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Two-stage hybrid electrocoagulation–adsorption in the removal of disperse dyes and inorganic salts from the textile dyeing effluent

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ABSTRACT

The conventional physical, chemical and biological treatment methods are less efficient, more time and energy-intensive, need more operational space and are less efficient in treating effluent-containing toxic elements. In the past few decades, electrocoagulation is gaining more attention in the treatment of textile dyeing effluent to remove color and chemical oxygen demand, because of its environmental compatibility and versatile nature. As a tertiary treatment for the removal of salts, capacitive deionization (CDI) is another electrochemical method that is effective in the removal of salts. In this study, high-performance hybrid TiO_2/Al and carbon aerogel electrodes-based electrocoagulation–adsorption technology have been applied to treat the dyeing wastewater from small-scale industries in batch as well as in continuous mode. The effect of operating parameters such as pH, initial concentration of dye, electrolyte concentration, current and reaction time on the decolorization removal efficiency has been investigated. From the experimental investigations, it was observed that 99% of dye was removed, when the initial concentration of dye was 90 mg/L at initial pH of 7.0, with DC power of 0.3 Å and the reaction time of 10 min. It was also noted that about 60% of chlorides in the electro coagulated treated wastewater was removed through CDI.

Keywords: Aluminum/TiO_2 electrode, Dye removal, Electrocoagulation, Capacitive deionization

1. Introduction

Textile industries are one of the most water-consuming industries in India. The effluent discharged from those industries contains a lot of salts and chemicals, which are toxic and carcinogenic that hinders photosynthetic activity because of less penetration of light. The conventional physicochemical and biological treatment methods like chemical coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration have major limitations such as consumption of more time and energy, difficulty in the regeneration of adsorbents and production of large amounts of sludge and its disposal [1–3]. In the past few decades, the electrochemical treatment methods have gained wide attention due to less maintenance, easy to operate, simplicity, economical, reliability, less production of sludge with no other chemical consumption. In the electrocoagulation process, the required amount of coagulant is generated *in-situ* by electro-oxidation of the sacrificial anode by the applied potential to the electrodes. The destabilization of colloidal pollutants, breaking down of emulsion and suspension of pollutants occur through electrostatic force of attraction towards the *in-situ* generated coagulant that compresses the diffuse double layer. Due to reduction in the electrostatic inter-particle repulsion, the flocs are formed which adsorb/entrap the dye molecules/colloidal pollutants present in the wastewater. Several studies have been carried out using batch and continuous flow electrochemical reactors with

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aluminum and iron electrodes to remove Methylene blue dye, crystal violet-blue, azo dye, acid black and acid yellow dye, blue reactive dye and disperse red dye with dye removal efficiency ranging from 70% to 98% with current density ranging from 10 to 40 M/m^2 [4–15].

This study presents the batch and continuous flow results of the hybrid electrocoagulation–adsorption method in the treatment of dyeing effluent using aluminum electrode coated with TiO_2 and carbon aerogel electrodes. The different influencing operational parameters such as applied current, the concentration of dye, pH, the concentration of electrolyte and reaction time on color removal efficiency (CRE) and salt were analyzed. These operational parameters have a great influence on the industrial application of electrochemical methods.

2. Dye removal mechanism

In this study, the TiO_2/Al electrodes are used as anode and cathode for *in-situ* generation of Ti^{4+} metal ions which has a tetravalent charge with better dye removal efficiency than Al^{3+} or Fe^{3+} ions. The Ti^{4+} ions will be released till the coating/thermally deposited Ti^{4+} gets dissolved into the solution, then after Al^{3+} ions may start getting dissolved. This type of nanocomposite electrode takes advantage of both metal ions in removing the dye from the effluent. The main reactions occurring in the reactor are: when the potential is applied to the metallic anode, the metal ions (Ti^{4+}, Al^{3+}) get dissolved into the solution, while the equivalent number of electrons pass through the circuit and dissociate water into H_2 (g) and OH^- ions at the cathode. The hydrogen gas is released at the cathode while oxygen is released at the anode [16–20]. In the presence of supporting electrolyte and with slow stirring, the electro-driven coagulants and hydroxyl ions come into contact to form both monomeric, polymeric metal hydroxides and poly-hydroxy metallic flocs like $Al_{13}(OH)_{34}^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_7(OH)_{17}^{4+}$, which finally get transformed to $Al(OH)_3$ based on precipitation kinetics, that adsorb/entrap the dye/ pollutants from the waste stream. Due to the formation of OH^- (aq) and consumption of protons at low initial pH, Al ions get dissolved from cathode to form aluminate $Al(OH)_4^-$ that increases the pH of the effluent in the reactor. Capacitive deionization is one of the efficient electro adsorption techniques for removing salt from aqueous solutions. When the electrodes are charged, the oppositely charged ions get adsorbed into the electrical double layer region on the surface of the respective electrodes (anions to anode and cations to cathode), thereby the concentration of anions and cations contributing to the increase in TDS gets removed. Then, during depolarization, due to a reduction in the cell voltage, the adsorbed ions get released into a waste stream [21–27].

