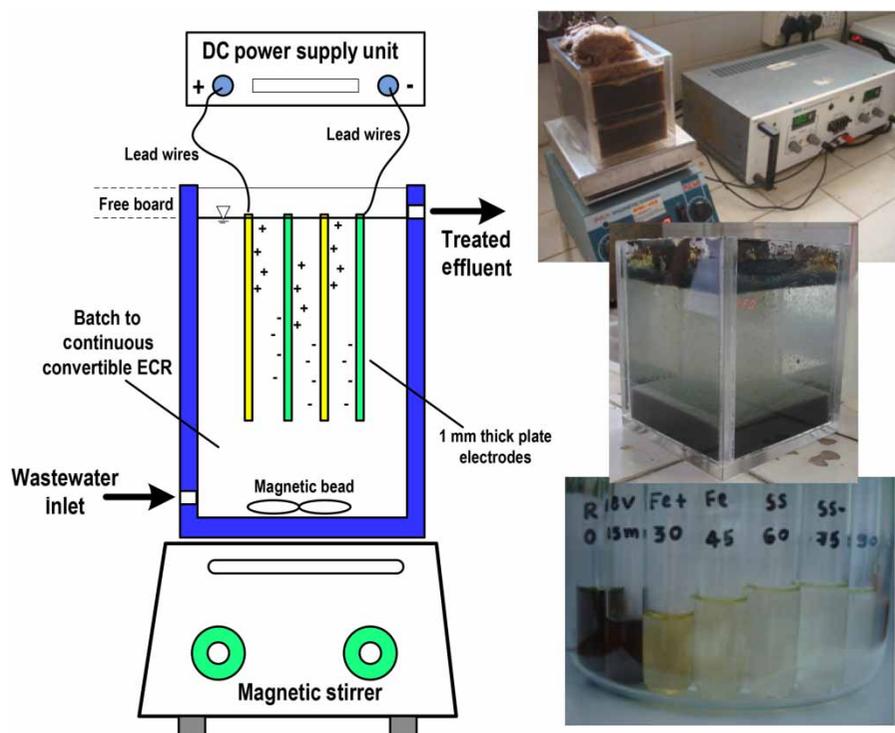

Figure 1 | Schematic experimental setup of 2D electrochemical reactor.

To check the effect of additives/coagulant aid on ECC of CPWW, PAC was added just before startup of the 2D ECC experiments, varying PAC doses in the range 20–100 mg/L.

Characteristics of raw coffee processing wastewater

Raw CPWW for use in ECC treatment was collected from an outfall conduit entering the equalization basin of a local coffee manufacturing industry which uses green coffee beans as raw material. Raw CPWW was characterized for various water quality parameters within 1 day of sampling using procedures according to standard methods (APHA 2005) for analysis of water and wastewater. The initial characteristics of CPWW used in the BECC are shown in Table 1. The discharge standards set by the Government of India for CPWW through the Central Pollution Control Board (CPCB), New Delhi, India, for the water quality parameters after proper treatment are also shown in Table 1.

RESULTS AND DISCUSSION

Effect of SS and Fe electrodes on pH of bulk solution

The initial pH of raw CPWW was 7.5 ± 0.2. pH of the bulk solution increased to 9.33–10.6 by 45 min ET in all the CDs

Table 1 | Physico-chemical characteristics of raw coffee processing wastewater

Parameters	Units	Range of values	Government of India CPCB standards
pH	–	7.5 ± 0.2	5.5–9.0
Color	PCU	6,800–9,200	–
Conductivity	$\mu S/cm^2$	2,805–2,868	–
Total solids	mg/L	3,400–3,550	–
TDS	mg/L	3,150–3,280	–
COD	mg/L	1,400–1,990	250
Biochemical oxygen demand (BOD)	mg/L	850–920	30
COD/BOD	–	1.6–2.1	–
Chlorides	mg/L	180–210	200
Total hardness as $CaCO_3$	mg/L	580–640	600
Total alkalinity as $CaCO_3$	mg/L	1,100–1,280	600
Nitrate	mg/L	87–147	100
Phosphate	mg/L	53–84	100
Sulfate	mg/L	181–221	400

and gradually increased to ~10.8 after 75 min ET showing stable values at 90 min ET. pH values increase with an increase in CD and ET, ascribed to the production of hydroxyl ions near the cathode face that aid the formation of flocs. Similarly, while using four Fe electrodes, pH significantly increased from 7.55 to above 10 at 45 min ET in all CDs and the trend continued to reach above pH 11 at CDs 80, 120 and 160 A/m^2 at 90 min ET (Supplementary information, Figure S1, available with the online version of this paper). Four Fe electrodes in the reactor showed bulk solution pH increase by 1 unit compared to the four SS electrodes. While using all four SS and four Fe electrodes, the pH increase at 15 min ET was high because of quick release of ferric ions into the bulk solution.

