Batch electrochemical coagulation of real textile wastewater using Cu-SS and SS-Cu electrode combinations and its settleability aspects

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ABSTRACT

Copper and stainless steel electrodes were used in batch electrochemical coagulation (BECC) for the treatment of real textile wastewater using 16 electrode combinations. Out of 16 Cu-SS and SS-Cu combinations (eight combinations each), only 4SS and 3SS-1Cu electrodes operated at cell voltage of 18 V and current density of 180 A/m² gave maximum color and chemical oxygen demand (COD) removals. The COD removal was observed to be 89.37% for 4SS and 72.34% for 3SS-1Cu electrodes from CODo 3,012 mg/L. Color removal was 97% and 98% from its initial value of 1,000 Pt-Co unit for 4SS and 3SS-1Cu combinations. Water quality parameters like total dissolved solids, chloride, nitrate, phosphate, and sulphate reduced from their initial values while using all 4SS and 3SS-1Cu electrode arrangements. Other control factors exercised for optimal operations were ECC floc settling pattern and sludge volume index (SVI). SVI values were found to be <100 mL/g for both electrode combinations.

Key words | batch electrochemical coagulation, electrode combinations, real textile wastewater, settleability, sludge volume index (SVI)

HIGHLIGHTS

- Limited work is carried out using Cu and SS electrode combinations for treating industrial wastewaters using bipolar mode reporting settling aspects of sludge generated during ECC.
- The intent of using Cu and SS electrodes is the redox potentials of aluminum is \(-1.662\) V, \(-0.440\) V for iron, copper is \(+0.337\) V respectively and with positive potential it is easily ionized in the electrolysis system.
- SS is that it resists corrosion more than iron, the rate of formation of Fe(OH)₂ is much higher than iron with relatively lower electrode dissolution.
- Copper serves as an active disinfectant and treats water to make fit for human consumption without generating secondary pollution.
- SVI values were less than the quality limit of 100 mL/g which can be used for designing secondary settling tanks.
Conventional treatment technologies are too slow and ineffective in treating textile wastewater (TWW) and tend to generate large quantities of sludge (Ahluwalia & Goyal 2011). On the other hand electro-Fenton, electro-oxidation, and catalytic oxidation have several technical benefits for the degradation of dyes but are high in cost, require expensive equipment and a high-energy requirement (Valero et al. 2013). Social concerns for environmental impacts caused by industry are growing and new laws are in demand for strict environmental protection; a search for ‘greener’ and more efficient methods for wastewater treatment is increasing (Mahesh et al. 2006a). In this sense, electrochemical coagulation treatment processes for pollutants/contaminant removal are unique because they prevent any sort of dilution, hazardous materials, and do not require any added chemicals as additives to carry out oxidation or reduction reactions (Drouiche et al. 2012).

Batch electrochemical coagulation (BECC) as a treatment option was chosen to be carried using copper (Cu) and stainless steel (SS) and its possible electrode combinations for the treatment of real TWW. The intent of using Cu and SS electrodes is because redox potential of aluminum is −1.662 V, −0.440 V for iron and copper is +0.337 V respectively. Thus the positive redox potential in Cu easily ionizes the electrolysis system (Hong et al. 2013), whereas a negative potential results in high activity. Another reason for using Cu as the electrode is because it serves as an active disinfectant and treats water to make it fit for human consumption (Halilović & Avdić 2015) without generating secondary pollution, since Cu is less reactive than iron and displacement of Cu in water is less. The reason for using SS is that it resists corrosion more than iron and the rate of formation of Fe(OH)$_2$ is much higher than iron with relatively less electrode dissolution (Yüksel et al. 2011).

Treatment using electrode combinations in 2D electrochemical coagulation (ECC) of contradictory or matching electrodes provide an extension of the ECC technique for removal of color and organics using Al, Fe, Cu, SS, Pb, Zn, Pt and boron-doped diamond electrodes. Most of the research is carried out on Fe-Al and Al-Fe, SS-Al and Al-SS electrode combinations using either real or synthetic wastewater. Limited work is carried out using Cu and SS electrode combinations for treating industrial wastewaters using bipolar mode reporting settling aspects of sludge generated during ECC. Therefore, research objectives were set to study the electrochemical degradation levels using 16 different Cu-SS and SS-Cu electrode combinations for the treatment of...
raw TWW, without dilution or modifications, for removal of chemical oxygen demand (COD), color, nitrate, etc. and to study the floc settling pattern, and sludge volume index.

**MATERIALS AND METHODS**

The chemicals required for parameter estimation were of analytical reagent grade purchased from Himedia Laboratories, Mumbai, India. The dimensional characteristics of the laboratory scale electrochemical reactor (ECR), electrodes and the configuration details are presented in Table 1. Electrode plates were cleared off for scales and oxides on their surface using 15% hydrochloric acid, rinsed using distilled water dried and then used for BECC experiments. The initial weights of all the electrodes were noted down to estimate the electrode consumption per unit volume. For conducting settling experiments on post ECC slurry, a cylindrical column was fabricated using organic glass giving an effective volume of 1 L.