3. Experimental investigations

The synthetic stock dye solution was prepared by dissolving an equal proportion of Coralene Navy RDRLSR, Coralene Red 3G, Rubru RD GLF I solid dye in distilled water. The batch experiments were conducted in a 250 mL beaker with 200 mL of initial dye solution. Two TiO_2/Al electrodes prepared by thermal decomposition method (using $TiCl_3$) as precursor were used as anode and cathode. The influence of operational parameters like initial concentration of dye, pH, electrolyte concentration, reaction/electrolysis time and current density on CRE was studied. The interelectrode distance maintained was 1 cm. The samples collected from the reactor tank were allowed to settle for 30 min, filtrated and analyzed for pH, EC, TDS and absorbance using a UV-Visible spectrophotometer (UV/V) at an observed peak wavelength of 568 nm. The characterization of sludge (functional group, surface morphology and structure) was done using scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM).

4. Effect of the operational parameter on the performance of electrocoagulation process

4.1. Effect of pH

The pH of the wastewater has a greater influence on the dissolution of the metallic ions from the sacrificial anode, formation of hydroxide species, the conductivity of the medium and the zeta potential of the colloidal pollutants residing in the wastewater. Based on the initial pH of the solution, the *in-situ* generated Al metal ions undergo different hydrolytic reactions resulting in the formation of mononuclear/monomeric and polynuclear/polymeric hydroxides. The higher positive charges carried by polymeric/polynuclear hydroxide species and their size, greatly influence the destabilization of colloidal pollutants. The metal hydroxides $Al(OH)_4^-$ and formed in the alkaline medium have got poor coagulation capacity. When the pH is less than 3, the rate of dissolution of Al at the anode is less and the dissolution occurs at Al cathode because the hydroxyl ions formed at the cathode are being consumed by protons in the acidic medium resulting in the formation of aluminate. The CRE at different pH is shown in Fig. 1. The CRE value after the 10 min operation of constant DC power supply with constant inter-electrode distance of pH 4, 5, 6, 7, 8 and 9 were 93% to 98%. The CRE value in optimization of pH increase constantly up to pH 7 and the decrease with increase in pH beyond pH 7. The solubility of metal hydroxide was lower between pH 5 and 8. The pH value after the electrocoagulation process was stabilized to pH 8–9 due to the isoelectric point of that solution. The CRE value for the pH 7 dye solution was 98.2%.

4.2. Effect of initial concentration of dye

The initial concentration of the dye has a greater effect on the performance of the EC process. When the concentration

Table 1
Characteristics of the waste

Parameter	Range
pH	8.1–8.45
Total dissolved solids, ppm	2,060–2,222
Initial absorbance due to dye	1.9143
Total suspended solids, mg/L	300–400
Chemical oxygen demand, mg/L	1,200–1,500

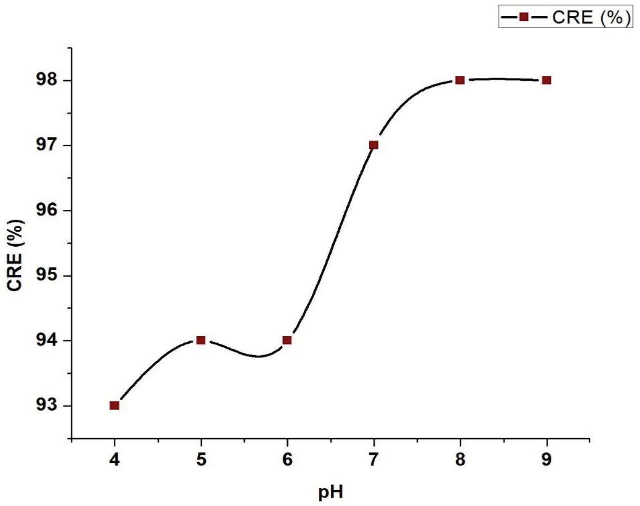

Fig. 1. CRE at different pH.