Effect of CD on COD, color, and TDS removals using SS electrodes

CD is an important parameter that determines the *in situ* coagulant dosage during the ECC process. The effect of CD on treating CPWW using four SS electrodes during ECC was explored over a CD range of 40–160 A/m^2 for wastewater having initial characteristics pH$_0$: 7.5 ± 0.2, COD$_0$: 1,984 mg/L, EC$_0$: 2,805 μS/cm^2, and TDS$_0$: 3,210 mg/L. COD degradation curves for different CDs as a function of ET are shown in Figure 2(a). It is important to reduce the COD value in a short treatment time (low HRT) before discharging the treated effluent. It may be observed from Figure 2(a) that lower and higher CDs showed poor COD removal ascribed to the fact that at lower CDs the M$^+$ ions released do not bear sufficient strength to attract negatively charged colloidal particles, while at higher CDs excess M$^+$ ions are released which tear apart the flocs formed, thus making the solution more turbid, causing low COD removals. At a higher CD of 160 A/m^2 at 45 min ET, a boom in COD value (2,624 mg/L) is observed; it is surmised that the re-entrainment of torn floc particles back into solution and the samples retrieved caused the increase in COD values. It was concluded that higher CDs do not necessarily remove COD from the solution. There always exists an optimal operating condition among different CDs. At CD 120 A/m^2, COD removals were stable and maximum at 90 min ET with COD decreasing to 256 mg/L (87.09% removal). Medium CDs provide a balanced release of M$^+$ ions into the solution, from the anode/anode face to develop matured flocs, to form Fe(OH)$_2$ which agglomerates as precipitates following Pourbiax pH patterns.
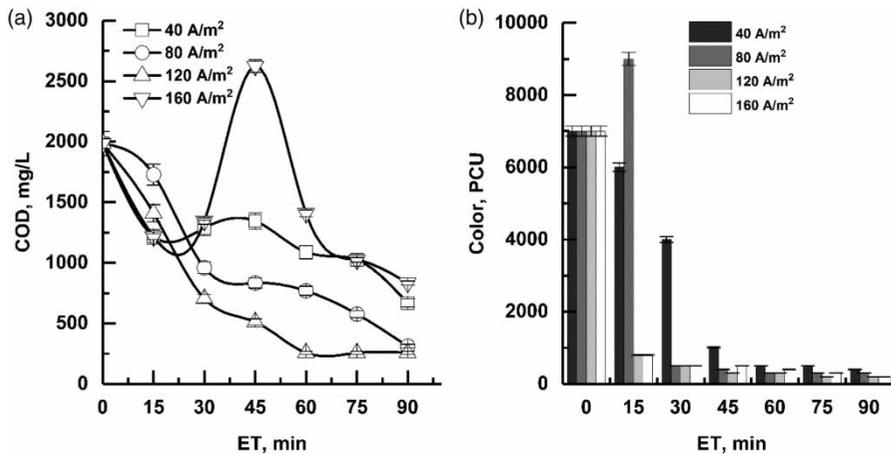
Figure 2 | COD (a) and color (b) removal using SS electrodes at CDs 40–160 A/m^2. Operating conditions: ECR: 1 L; electrode arrangements: bipolar; pH$_0$: 7.55; COD$_0$: 1,984 mg/L; color$_0$: 7,000 PCU; ET: 90 min; agitation speed: 350 rpm.

Figure 2(b) shows color removal during ECC for different operating CDs of 40–160 A/m^2. At CD 120 A/m^2, 97.1% color was removed at 75 min ET with a further slight increase in color removal at 90 min ET. Therefore, 75 min ET was felt sufficient at CD 120 A/m^2. The increase and decrease in color concentrations in the initial stages is because of the color imparted by ferric ions released by ED that aid floc formation. CDs of 120 and 160 A/m^2 show maximum color removal of 300 PCU at 90 min ET. TDS values are indicative of an aesthetic characteristic marking the presence of a broad array of chemical contaminants in wastewater (Mahesh *et al.* 2014). High TDS removal was observed at CD 120 A/m^2 showing 1,372 mg/L. At CDs

of 40, 80, 120 and 160 A/m^2, TDS removal efficiencies were found to be 49.8%, 56.4%, 57.25%, and 52.65%, respectively, in comparison with initial TDS value of 3,210 mg/L at 90 min ET.