**Instruments and analytical equipment**

Water quality parameters were analyzed in duplicate using various instruments and equipment following the procedures in the APHA guidelines (APHA, 2005). pH was measured using an inoLab WTW pH-meter, color by Platinum-Cobalt method and COD by closed reflux method using a digestion unit (DRB 200, HACH, USA). The electrical conductivity (EC) and total dissolved solids (TDS) values were measured using an MH Digital-TDS/EC meter.

**BECC analysis**

All the ECC test runs were performed at ambient temperature, 25–27 °C. BECC experiments on raw TWW for removal of COD, color and other contaminants were performed in duplicate with error bars representing deviation from the true value. BECC studies on 16 (8 Cu-SS and 8 SS-Cu) electrode combinations were carried out because to check the electrode face acting in the 1st position (anode) in both Cu and SS electrodes. In the first set of experiments, four copper (4Cu) electrodes were used with extreme electrodes (1st and 4th electrode) connected to the positive and negative terminals of the DC power supply unit. Seven other combinations that followed were 1Cu-5SS, 2Cu-2SS, 2Cu-1SS-1Cu, 3Cu-1SS, 1Cu-1SS-1Cu-1SS, 1Cu-2SS-1Cu and 1Cu-1SS-2Cu respectively. Similarly, in the second set of BECC experiments, the first experiment was carried using 4SS electrodes followed by seven other electrode combinations; that is, 1SS-3Cu, 2SS-2Cu, 2SS-1Cu-1SS, 3SS-1Cu, 1SS-1Cu-1SS-1Cu, 1SS-2Cu-1SS, and 1SS-1Cu-2SS. The samples were retrieved (approximately 2–3 mL) at time intervals of 15 min during treatment and at the end of the electrolysis time (ET) the treated effluent was filtered through Whatman 42 filter paper and analyzed for pH, COD, color and other water quality parameters. All the BECC experiment runs lasted for a small hydraulic retention time of 60–75 min ET.

**Settling**

The post-ECC TWW slurry was kept to observe the settling pattern characteristics. The post ECC slurry pre-loaded with charged flocs was homogenized and well mixed to release gas bubbles and then used in settling studies. Settling behavior of solids in the ECC treated solution was measured as a function of time for all the Cu and SS electrode combinations without stirring or addition of any chemicals. All settling studies were limited to a maximum of 30 min as per the requirements of a good settling tank design where the vertical settling velocity \( v_s \) has to be achieved. The plot of H/Ho versus time was drawn for all the Cu-SS and SS-Cu electrode combinations.

**Reactions mechanisms while treating textile wastewater**

Two sorts of reactions occur in the ECC treatment process: (a) electrode reactions and (b) water quality related reactions.
Electrode reactions

The chemical reactions when using Cu and SS electrodes describes Equations (1)–(4) (Parga et al. 2012; Kobya et al. 2014).

Stainless steel

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \] (1)
\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \] (2)
\[ \text{Fe} \rightarrow \text{Fe}^{3+} + 3e^- \] (3)

Copper

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \] (4)

The metal ions Fe\(^{2+}\), Fe\(^{3+}\) and Cu\(^{2+}\) following the Pourbiax curves combine with the negatively charged hydroxide ions (OH\(^-\)) to form the respective hydroxides in the ECR. The real textile wastewater used in BECC experiments was slightly alkaline with pH value 7.25–7.89. During ECC, the pH\(_0\) value tend to change (increase or decrease) from its initial value depending on the electrode used. Under alkaline conditions of the bulk solution electrochemical oxidation of iron produces Fe\(^{2+}\), Fe\(^{3+}\) and copper produces Cu\(^{2+}\) ions, which hydrolyze to produce insoluble Fe(OH)\(_2\) and Cu(OH)\(_2\) presented in Equations (5) and (6).

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \] (5)
\[ \text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 \] (6)

Under acidic conditions in the ECR, Fe\(^{2+}\) and Cu\(^{2+}\) ions combine with oxygen to form a mild acid which lowers the bulk solution pH as shown in Equations (7) and (8).

\[ 4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O}_4 \rightarrow \text{Fe}^{3+} + 4\text{OH}^- \] (7)
\[ 4\text{Cu}^{2+} + \text{O}_2 + 2\text{H}_2\text{O}_4 \rightarrow \text{Cu}^{3+} + 4\text{OH}^- \] (8)

When iron and copper undergo hydrolysis under acidic conditions, Equation (8) takes the form as shown in Equation (9).

\[ \text{Fe} + 6\text{H}_2\text{O} \rightarrow \text{Fe(H}_2\text{O)}_4(\text{OH})_2 + 2\text{H}^+ + 2e^- \] (9)