of the dye/pollutant increases beyond the optimum level, the generated *in-situ* metal ions from the electrodes may be sufficient to form floc to have higher CRE. To achieve higher CRE, more reaction/electrolysis time is required which in turn increases more energy/power consumption. From the study on the influence of the initial concentration of dye (50–200 mg/L) on CRE at constant current density it was observed that the CRE was decreasing with an increase in the initial concentration because at higher concentrations (50 and 200 mg/L), longer reaction time was necessary to achieve good efficiency. According to Faraday's law, since the same amount of TiO^{4+} or Al^{3+} is released into the solution at a constant power supply for all concentrations of dyes, the generated flocs at high concentrations of dye were unable to adsorb the dye molecules further. At constant pH of 7, after 10 min of reaction time, the CRE value for the removal of different concentration of dye of 50, 70, 90, 120 and 150 mg/L were 97.97%, 99.17%, 98.46%, 83.68% and 34.10% respectively. The CRE value for the optimization of the initial concentration of dye decrease with an increase in CDI. The optimum value CRE value was obtained in 0.009% dye solution with 98.46% as shown in Fig. 2.

4.3. *Effect of anions and electrolytes*

The presence of anions (SO_4^-, Cl^-, NO_3^- and PO_4^-) in the wastewater also affects the formation of metal hydroxide based on the nature of their electronegativity and their affinity towards the metal ions and presence of the positive sites on the surface of the precipitates of metal hydroxide. In the above mentioned four anions, SO_4^- has strong coordination with metal ions than NO_3^- and Cl^-. The supporting electrolytes like NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ have great influence on the performance of the EC process. The presence of SO_4^- ions which are passivating agents reduce the generation of *in-situ* coagulant from the electrodes resulting in more power consumption while the presence of Cl^- ions initiate the breakdown of passive layer and induces pitting corrosion. In order to break down the formed passive layer, the ratio of Cl^-/SO_4^- should be more than 0.1. The presence of a high concentration of other salts may get precipitated on the surface of the electrodes which leads to more power consumption. In addition to that, the presence of anions like SO_4^-, Cl^-, NO_3^- and PO_4^- compete with another anion like F^- which is a pollutant to be removed. The SO_4^- ion competes with F^- in getting attached to Al metal ions, while arsenate and fluoride ions compete with PO_4^- ion when it is pollutant to be removed. The type of anions presents in the wastewater and the current density influence the current efficiency. By varying NaCl concentration from 2 to 6 mL, the recorded CRE values are from 54.3% to 99%. The removal of dye was low at the 2 mL concentration of electrolyte due to insufficient amount to transfer ions to carry electrocoagulation process. The optimum concentration of electrolyte solution was 3 mL with 99% dye removal with a minimum amount of sludge generation.

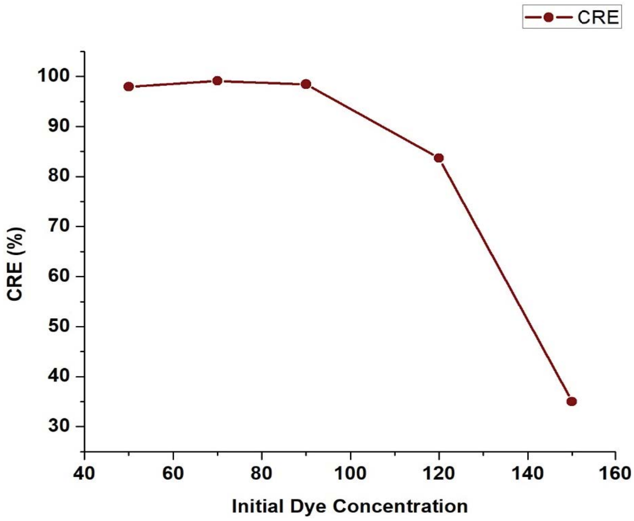

Fig. 2. Effect of concentration of dye on CRE.