Effect of current density on COD, color, and TDS removal using Fe electrodes

The effect of CDs on treating CPWW using Fe electrodes (four Fe) was explored applying CDs 40, 80, 120, and 160 A/m^2 on raw CPWW having initial characteristics shown in Table 1. COD removal as a function of ET is represented in Figure 3(a). A significant decrease in COD is
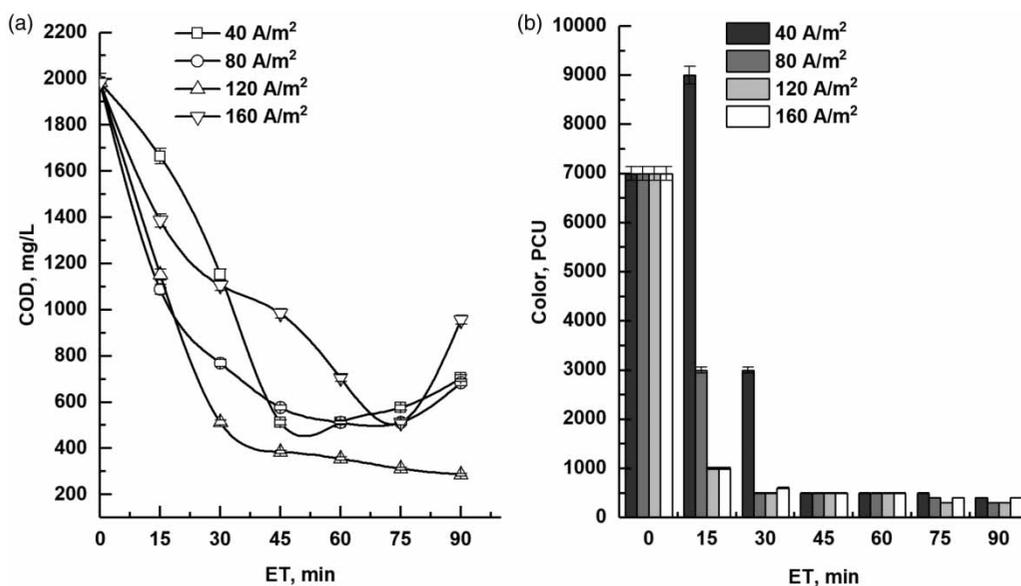

Figure 3 | COD (a) and color (b) removal using Fe electrodes at CDs 40–160 A/m^2. Operating conditions: ECR: 1 L; electrode arrangements: bipolar; pH$_0$: 7.55; COD$_0$: 1,984 mg/L; ET: 90 min; agitation speed: 350 rpm.

obtained at 60 min ET for all CDs. At lower CDs of 40 and 80 A/m^2 COD removal was ~65%. Release of metal ions and formation of precipitates contributed to the decrease in COD values. At 90 min ET COD removal was maximum showing a COD residual of 286 mg/L (85.58% removal) from its initial value of 1,984 mg/L. CD 160 A/m^2 had minimum effect on COD removal at 90 min ET because of excess release of metal ions tearing off the agglomerated flocs and increased production of sludge.

Figure 3(b) presents color removal for CDs 40–120 A/m^2 using Fe electrodes. At CD 40 A/m^2 at 15 min ET, color increased from 7,000 PCU to 9,000 PCU as a result of *in situ* release of metal ions (M$^+$) into solution which add to the existing color, turning the solution more murky. At CD 80 and 120 A/m^2, color reductions were over 95.7% with residual true color of 300 PCU at 90 min ET. Color removals were relatively high compared to COD removal as a result of anodic dissolution together with the presence of OH$^-$ ions to remove pollutants/contaminants by adsorption followed by flotation (Cotillas *et al.* 2013). Removal of the residual true color of ~300 PCU requires a polishing treatment downstream, such as adsorption. TDS removal was also high for Fe electrodes at CD 120 A/m^2 achieving 1,220 mg/L (61.9% removal) compared to 56.4% removal by SS. At CDs 40, 80, 120, and 160 A/m^2, TDS removal efficiencies were 44.6%, 53.25%, 61.9%, and 53.65% from its initial value of 3,210 mg/L. Lower CDs, 40 and 80 A/m^2, and higher CD 160 A/m^2 showed less color and COD removal compared

to CD 120 A/m^2. Therefore all further BECC experiments were studied applying 120 A/m^2 CD for electrode combinations and use of additives.