Triaquatrihydroxy iron (III) begin to precipitate flocs displaying yellow color and rust forms on the copper/iron electrodes, ascribed to the reaction shown in Equation (10).

\[ 2\text{Fe} (\text{H}_2\text{O})_3(\text{OH})_3 \leftrightarrow \text{Fe}_2\text{O}_3(\text{H}_2\text{O})_6 \] (10)

When the wastewater pH turns alkaline during ECC with pH values near to 9, precipitation of Fe\(_2\)O\(_3\)(H\(_2\)O)\(_6\) continues and Fe(OH)\(_2\) precipitate giving a dark green floc which marks byproducts degradation of Cu and SS electrodes having tetra aquadihydroxy iron (II) and Equation (11) is formed as reported by Thirugnanasambandham et al. (2015).

\[ \text{Fe(H}_2\text{O)}_4(\text{OH})_2(\text{aq}) \rightarrow \text{Fe(H}_2\text{O)}_4(\text{OH})_2(\text{s}) \] (11)

Because of polymerization of iron oxyhydroxides, flocs produces and formation of dehydrated hydroxides takes place. The various ECC byproducts formed are as shown through Equations (12)–(15) (Parga et al. 2005, 2012).

\[ 2\text{Fe(OH)}_3 \leftrightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \] (12)
\[ \text{Fe(OH)}_2 \leftrightarrow \text{FeO} + 3\text{H}_2\text{O} \] (13)
\[ 2\text{Fe(OH)}_3 + \text{Fe(OH)}_2 \leftrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \] (14)
\[ \text{Fe(OH)}_3 \leftrightarrow \text{FeO(OH)} + \text{H}_2\text{O} \] (15)

Water quality related equations

Water electrolysis is the process of electrically splitting water into oxygen and hydrogen. The overall water electrolysis is represented by Equation (16).

\[ 2\text{H}_2\text{O} \rightarrow 4\text{e}^- \rightarrow \text{O}_2 + 4\text{H}^+ \] (16)

When using stainless steel and copper, water reduces on the cathode face producing gaseous hydrogen and hydroxide ions shown in Equations (17)–(19).

\[ 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O} \] (17)
\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \] (18)
\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \] (19)

The electro-generated Fe ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, depending upon the pH range of the bulk solution during electrochemical degradation. A large number of oxyhydroxy iron species may be present in the bulk aqueous solution. Because of the polymerization of hydroxy species, a number of iron species such as Fe(OH)\(^3+\), Fe(OH)\(^2+\), Fe\(_2\)(OH)\(_4^+\), Fe(OH)\(^4+\), Fe(H\(_2\)O)\(_2^+\), Fe(H\(_2\)O)\(_3\)OH\(^2+\), Fe(H\(_2\)O)\(_4\)(OH)\(^2+\),
Fe(H$_2$O)$_8$(OH)$_2$ and Fe$_2$(H$_2$O)$_6$(OH)$_4$ may be present (Mahesh et al. 2006a; Lemlikchi et al. 2012) in the solution. Similarly, Cu$^{2+}$ ions hydrate and hydrolyze to form monomeric and polymeric species like Cu(OH)$_2$, CuOH$_2$, Cu$_2$(OH)$_3$, Cu(OH)$_4$, Cu(H$_2$O)$_2$, Cu$_2$(OH)$_3$, Cu$_2$(H$_2$O)$_3$, etc. (Sahu et al. 2014). During ECC, few water quality parameters values increase or decrease as result of chemical interactions between electrodes and the water quality constituents. Chlorine produced in wastewater containing chlorides and the removal of water quality parameters with different electrode combinations plays a significant role in electrolysis. Various chlorine species form in the reactor which mainly depend on pH within 6–9. In this study, during characterization of raw TWW, a significant chloride concentrations of 760 mg/L was observed. During the ECC process, chlorine gas generated at the anode and formed other chlorine species like HOCl and ClO$^-$ depending upon the pH. The chlorine anions generated during ECC treatment are governed by the reactions presented in Equations (20)–(22).

\[
\begin{align*}
2\text{Cl}^- + 2e^- & \rightarrow \text{Cl}_2 \\
\text{Cl}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ \\
\text{HOCl} & \leftrightarrow \text{ClO}^- + \text{H}^+
\end{align*}
\]

Table 2 | Physico-chemical characteristics of raw textile wastewater

| Sl. no. | Characteristics | Unit | Parameter value |
|--------|----------------|------|-----------------|
| 1      | pH             | –    | 7.25–7.89       |
| 2      | Color          | Physical color- Dark bluish purple | Platinum-Cobalt units (PCU) | 900–1,100 |
| 3      | Oil and grease | mg/L | 20–42           |
| 4      | Conductivity   | mS/cm | 2.4–2.9        |
| 5      | Total hardness (TH) as CaCO$_3$ | mg/L | 10–14          |
| 6      | Total alkalinity (TA) as CaCO$_3$ | mg/L | 20–28          |
| 7      | Chlorides      | mg/L | 760–1,320      |
| 8      | Total solids   | mg/L | 2,540–3,290    |
| 9      | TSS            | mg/L | 980–1,230      |
| 10     | TDS            | mg/L | 1,560–2,060    |
| 11     | COD as mg/L of O$_2$ | mg/L | 2,728–3,200 |
| 12     | BOD            | mg/L | 820–890        |
| 13     | COD/BOD        | Ratio | 3.32–3.59     |
| 14     | Nitrate        | mg/L | 18–28          |
| 15     | Phosphate      | mg/L | 150–220        |
| 16     | Sulphate       | mg/L | 55–78          |
| 17     | Cl$^-$/SO$_4$  | Ratio | 13.81–16.92   |