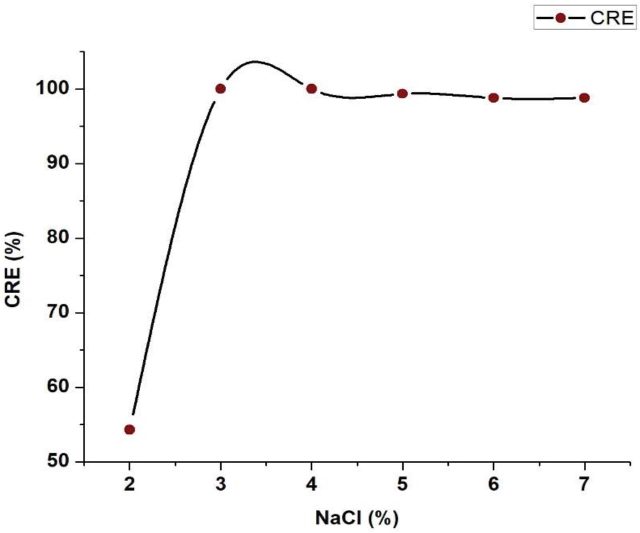

Fig. 3. Influence of electrolyte with CRE.

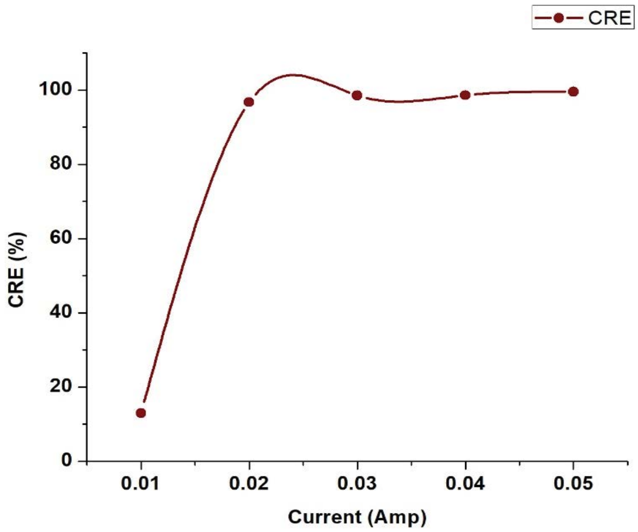

Fig. 4. Effect of current on CRE.

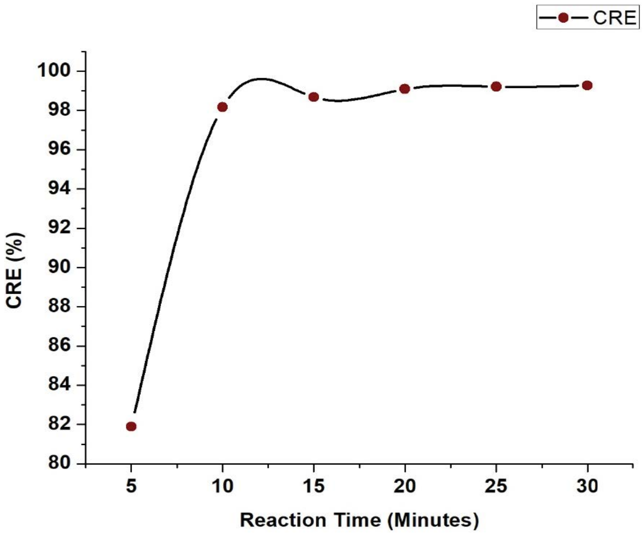

Fig. 5. CRE at a different time interval.