2D BECC combining SS and Fe electrodes

BECC experiments on raw CPWW were performed in duplicate for removal of COD and color using combinations of 2D Fe and SS electrodes: Fe-Fe-SS-SS, Fe-SS-Fe-SS, SS-SS-Fe-Fe, and SS-Fe-SS-Fe with an optimal CD 120 A/m^2 for 90 min ET.

The pH variation, COD and color degradation curves for the said electrode combinations are shown in Figure 4. Electrode combinations SS-SS-Fe-Fe and SS-Fe-SS-Fe showed pH increase by 3 units from its initial value at 90 min ET. Similarly, Fe-Fe-SS-SS and Fe-SS-Fe-SS electrode combination showed pH increase by 2 units at 90 min ET (Figure 4(a)). pH increase is ascribed to release of metal cationic species in large quantities into the bulk solution to reach a state of floc maturity and the formation of (MOH)$_3$ and other precipitates. By providing a time lapse of 1–2 h after ECC, the pH values recede back to ~8.6 as the hydroxide flocs form sludge with residual H$^+$ ions causing the decrease in pH.

Figure 4(b) shows COD removal for SS-SS-Fe-Fe and SS-Fe-SS-Fe. In the initial 15 min ET COD values increased from 1,280 mg/L to 1,600 mg/L for both electrode combinations, which gradually decreased after 45 min reaching 256 mg/L achieving 80% removal. This is explained by the
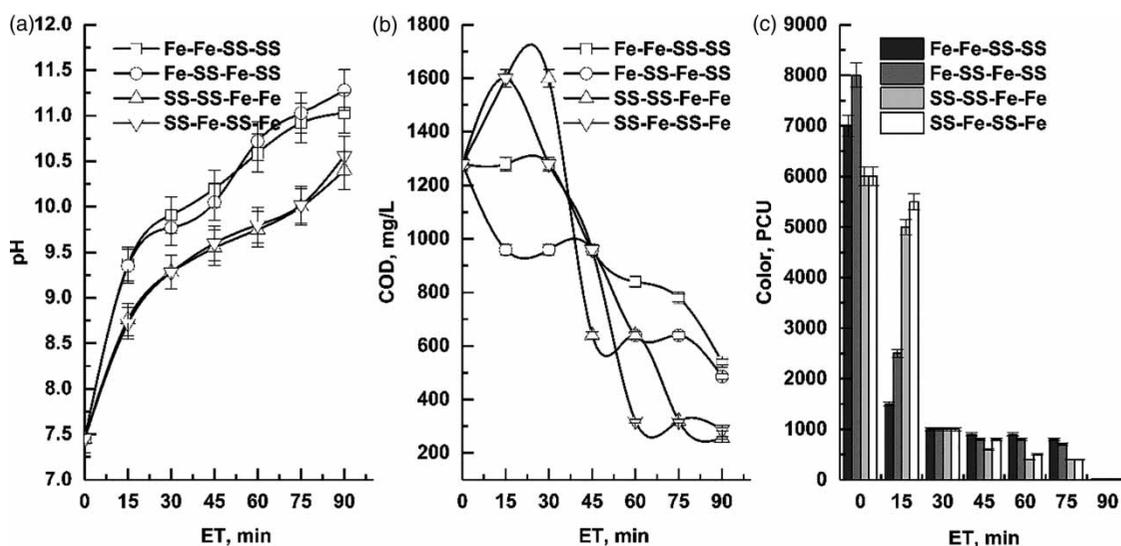

Figure 4 │ pH (a), COD (b) and color (c) variations for Fe-Fe-SS-SS, Fe-SS-Fe-SS, SS-SS-Fe-Fe, and SS-Fe-SS-Fe electrode combinations at optimal CD 120 A/m^2. Operating conditions: ECR: 1 L; electrode arrangements: bipolar; pH$_0$: 7.55; COD$_0$: 1,280 mg/L; ET: 90 min; agitation speed: 350 rpm.

extent of anodic dissolution of SS resulting in higher precipitate formation, enhancing COD removal. In Fe-Fe-SS-SS combinations, COD removals were ~60% at 90 min ET. In all the combinations, maximum COD removals of ~80% were achieved when SS was used as an anode compared to COD removals with Fe as anode.