Characteristics of raw textile wastewater

Raw TWW for use in batch ECC treatment was collected from an outfall conduit entering the equalization basin of a local textile mill which uses silk (drawn from cocoons) as raw material. The dyes used on the fabric are acid dyes, direct dyes and vat dyes. The dye constituents unable to stay in the fabric end up in the waste stream adding color values to >3,000 platinum cobalt units (PCU). Raw TWW was characterized for various water quality parameters using procedures accorded in the Standard methods for analysis of water and wastewater. The initial characteristics of raw TWW used in the BECC are shown in Table 2.

RESULTS AND DISCUSSION

Effect of Cu and SS electrode combinations on COD and color removal

Electrode combinations are a crucial feature to increase anodic oxidation that improves elimination of dye and organics. Four electrodes with a surface area to volume (SA/V) of 20 m$^2$/m$^3$ showed maximum COD removal and
therefore extensive BECC experiments in a 1.5 L cuboidal reactor was carried out for 16 different electrode combinations using Cu and SS electrodes in the parallel bipolar arrangement. For an SA/V of 20 m²/m³ cell voltages of 6, 12, 18, and 24 V, giving corresponding current densities (CD) of 20, 60, 180 A/m² and 260 A/m², BECC experiments were carried out. The agitation speed was pre-optimized at 400 rpm because higher agitation speed over 400 rpm causes floc breakage in the reactor. BECC experiments were carried out with two sets of electrode combinations: (i) 4Cu and Cu-SS electrode combinations and (ii) 4SS and SS-Cu electrode combinations. The electrode arrangements in bipolar mode adopted in BECC using 4Cu and Cu-SS electrode combinations and with 4SS and other SS-Cu electrode combination are shown in Figure 1.

4Cu And Cu-SS combinations

In the first instance, all 4Cu electrodes used within the electrodes (1st and 4th position) were connected by lead wires to the positive and negative terminals of the DC power supply unit. Seven other combinations used in the succeeding experiments were 1Cu 3SS, 2Cu 2SS, 2Cu 1SS 1Cu, 3Cu 1SS, 1Cu 1SS 1Cu 1SS, 1Cu 2SS 1Cu and 1Cu 1SS 2Cu. In all these eight sets of Cu-SS electrode combinations, the pH of the bulk solution increased to a little over 10 after 60 min ET (Figure 2) because of the release of Cu²⁺ ions in large quantities into the bulk solution (Jung et al. 2018).

In all eight electrode arrangements, maximum COD removals were achieved at <45 min ET as the M⁺ ions could pick moving micro flocs from the bulk solution forming Cu(OH)₂. This trend continued up to 60 min ET, by which time most organics were removed with other water quality parameters under control. At 75 min ET, with the pH of the bulk solution at 11, COD and color removal showed a decreasing trend because the dissolution of copper oxides did not have any more flocs remaining in the reactor for removal as scum. The Cu electrode in the reactor near the positive terminal (Cu as a 1st electrode) showed increase in pH by two units in the bulk solution because the dissolution of copper oxides did not have any more flocs remaining in the reactor for removal as scum. The Cu electrode in the reactor near the positive terminal (Cu as a 1st electrode) showed increase in pH by two units in the bulk solution after 60 min compared to other SS-Cu electrode combinations. In general, the electrode consumption was high while using Cu-SS electrode combinations compared to SS-Cu electrode combinations.

From Figures 3 and 4 it may be observed that of all the Cu-SS electrode combinations, 4Cu, 3Cu 1SS and 2Cu 1SS 1Cu electrode combinations showed lower COD removal of 526–658 mg/L from the initial value of 3,012 mg/L, and simultaneous color removals limited to 100 PCU at 75 min ET from the initial value of 1,000 PCU. Further, during electrolysis when the bulk solution pH reached 9.5 at 60 min ET, the color of the bulk solution changed to black from its initial pink-purple color. The change in black color is ascribed to excess release of metal ions into the solution making it more murky and dirty (Sujit et al. 2019). Because of these aforesaid limitations viz., high bulk solution pH, high electrode dissolution, low COD removal and black color of treated TWW, all experiments that followed were investigated using SS-Cu electrode combinations. Figure S1 (supplementary material) shows the electrode dissolution and corrosion at the bottom and sides of the Cu electrode. The Cu electrode (at 1st position) was
used continuously for ∼30 number of cycles. Figure S1 shows floc deposition on the active sites with pitting corrosion and edge corrosion on the plates with ∼1 cm (width) electrode corrosion along the periphery of the electrode.