4.4. Effect of current density

The applied current density has a significant influence on the potential of the electrode which defines the type of electrochemical reactions occurring on the surface of the electrode and their rate. The amount of *in-situ* generated coagulant from the sacrificial electrode is calculated by Faraday's law, $Q = CD \times t \times M/n \times F$, where 'CD' is the applied current density in mA/cm^2, '*t*' is the reaction/electrolysis time, '*M*' is the molar mass of the electrode material, '*n*' is the number of electrons released during a redox reaction, '*F*' is the Faraday's constant. In the case of Al electrodes, at acidic and neutral pH, for the given applied potential, the dissolution of the metal ions from the sacrificial anode is the major type of reaction in the reactor. At a given time and reaction time, the amount of *in-situ* generation of metal ions from the sacrificial anode is calculated by Faraday's law. In the case of Al electrodes, at pH less than 3, the total amount of *in-situ* generated coagulant includes both the dissolution of Al anode and Al cathode. It is also reported that as the current density decreases over time at a constant charge per volume, the amount of the *in-situ* generation of Al increases indicating that even at low current densities (<0.1 A/cm^2), the dissolution reaction occurs at the Al cathode. At higher current, due to high electrooxidation at anode, oxygen is being released from the anode and the hydrogen from the cathode. The size of hydrogen and oxygen bubbles produced in electrofloation is in the range from 17 to 50 µm that provides more surface area for attachment of dye or pollutant. The CRE value at varying current density (0.03 Å, 0.04 Å, 0.05 Å and 0.06 Å) was 96.68%, 98.48%, 98.62% and 99.49% respectively. At higher current density, the generation of gases favors the electrofloation process.

4.5. Effect of reaction time

The dye removal efficiency depends directly on the concentration of metal ions generated at the anode through the anodic electro-dissolution. The formation of more hydroxide (monomeric and polymeric) flocs at higher reaction time leads to higher CRE. The effect of time of electrolysis was studied at a constant current of 0.03 Å and initial pH 7. As shown in Fig. 5, an increase in the time of electrolysis from 5 to 25 min results in an increase in the dye removal efficiency from 81% to 99%. It also could be noticed that after 10 min, only 2% further removal could be achieved which is not economical.

5. Continuous-flow electrocoagulation

The study of electrocoagulation was further extended to the continuous flow laboratory study with a single pair of aluminum/TiO$_2$ electrodes and parameters with a flow rate of 50 mL/min, initial concentration of 200 mg/L and the current density of 1 Å (Fig. 6). The weight and thickness of the electrode were measured regularly. The continuous flow experiments were carried out for 10 d and samples were collected from the electrocoagulation unit, settling tank and filter unit for analysis of pH, TDS, EC and absorbance. The sludge from the electrocoagulation was collected and characterization was done using SEM, XRD, EDX and Fourier-transform infrared spectroscopy (FTIR). It was observed that there was 99% dye removal through the continuous flow studies.

6. Energy and electrode consumption

The energy consumption by the electrodes can be determined by the equation, '*C* energy' = $U*I*t/V$, where *C* energy = energy consumption for each m^3 of wastewater (kWh/m^3); '*C* electrode' = electrode consumed for treatment of one m^3 of wastewater (kg/m^3); *a* = electricity cost 500 paisa/kWh and *b* = standard cost of aluminum Rs. 403/kg, *U* = voltage (V), *I* = current (A), *t* = residence time (h) and *V* = volume of wastewater (L), respectively. In this study, the overall electrical energy consumption was computed using (*C* energy) *S* and (*C* energy), where (*C* energy) *S* represents the value of the electrical energy; (*C* energy) *M* represents the value of the electrode. The values of ‘*C* energy’ and ‘*C* electrode’ calculated based on the above-mentioned expressions are 0.023 kWh/m^3 and 0.083 kg/m^3, respectively.

7. Characterization studies

7.1. TEM analysis

TEM was used to examine the particle size, crystallinity and morphology of samples. It is clearly seen that the TiO_2 powders in the rutile phase consist of both spherical and rod shapes but the particle of TiO_2 powders in the anatase phase is mostly spherical morphology. The darker regions of the TEM image due to titanium hydroxide precipitate resemble folds in a scrap of fabric as if the had wrinkled and overlapped on itself (Fig. 7). The precipitate which is not as thick is indicated by the lighter regions, particularly near the edges of the floc. The scrap from the cathode has a geometrical resemblance which indicates that