Figure 4(c) shows color reduction for different Fe and SS combinations. Electrode combinations Fe-Fe-SS-SS and Fe-SS-Fe-SS showed meager removal of color in the initial part of the BECC process. At 90 min ET, color concentrations reduced from 9,000 PCU to 800 (91.1% removal) and 700 PCU (92.2% removal) for the said electrode combinations. When using SS as anode (first electrode as SS), both SS-SS-Fe-Fe and SS-Fe-SS-Fe electrode combinations achieved 95.5% color removal at 90 min ET. It was finally inferred that SS-SS-Fe-Fe electrode combination showed highest color and organics removal compared to other electrode combinations. The flocs generated with the first two electrodes of SS in a bipolar arrangement produced sturdy and stable interlocking flocs giving maximum pollutant removal. Therefore, it was decided to use this combination when applying additives/coagulant aid in further BECC experiments.

BECC using SS-SS-Fe-Fe electrode combinations with additives

PAC was added in various concentrations (20–100 mg/L) into the ECR to observe its effect on pollutant/contaminants removal during ECC of raw CPWW for CD 120 A/m^2 using SS-SS-Fe-Fe electrode combination.

Figure 5(a) shows pH changes during ECC for SS-SS-Fe-Fe without and with PAC doses: 0, 20, 50 and 100 mg/L in discrete BECC runs applying CD 120 A/m^2 for 90 min ET. pH values for PAC doses of 0, 20, 50, and 100 mg/L at 90 min ET showed an increase in pH values from 7.8 to 10.22, 10.15 and 10.72. pH was higher (pH 11.03) in a no-additive condition compared with the addition of 20 and 50 mg/L dosages because at high pH, OH$^-$ ions compete with organic compounds for metal adsorption sites and metal hydroxides precipitate by co-precipitation (Stephenson & Duff 1996). Figure 5(b) presents the COD degradation curves with ET. ECC experiments without any additive showed maximum COD removal of 75% from its initial value of 1,280 mg/L. With PAC doses of 20, 50, and 100 mg/L at 90 min ET, COD concentrations were 320 mg/L (75% removal), 256 mg/L (80%), and 384 mg/L (70%) respectively. BECC experiments without aid and 20 mg/L PAC dose showed 91% color removal whereas 50 and 100 mg/L doses showed 94.4% and 93.3% of color removal (Figure 5(c)). The color removal was very effective showing removal of 97.1% for four SS electrode, 95.7% using four Fe electrodes and 95.5% in SS-SS-Fe-Fe electrode combinations compared with color removal with PAC dosages. It is concluded that PAC does not serve as an effective coagulant aid for the removal of color and organics from CPWW wastewater; however, it aids in quick settling of flocs and good filterability giving clear supernatant.
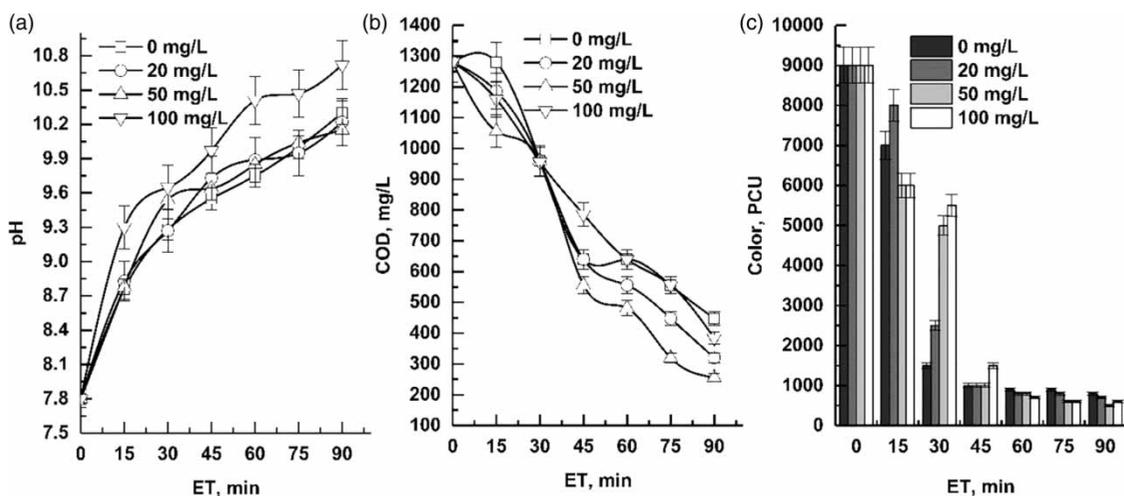