### 4SS and SS-Cu combinations

Firstly, all 4SS electrodes with SEA/V of 20 m$^2$/m$^3$ were used. Seven other electrode combinations used were 1SS
3Cu, 2SS 2Cu, 2SS 1Cu 1SS, 3SS 1Cu, 1SS 1Cu 1SS 1Cu, 1SS 2Cu 1SS and 1SS 1Cu 2SS. The pH of the solution in all the combinations before and after ECC were 7.53 to ∼8.57 at 60 min ET showing stable removal at 75 min ET as shown in Figure 5.

Maximum COD and color removals were obtained between 45 and 60 min ET for cell voltage of 18 V due to the formation of Fe(OH)₂ from SS electrodes following Pourbix pH patterns (Figures 6 and 7). Between 60 and 75 min ET, SS-Cu electrode combinations showed a marginal decrease in COD and color removals because an increased amount of dissolved iron led to the formation of heavy gelatinous Fe(OH)₂ ending up in lesser floc entrapment and pollutant
removal. For all the electrode combinations, a foam-like gel of black-green color formed atop the reactor near the electrodes close to the negative terminal because of deposits of iron oxides on the positive side of the SS electrode faces (Li et al. 2013). Pitting corrosion was high while using SS electrodes on the anode face, which was ascribed to the high chloride value of 760 mg/L in raw TWW. Similarly, area corrosion was observed while using Cu-SS electrode combinations.

From Figures 6 and 7 it is observed that out of all the SS-Cu electrode combinations, only 4SS and 3SS 1Cu electrode combinations showed higher COD removal of 320 mg/L from COD$_0$ 3,012 mg/L and color removal of 20–30 PCU.

From the above set of results, since Cu-SS (Cu in the first
position) electrode combinations showed poor removal of organics and high electrode dissolution compared to SS-Cu combinations, all the experiments that followed were conducted using 4SS and 3SS 1Cu electrode combinations.

The performance of an ECC treatment process is greatly assessed and valued by the quality characteristics of water after electrolysis. From Figures 3–7, it may be observed that only 4SS and 3SS 1Cu electrode combinations at CD 180 A/m² showed good COD and color removal compared

Figure 5 | pH vs ET using 4SS and SS-Cu electrode combinations for TWW.
to CDs 20, 60 and 240 A/m². Therefore, the post ECC supernatant was checked for several important water quality parameters for 4SS and 3SS 1Cu at a cell voltage of 18 V and CD 180 A/m² as listed in Table 3.

Though pH values of BECC treated effluent were slightly higher after treatment, pH recedence was observed after a time lapse of 1–2 h close to the CPCB (India) discharge standard limits of 6.5–9.0. TA values were seen to increase after treatment to 98 mg/L and 99 mg/L from the initial value of 20 mg/L because dissolution of electrodes forms metallic hydroxides that tend to increase the alkalinity values. Similarly, nitrates and phosphates also decreased significantly from their initial values with only marginal sulphate removal. Summarizing, it was concluded

Figure 6 | COD removal as a function of ET for 4SS and SS-Cu electrode combinations for TWW.
that addition of one Cu electrode as the fourth electrode (4th position of four electrodes) in the bipolar arrangement with 3SS (first electrode connected to the positive terminal of the DC unit) provides an excellent water quality after ECC as seen in Table 3.

**Figure 7** | Color removal as a function of ET for 4SS and SS-Cu electrode combinations.

**Discrete time BECC for discrete ET**

Batch ECC for discrete ET of 5, 15, 30, 45 and 60 min were conducted for 4SS and 3SS 1Cu electrode combinations to the observed removal pattern for the following aspects:
(i) removal of COD and color, (ii) post ECC water quality, (iii) sludge settling at 30 min, and (iv) sludge volume index (SVI).