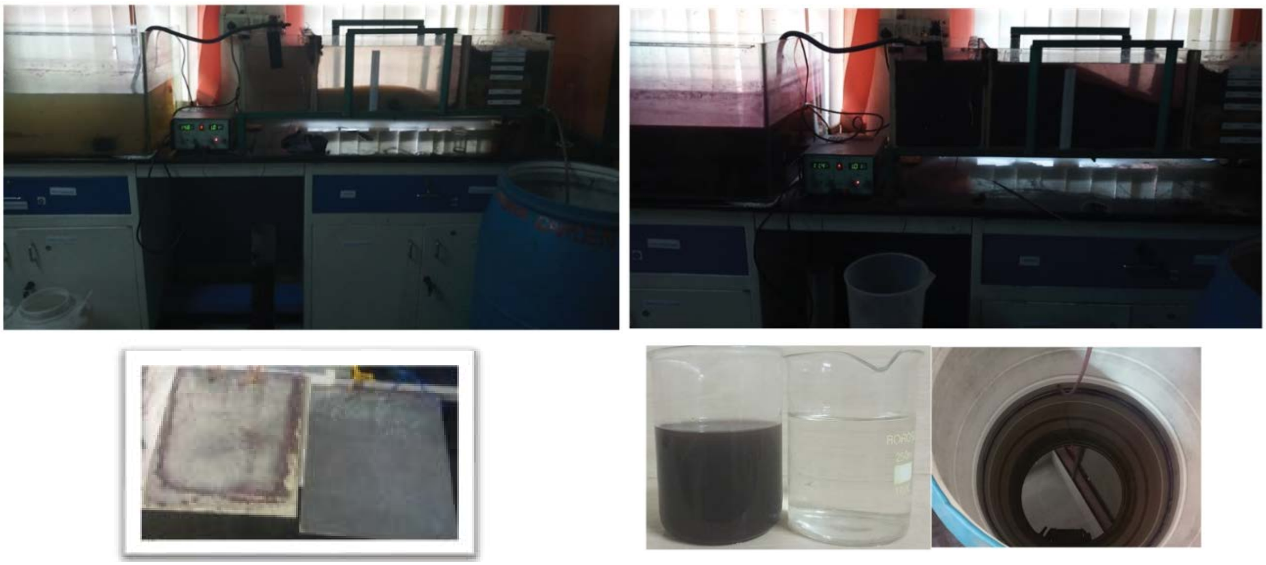

Fig. 6. Continuous flow studies treated effluent and electrodes after 7 d.

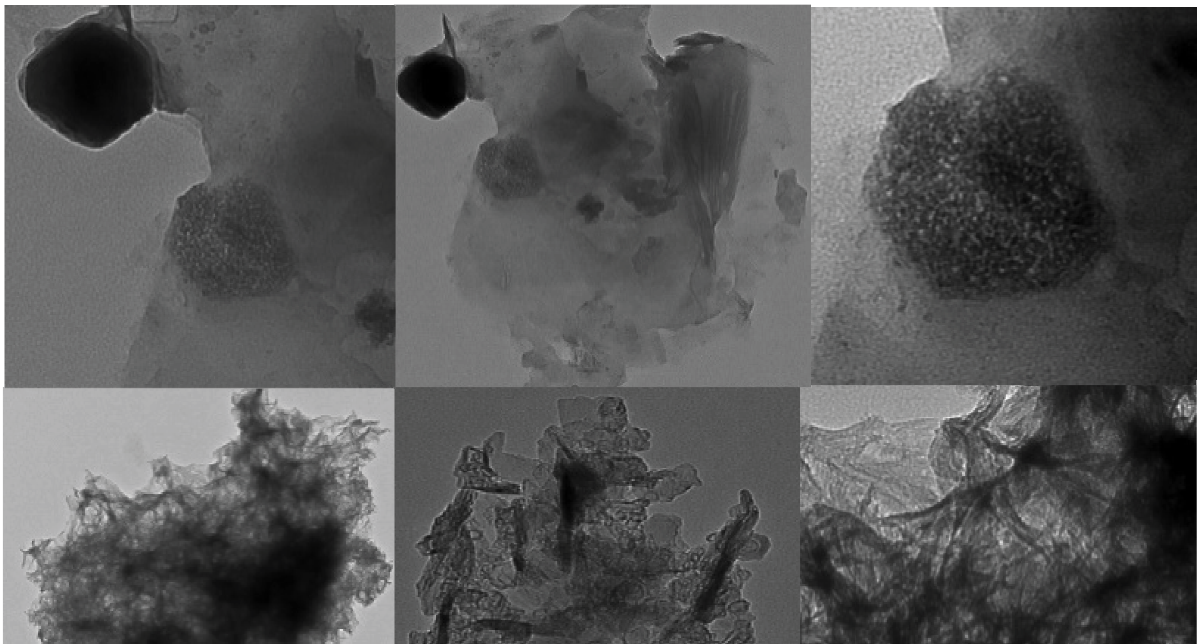

Fig. 7. TEM images of sludge in the settling tank.

repeating, self-similar structures existed, which is essential to the definition of a fractal object (Fig. 7). Similar patterns have been reported in the article.