Figure 5 | pH (a), COD (b) and color (c) variations for SS-SS-Fe-Fe electrode combinations, CD 120 A/m^2 using 20, 50, and 100 mg/L of PAC dosages. Operating conditions: ECR: 1 L; electrode arrangements: bipolar; pH$_0$: 7.55; COD$_0$: 1,280 mg/L; ET: 90 min; agitation speed: 350 rpm.

Electrode dissolution pattern

At the end of each BECC experiment, ED was calculated by taking the difference in weight of the electrodes and also the weight of dry sludge. At CD 40 and 80 A/m^2, ED of four SS electrodes was 1.45 g/L and 2.52 g/L and the corresponding weight of dry sludge was 4.02 g/L and 5.85 g/L respectively. Similarly at CDs 120 and 160 A/m^2, dissolution of SS electrodes was 3.46 g/L and 5.13 g/L with the corresponding sludge production of 7.68 g/L and 10.24 g/L, respectively. It was commonly observed that both ED and sludge production increase with the increase in CDs. Similar observations were reported by Bouhezila *et al.* (2011) while treating landfill leachate using ECC. ED for iron electrodes for CDs 40, 80, 120 and 160 A/m^2 was found to be 1.68, 2.80, 4.74 and 6.12 g/L, respectively. Similarly, dry sludge weight was 4.66, 6.34, 8.12 and 12.72 g/L, respectively. The ED patterns while using Fe-Fe-SS-SS, Fe-SS-Fe-SS, SS-SS-Fe-Fe, and SS-Fe-SS-Fe were 4.76, 4.64, 4.12 and 4.08 g/L respectively. ED patterns were significant when using SS-SS-Fe-Fe electrode combination for different PAC doses.

Characterization of ECC-generated sludge

The ECC sludge generated after treating CPWW operated at CD 120 A/m^2 using SS electrodes was analyzed for physico-chemical parameters, proximate and ultimate analysis, and EDS for metal quantification. The physico-chemical parameters studied were pH, total solids, density, specific gravity and pH$_{PZC}$. Table 2 shows the results of physico-chemical analysis of CPWW ECC sludge. CPWW ECC dry sludge applying CD 120 A/m^2 was dark brownish in color. The pH of sludge was near neutral value, from 6.75–6.76, which can be considered suitable for sludge being used as

Table 2 │ Physico-chemical analysis of CPWW ECC sludge

Parameters	Units	Values
pH	–	6.75–6.76
Solids content		
Total solids	%	94.80
Volatile solids	%	18.88
Fixed solids	%	81.12
Density	kg/m^3	2,220
Specific gravity	–	1.58
pH$_{PZC}$	–	8.70

soil supplement considering other quality parameters. The specific gravity of the solids content in the sludge was 1.58 and bulk density was 2,220 kg/m^3. The volatile solids in CPWW ECC sludge were as low as 18.88%. The fixed solids content in the sludge was 81.12% indicating the presence of large amount of inorganic solids in the EC-generated CPWW sludge. The volatile solids content was much lower compared to the fixed solids.

Proximate and ultimate analysis of CPWW ECC sludge

The proximate analysis of CPWW ECC sludge comprised moisture, volatile matter, ash, and fixed carbon. Table 3 presents the results of proximate analysis of CPWW ECC sludge. The moisture content in CPWW ECC dry sludge was as low as 5.9%. The volatile matter in the sludge was 76.6% and ash 17.6%. Low fixed carbon value of 5.8% is ascribed to less free carbon element in the CPWW ECC sludge.