**COD and color removal**

Raw TWW having COD$_0$ 3,012 mg/L, color$_0$ 1,000 PCU and pH$_0$ 7.53 was subject to BECC using 4SS and 3SS 1Cu electrode combinations for the aforesaid ETs. After each discrete BECC, water quality checks were made for color, COD, etc. When using all 4SS electrodes, COD residues in solution were 768 mg/L, 960 mg/L, 768 mg/L, 256 mg/L and 1,280 mg/L with corresponding color removals of 900, 800, 200, 30 and 60 PCU after 5, 15, 30, 45 and 60 min ET. The color removal using 4SS is mainly because SS electrodes are quick in producing additional hydroxyl radicals, expanding the productivity of treatment and immediately oxidizing the processes (Wang et al. 2008). Similarly, for 3SS 1Cu, COD residues were 1,536 mg/L, 768 mg/L, 528 mg/L, 256 mg/L and 1,024 mg/L after 5, 15, 30, 45 and 60 min ET with corresponding color values of 900 PCU, 800, 600, 300 and 20 PCU respectively. It was observed that COD removals do not necessarily synchronize with simultaneous color reduction during ECT. The optimum pH to remove color and organics is $\sim$8.5 pH because at optimum pH (Liu et al. 2014) charge neutralization and coagulation allows solid particles to agglomerate by Van der Waal’s mechanism, which finally results in the ultimate phase of ‘sweep flocculation.’ This state increases the particle size at optimum pH and allows good sludge settling, giving the highest COD and color removal efficiencies (Mondal et al. 2012). After the lead wires were removed from the electrodes, the sludge settled to the bottom of the ECR and in one min or so, the bulk solution reached a state of maturity giving the highest COD and color removal efficiencies.

**Post ECC water quality check**

Secondly, the performance of BECC is influenced by the water quality characteristics of treated effluent. The

| Table 3 | Post-BECC water quality for 4SS and 3SS 1Cu electrode combinations for CD 180 A/m$^2$ (18 V) at 75 min ET |
|---|---|
| **Post-BECC water quality parameters** | **Raw TWW before ECC** | **4SS after ECC** | **3SS 1Cu after ECC** |
| pH | – | 7.53 | 8.24 | 8.76 |
| Color | PCU | 900–1,100 | 60 | 20 |
| Electrical conductivity (EC) | mS/cm | 2.4–2.9 | 2.8 | 2.7 |
| Total dissolved solids (TDS) | mg/L | 1,560–2,060 | 1,218 | 753 |
| Total alkalinity (TA) | mg/L | 20–28 | 98 | 99 |
| Total hardness (TH) | mg/L | 10–14 | – | – |
| Chloride (Cl$^-$) | mg/L | 760–1,320 | 524 | 317 |
| COD | mg/L | 2,728–3,200 | 320 | 768 |
| Nitrate (NO$_3^-$) | mg/L | 18–28 | 2.124 | 1.825 |
| Phosphate (PO$_4^{3-}$) | mg/L | 150–220 | 61.34 | 34.73 |
| Sulphate (SO$_4^{2-}$) | mg/L | 55–78 | 21.17 | 14.05 |

| Table 4 | Post-BECC water quality of TWW for 4SS electrode combinations for CD 180 A/m$^2$ at discrete 5, 15, 30, 45 and 60 min ETs |
|---|---|
| **Parameters** | **Units** | **Initial** | **5 min** | **15 min** | **30 min** | **45 min** | **60 min** |
| pH | – | 7.53 ± 0.3 | 7.84 | 8.17 | 8.18 | 8.3 | 8.41 |
| Color | Color units | 900–1,100 | 900 | 800 | 200 | 20 | 20 | 60 |
| EC | mS/cm | 2.4–2.9 | 2.9 | 2.8 | 2.7 | 2.7 | 2.7 |
| TDS | mg/L | 1,560–2,060 | 2,269 | 1,940 | 1,160 | 728 | 853 |
| TA | mg/L | 20–28 | 98 | 99 | 98 | 98 | 98 |
| TH | mg/L | 10–14 | – | – | – | – | – |
| Chloride | mg/L | 760–1,320 | 702 | 616 | 489 | 356 | 388 |
| COD | mg/L | 2,728–3,200 | 768 | 960 | 768 | 256 | 1,280 |
| Nitrate | mg/L | 18–28 | 19.211 | 16.106 | 9.985 | 1.784 | 2.241 |
| Phosphate | mg/L | 150–220 | 172.26 | 116.89 | 74.65 | 58.31 | 62.03 |
| Sulphate | mg/L | 55–78 | 54.64 | 47.12 | 32.89 | 20.65 | 21.44 |
post-ECC supernatant of 4SS and 3SS 1Cu electrode combinations was checked for several important water quality parameters listed in Tables 4 and 5. The post ECC water quality was checked after the settling and filtration studies (after 45–60 min of BECC). The values of all water quality parameters except total alkalinity and pH were found to gradually decrease up to 45 min ET, after which alkalinity values increased just after 60 min ET. The increase in total alkalinity for both electrode combinations is because electrode dissolution will be in the form of metallic hydroxides that generates microflocs causing increase in the alkalinity values (Zhang et al. 2014). After 45 min, ET parameters like TDS, chloride, nitrate, phosphate and sulphate reduced to 728, 356, 1.784, 58.31 and 20.68 mg/L when using 4SS electrode combinations. Similarly, in 3SS 1Cu electrode arrangement TDS, chloride, nitrate, phosphate and sulphate reduced to 680, 317, 1.115, 31.31 and 10.22 mg/L from its initial values of 2,914, 760, 21.37, 180.44 and 66.53 mg/L. Of the 4SS and 3SS 1Cu electrode combinations, 4SS electrodes showed higher removals of color and organics. 3SS 1Cu showed high TDS, chloride, nitrate, phosphate, sulphate removals than the 4SS electrode arrangement. Nitrates and sulphate removal can be explained that at higher CDs the coagulating species are discharged and flocs generated will have higher adsorption capacities, resulting in removal of nitrates and sulphates (Xu et al. 2018). Removal of phosphate in the bulk solution is because of coagulation with Fe3+ salts resulting in the arrangement of FeHO5P that adsors unto Fe3+ ions.