7.2. FTIR analysis

The first band is the broadest, and is observed at 3,500 cm^{-1}, corresponding to the stretching vibration of the hydroxyl group O–H of the TiO_2; The second band is observed around 1,630 cm^{-1}, corresponding to bending modes of water Ti–OH; prominent peak at 1,383 cm^{-1} related to Ti–O modes; The peaks at 3,438.70 and 1,640.26 cm^{-1} in the spectra are due to the stretching and bending vibration of the –OH group; The peaks at 523.88 cm^{-1} show stretching vibration of Ti–O and peaks at 1,416.38 cm^{-1} shows stretching vibrations of Ti–O–Ti (Fig. 9).

8. Capacitive deionization

The industrial capacitive deionization unit which works on the electro adsorption principle, has 200 pairs of static/flow porous carbon aerogel electrodes separated by either a porous dielectric material or open channel in-between. The feed water flows through these carbon electrodes while applying potential. While the carbon aerogel electrode pairs are charged with potential difference ranging from 1–1.4 V, the ions migrate into the electrical double layer (EDL) along the surface of the electrodes and get separated. These ions remain in EDL till the potential is stopped or polarity is reversed. The adsorbed ions get released into the waste stream. About 75% of salts is removal by this electro-adsorption process.

9. Conclusions

In the current work, the performance of dye and salt from dyeing wastewater and the influence of operational parameters like initial concentration, current density, pH, electrolyte concentration and electrolysis time in treating textile dyeing effluent were carried out in both batch and continuous flow studies. It was observed that within 10 min of reaction/electrolysis time there was more than 99% removal of dye using EC process with electrodes kept at a distance of 1 cm and current of 0.3 Å. The continuous flow studies were conducted with a flow rate of 50, 100 and 200 mL/min for nearly 150 h. The sludge of scrap from the electrode surface and settled flocculated sludge were taken daily and collected from the EC unit. It was observed that using hybrid electrocoagulation–adsorption reaction, there was color removal efficiency in the range of 81%–99.59%

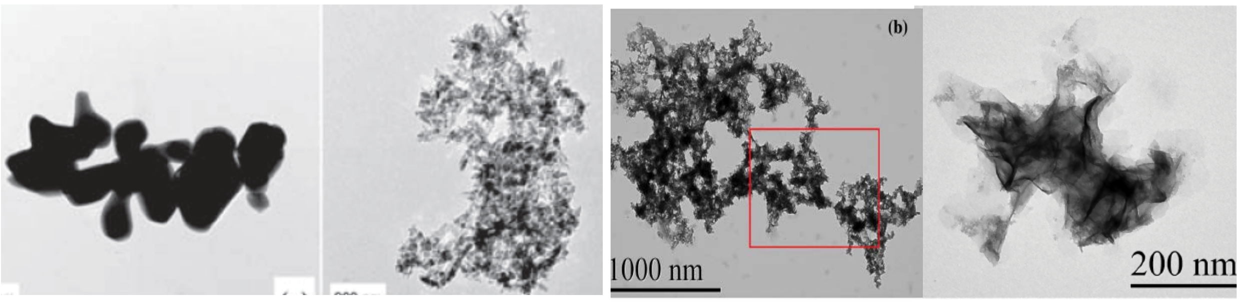

Fig. 8. *Source*: Growth and structure of flocs following electrocoagulation, 2016.