Point of zero charge

The pH where the net particle is zero is called 'point of zero charge'. It is one of the characteristic properties for using sludge as an adsorbent. pH$_{PZC}$ for a given sludge is the pH at which that surface has a net neutral charge. The pH$_{PZC}$ was determined using 'solid addition' method using NaCl. The sludge surface having positive charge at solution pH < PZC tends to absorbs anions. On the other hand, sludge surface having negative charge at solution pH > PZC tends to absorb cations. The sludge generated during the experiments conducted using SS electrodes (four SS) at CD 120 A/m^2 was used for determining pH$_{PZC}$. The pH$_{PZC}$ of SS-generated sludge is presented in Figure 6. Six Erlenmeyer flasks each of 100 mL volume were filled with 0.01 M NaCl solution and the flask contents were adjusted to pH 2, 4, 6, 8, 10 and 12, respectively, and noted as pH$_0$. To each of these flasks 0.15 g of ECC sludge generated from SS electrodes was added and kept under quiescent condition for 48 h and then the final pH (pH$_f$) values in

Table 3 │ Proximate analysis of CWW ECC sludge

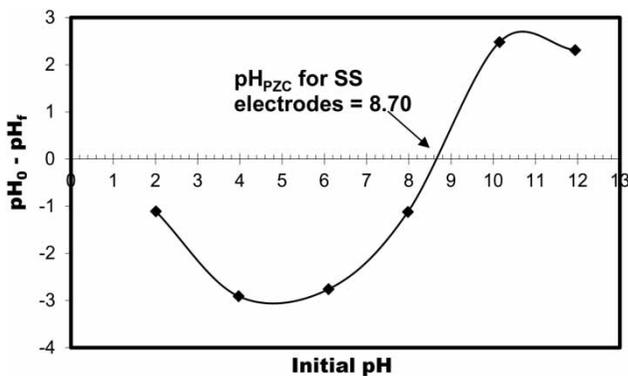| Parameters	Values (%)
Moisture	5.9
Volatile matter	76.6
Ash content	17.6
Fixed carbon	5.8

Figure 6 │ Point of zero charge (pH_{PZC}) of 2D BECC-generated sludge using SS electrodes at CD 120 A/m^2.

each flask were noted. The difference between pH_0 and pH_f values were then plotted as a function of the pH_0 to obtain the pH_{PZC} curve. The pH_{PZC} of the sludge is the point where the curve cuts the pH_0–pH_f line. pH_{PZC} value of SS-generated sludge is 8.70 indicating suitability of the sludge for use as adsorbent for removing specific contaminants from acidic wastewater streams.

Energy dispersive X-ray spectroscopy analysis

The post-ECC sludge samples of SS and Fe electrodes were subjected to EDS. EDS results show percentage weights of various elements present in ECC sludge. After 90 min ET, the settled sludge was kept for drying in a hot air oven for 24 h, weighed and quantified for sludge produced per unit volume of wastewater treated. Sludge samples were collected and analyzed for morphological and chemical characteristics (Supplementary information, Figure S2, available with the

online version of this paper). Figure 7(a) shows the results of EDS of the sludge generated at a CD of 120 A/m^2 using iron as electrodes with inter-electrode spacing of 1 cm. The figure shows percentage weight of various elements present in the ECC sludge. EDS analysis showed the presence of 13.2% carbon, 44.47% oxygen, 8.07% sodium, 3.16% chloride, 0.9% potassium and 30.19% iron. Similarly, the results of EDS of the sludge generated at optimal CD 120 A/m^2 using SS is shown in Figure 7(b). The constituents of the sludge showed 13.96% carbon, 50.93% oxygen, 4.57% sodium, 0.73% magnesium, 0.57% sulfur, 1.50% chloride, 0.83% calcium, 5.53% chromium, 1.91% nickel and 19.46% iron. Summarizing, the results show that sludge obtained from four Fe electrodes had higher amounts of metals compared to the sludge obtained using all four SS electrodes. Carbon was found to be a little higher in four SS electrode sludge than in four Fe electrode sludge. A comparative study was made with the results reported by Kozlov *et al.* (2015) on proximate and ultimate analyses of various solid fuels with CPWW ECC sludge. Table 4 compares various materials with that of CPWW ECC sludge. The C and O composition, 42.75% and 42.55% respectively, of CPWW ECC sludge is similar to sawdust aspen, and therefore it was surmised that the ECC sludge can be used as a sawdust aspen supplement or similar such use.