### Characteristics of EC generated sludge

**ECC floc settling pattern.** The velocity of the settling floc particles in the graduated cylinder and its settling pattern (Type I, II, III and IV) controls the design size of the clarifier-floculator unit. The settling pattern of ECC flocs shown in Figure 8 follow a particular pattern, skipping Type II settling for 4SS and 3SS-1Cu electrode combinations at CD 180 A/m².

The settling process was initiated, giving a time lapse of 10 min after ECC to drive away entrapped gases in the slurry. In the event, the settling process is initiated immediately after the ECC process, the sludge does not settle to the bottom of the container/sludge tank prompting a reverse settling tank design by drawing off the clarified supernatant at the bottom of the reactor. During ECC, a fluffy viscous jelly scum like material accumulate atop the ECR. The ECR content after each batch ECC was homogenized and well mixed for a minute or two for releasing the entrapped bubbles in the gel matrix. After a time lapse of 10 min, the slurry for all 16 different electrodes (Cu and SS) combinations were subject to gravity settling in a 1,000 mL graduated glass cylinder. The settling sludge-clear water interface in mL was noted every 5 min with the cylinder kept in quiescent condition for all the electrode combinations. Using this data, H/Ho vs. settling time plots were generated for all 16 Cu-SS and SS-Cu electrode combinations.

#### Table 5 | Post BECC water quality of TWW for 3SS 1Cu electrode arrangements for CD 180 A/m² at discrete 5, 15, 30, 45 and 60 min ETs

| Parameters | Units | Initial | 5 min | 15 min | 30 min | 45 min | 60 min |
|------------|-------|---------|-------|--------|--------|--------|--------|
| pH         | –     | 7.53 ± 0.3 | 7.84 | 8.17 | 8.18 | 8.3 | 8.41 |
| Color      | Color units | 900–1,100 | 800 | 600 | 300 | 30 | 20 |
| EC         | mS/cm | 2.4–2.9 | 2.9 | 2.8 | 2.7 | 2.6 | 2.6 |
| TDS        | mg/L | 1,560–2,060 | 2,571 | 1,819 | 968 | 680 | 912 |
| TA         | mg/L | 20–28 | 98 | 98 | 99 | 99 | 98 |
| TH         | mg/L | 10–14 | – | – | – | – | – |
| Chloride   | mg/L | 760–1,320 | 628 | 497 | 398 | 317 | 452 |
| COD        | mg/L | 2,728–3,200 | 1,536 | 768 | 528 | 256 | 1,024 |
| Nitrate    | mg/L | 18–28 | 18.850 | 14.228 | 7.864 | 1.115 | 1.926 |
| Phosphate  | mg/L | 150–220 | 166.85 | 102.55 | 61.13 | 31.31 | 34.98 |
| Sulphate   | mg/L | 55–78 | 52.59 | 48.22 | 21.54 | 10.22 | 14.48 |
flocs in the column, a ‘local choking effect’ was observed in the Cu-SS electrode combinations compared to SS-Cu electrode arrangements with settling water gaps in the column. Because of this choking effect, particularly for Cu-SS arrangements, the air voids are generated en masse between settling sludge were seen as broken cylindrical blocks and therefore slurry modifications were made by adding a small quantity of alum to blow off the bubbles and aid in particle settling. Electrode combinations other than 4SS and 3SS-1Cu required slight modifications to complete the settling process by adding additives/coagulant.

Of all the electrode combinations, 4SS and 3SS-1Cu showed good settling at CD 180 A/m² for discrete ECC times of 5, 15, 30, 45 and 60 min as shown in Figure 8(a) and 8(b). The initial color of the slurry was green for 4SS and 3SS-1Cu. After settling for 30–40 min in the column, the supernatant was slightly murky and the color of supernatant turned mild algal green. Discrete settling was observed with a rather slow settling rate because of entrapped gases up to 15 min after initiating settling, followed by a quick ‘zone settling’ and finally ‘compression settling.’ Use of SS electrodes alone and 3SS-1Cu electrode combinations provided a reasonably good settling pattern as seen in Figure 8 in the first 10 min.