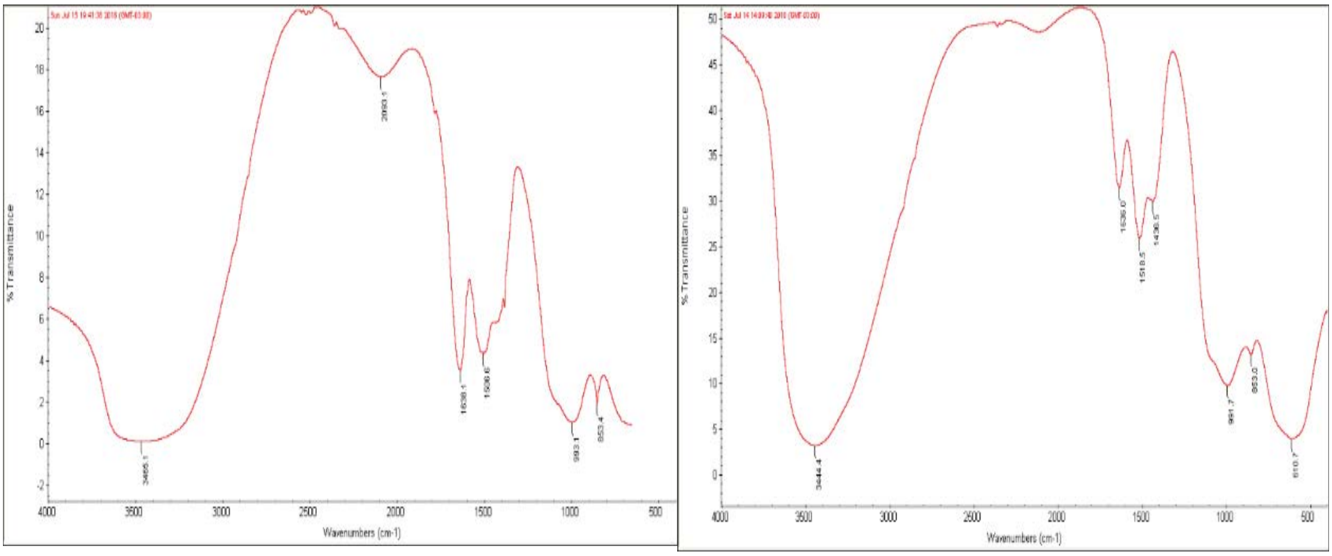

Fig. 9. FTIR spectrum of electrocoagulation sludge and anode scrap.

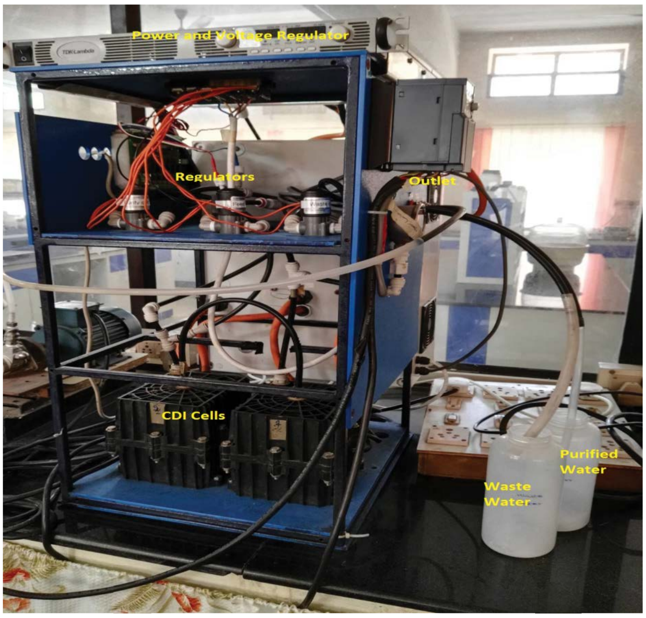

Fig. 10. Industrial capacitive deionization unit.

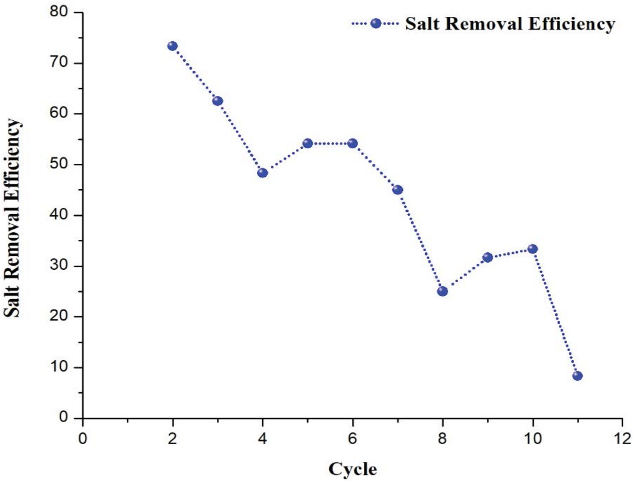

Fig. 11. The efficiency of removal of salts in 10 cycles using CDI.

and salt removal was 30%–75%. This hybrid electrocoagulation–adsorption technology can be an effective treatment in small-scale industries.

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