CONCLUSION

Raw CPWW was treated electrochemically using SS and Fe electrode combinations for a pre-optimized SA/V of 20 m^2/m^3. Optimal operating conditions in BECC were
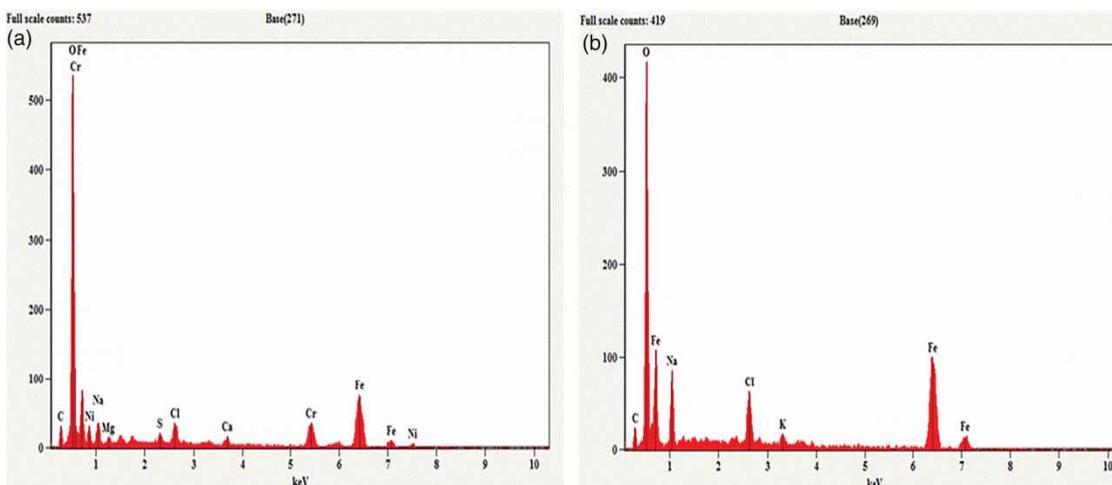

Figure 7 │ EDS of sludge generated at a CD of 120 A/m^2 using SS (a) and Fe (b) electrodes.

Table 4 | Comparison of results of the proximate and ultimate analyses of various solid fuels with CPWW ECC sludge

Sample	Moisture (%)	Ash content (%)	C (%)	O (%)
Lignite coke[a]	0	33.09	88.45	10.24
Charcoal[a]	1.26	2.97	80.33	17.94
Brown coal (Azeya)[a]	12.20	7.60	77.64	16.97
Brown coal (Mugunsky)[a]	5.90	13.70	76.28	11.45
Brown coal (Haranutsky)[a]	2.67	26.46	74.97	15.66
Black coal (Cheremhovsky)[a]	4.04	14.72	73.47	21.85
Brown coal (Glinka)[a]	4.34	10.10	78.28	14.11
Straw[a]	2.53	6.12	56.35	26.85
Lignin[a]	72.00	19.5	54.20	39.70
Sawdust pine[a]	3.47	1.12	54.28	40.53
Sawdust beech[a]	3.10	1.40	46.61	47.23
Sawdust aspen[a]	2.00	1.68	47.77	43.52
Sewage sludge[a]	1.34	5.4	37.52	47.37
CPWW ECC sludge	5.9	17.6	42.75	42.55

[a]Kozlov et al. (2015).

based on process parameters COD and color removal, CD, ET present in wastewater, quick settleability, low SVI and good filterability of ECC-generated slurry. Compatible electrode combinations complement each other for complete performance, removing maximum pollutants/contaminants from wastewater. BECC shows good potential in removing COD, color, and TDS from CPWW operated at 120 A m^{-2} CD, achieving over 87% COD removal for SS electrodes and 85.58% for Fe electrodes with corresponding color removals of over 95% each. Post-ECC water quality could be kept at the desired level for its possible primary/secondary use on soil.

Of all the SS and Fe electrode combinations, SS-SS-Fe-Fe electrode combinations showed higher color and organics removal. PAC as external aid was not effective in color and COD removal through settling and filterability properties improved. ED pattern could be well controlled depending on post-ECC water quality needs. Sludge production was relatively high in Fe electrodes compared to SS electrodes. The latter electrodes were preferred as they do not develop bleak yellow rusty sludge as in Fe electrodes.

The ECC-generated sludge operated at CD 120 A/m^2 using SS electrodes was analyzed for physico-chemical parameters, proximate and ultimate analysis, and EDS for metal quantification. The pH of sludge was 6.75–6.76, specific gravity of the solids content was 1.58 and bulk density was 2,220 kg/m^3. Proximate analysis of CPWW ECC dry sludge portrayed its usefulness as soil/sawdust supplement with fixed carbon value of 5.8%.

Summarizing the results obtained, it was concluded that SS electrodes with Fe electrodes in the ratio of 3:1 can be used effectively to treat raw CPWW wastewater, with clean water reclamations of up to 90%. The ECC sludge may also be used as an adsorbent material and as a replacement for coal for further recovery of energy.

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