‘Discrete settling’ pattern and ‘compression settling’ pattern is seen as predominant over the other two settling types. As seen in the figure, the discrete settling pattern is a bit skewed between 0 and 5 min because of the microbubbles of O₂, H₂ or Cl₂ entrapped in the floc matrix yet to be thrown out (Khorram & Fallah 2018). This causes a density drop – a temporary effect after which the gravity pull takes over, which settles at ease. Lower ETs provide fewer solids during settling. Clear supernatant interfaces were observed for 30, 45 and 60 min ET with <300 mL mark at 30 min settling time. Only 45 min ET showed good settling characteristics with <250 mL in the graduated cylinder because at a particular current Fe(OH)₂ ions adsorb the pollutants rapidly, making the slurry heavy and it settles down since the atomic mass of Fe is 55.847 amu.

**Sludge volume index.** The settling characteristics of ECC generated sludge is commonly quantified using the sludge volume index. The SVI values were estimated using the relation provided by Mahesh et al. (2006b) and shown in Equation (23).

\[
SVI = \frac{1000 \times H_{30}}{H_0 \times X_0}
\]

where \(H_{30}\) is the height of the sludge-water interface at the bottom of the settling column under a quiescent condition at 30 min, \(H_0\) is the initial height of the mixed liquor in cm in the settling column and \(X_0\) is the initial solids concentration of the slurry mg/L in the entire column. SVI is the volume occupied by 1 g of the sludge at 30 min settling in a graduated cylinder. SVI values of the ECC slurry after 75 min ET for both Cu and SS with different electrode combinations are given in the supplementary material as Table S1. SVI values <100 mL/g for biological sludge indicate obtaining quality sludge surmising a small cost.
footprint in the design of secondary settling tanks (SSTs). In supplementary Table S1, it may be observed that only 4SS and 3SS-1Cu electrode combinations showed low SVI values of 92.80 and 95.23 mL/g for CD of 180 A/m². The ECC slurry containing floc particles settled quiescently without requiring any additives for 4SS and 3SS-1Cu while other 12 electrode combinations required a small quantity of additives (alum <1 g was added as an external additive) to induce settling. Use of copper as electrodes generates more gases at the electrode faces, which interlocks into the gel floc matrix thus curtailing the gravity value of particle settling. Settleable sludge was not formed at lower CDs (20 and 60) A/m² because of low charge on the M⁺ ions and low strength to pick colloidal particles from the solution to form flocs.

It was finally concluded that as the CD increases, SVI also increases. It is the SVI value that gives maximum removal of COD, color and other pollutants/contaminants for identifying the best-operating conditions that have to be used in the design of the underflow of the SST unit. SVI values were found to be satisfactory at CD 180 A/m² for 4SS and 3SS-1Cu electrode combinations and so discrete ET studies were carried out to observe the SVI values for different ETs.

Table 6 shows SVI values of post-ECC slurry using 4SS and 3SS-1Cu electrode combinations obtained at cell voltage 18 V and CD 180 A/m² for discrete ET of 5, 15, 30, 45 and 60 min. The moment all the five steps occur in the coagulation-flocculation (M⁺ ion release, double-layer compression, adsorption and charge neutralization, intra-particle bridging and sweep flocculation) at half the ET and with no other un-settleable solids available in the bulk solution, M⁺ ions continue to release into solution picking up the remaining micro flocs; this situation in the ECR marginally increases the SVI values from 97.82 to 128.57 mL/g from 45 to 60 min ET. At the 45th min, SVI values were 90.90 and 97.82 mL/g for 4SS and 3SS-1Cu electrode combinations.

### Table 6

| ET (min) | Sludge volume index (mL/g) for 18 V, CD: 180 A/m² |
|----------|--------------------------------------------------|
|          | 4SS | 3SS-1Cu |
| 5        | No sludge formation; micro flocs only | No sludge formation; micro flocs only |
| 15       | 204.54 | 181.81 |
| 30       | 132.35 | 125  |
| 45       | 90.90  | 97.82  |
| 60       | 118.42 | 128.57 |

Sixteen electrode combinations using Cu and SS were used in BECC for the treatment of real textile wastewater. Results reveal that the BECC process showed good potential to remove COD, color, and other water quality parameters from raw TWW using 4SS and 3SS-1Cu electrode combinations operated at an applied cell voltage of 18 V and CD of 180 A/m². A maximum COD removal of 89.37% for 4SS and 72.34% for 3SS-1Cu electrodes was achieved. Similarly, color removals of 97 and 98% were achieved for 4SS and 3SS-1Cu combinations. After 45 min, ET parameters like TDS, chloride, nitrate, phosphate and sulphate reduced to 728, 356, 1.784, 58.31 and 20.68 mg/L when using 4SS electrode combinations. Similarly, in the 3SS 1Cu electrode arrangement, TDS, chloride, nitrate, phosphate and sulphate reduced to 680, 317, 1.115, 31.31 and 10.22 mg/L from initial values of 2,914, 760, 21.37, 180.44 and 66.53 mg/L. SVI values were less than the quality limit of 100 mL/g for 4SS and 3SS-1Cu combinations, which can be used for designing secondary settling tanks, while other 12 electrode combinations required the addition of <1 g of alum to induce settling.

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### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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