Chapter 8. Removal of organic dyes and tannins by electrochemical techniques

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Abstract: Removal of organic dyes, tannins and phenol based molecules from aqueous solutions and the amenability of electrochemical techniques for the treatment of dye bath and tannery effluents was discussed. In the case of electro-coagulation/flotation, aluminum and steel were used as electrodes whereas graphite and $IrO_2/TaO_2/RuO_2$ coated Ti electrodes were tried for electro-oxidation. The degradation of dyes such as CI reactive blue 221 and CI Acid orange 10, phenol based tannins and phenolics such as resorcinol, pyrogallol, catechol and phloroglucinol was studied both by electrocoagulation and electro-oxidation techniques. The decolourization and degradation of the dye molecules was monitored by UV-Visible spectrophotometer and the mineralization trend of all these compounds was followed by chemical oxygen demand (COD) and total organic carbon (TOC) measurements. The effect of operating parameters such as nature of the electrolyte, pH, and applied current density were discussed. The generation of chlorine based in situ oxidants has been confirmed by cyclic voltammetric technique. Electro-oxidation of the dyes and tannin molecules was evaluated and found that the graphite material was effective to achieve the complete mineralization. Although, $IrO_2/TaO_2/RuO_2$ coated Ti anode is chemically inert and structurally stable, it fails to generate more molecular oxygen and hydroxyl radicals. The purification of textile and tannery effluent was successfully achieved by electrochemical treatment processes.

INTRODUCTION

Water, a major natural resource essential for human life, is continuously contaminated with different hazardous chemicals released from various industries. Rivers, canals, estuaries and other water-bodies are being polluted by indiscriminate discharge of industrial effluents as well as other anthropogenic activities and natural processes. The continuous depletion of ground water, shortage in rainfall and huge consumption of water by industries has made clean water as a scarce commodity. Textile and tannery industries are considered to be most polluting sector in terms of effluent composition and discharge volume. These effluents are not only aesthetic by their color but also interfere in the

penetration of light. Furthermore, it contains organic and inorganic chemicals that are toxic, carcinogenic, and mutagenic/teratogenic for microbes and fish species. Exposure of skin to tannins may cause discoloration, local irritation, eczema or even death due to absorption. Most of the textile units in India are situated at Tirupur, Ludiyana and Surat. In Tirupur alone there are 712 dyeing and bleaching industries that generate 87,000 m3/d of wastewater. Studies carried out on nearby aquatic systems have revealed that the ground water around Tirupur area is contaminated with substances capable of inducing DNA damage in human cells [1]. In order to avoid further deterioration, pollution control board of Tamil Nadu, India has enforced zero discharge concepts within a defined timeframe throughout the state.

The azo and reactive dyes are widely used due to their variety of color gamut, brightness of shade, flexible application procedure, and better color fastness of the resultant dyeing. Mineralization of CI Reactive Blue 221 and CI acid orange 10, basic phenolic molecules and purification of textile and tannery effluents was reported in the present manuscript. The CI Reactive Blue 221 belongs to the group of hetero bi-functional reactive dyes with complex aromatic structure consisting of mono chloro triazine and sulphato ethyl sulphone derivatives as functional groups. During the application process, part of the dye is hydrolyzed and remains in aqueous solution due to its poor reactivity with fiber. Depending on the reaction conditions, 20-40 % of the dye derivatives invariably remain in aqueous phase. It was reported that the wastewater from vinyl sulphone reactive dye bath is potentially toxic to anaerobic bacteria [2]. Another dye, extensively used in the textile industry and considered to be a potential health hazard is CI Acid orange 10. The reductive cleavage of azo bond leads to the formation of aniline which inhibits the microbial activity and affects anaerobic biomass in aqueous solutions. Long exposure of CI Acid orange 10 may lead to irritation to the respiratory and gastrointestinal tracts. The tannery wastewater contains high COD and dissolved solids like sodium chloride, sulfides, sulfate, ammonia, chromium and organic substances like fats, proteins, tannins and dyes. Tannins are extensively used to convert hides and skins in to leather. Skins are tanned to achieve the desired flexibility in dried condition and to protect from microbial attack or hydrolysis when moist. Extensive exposure of skin to hydroxy phenols may cause discoloration, local irritation, eczema or even death due to absorption.

Generally, the existing physical, chemical and biological methods are inadequate for the effective removal of pollutants from dye-house and tannery effluents. It is very difficult to oxidize dyestuffs with complex organic structure especially at low concentrations by conventional oxidation treatment [3]. Similarly biological

treatment is ineffective as 53% of 87 colors are non-biodegradable. Most of the commercial dyes are toxic to the microorganisms and result in huge volume of biological sludge. The detoxification of the effluents containing CI Reactive blue 221 was achieved only to the extent of 4.1% by microbiological enzymatic treatment [4]. Though the decolorization of Reactive Blue 221 using fungal laccases was reported, the complete degradation of dye could not be achieved [5]. The tannery effluents mainly contain high concentration of chloride and complex tannin compounds. The inclusion of such chemicals has rendered the biological treatment of tannery wastewater difficult and more complicated due to their low biodegradability. The tannin materials inhibit the activity of microorganism in activated sludge and aerobic lagoon treatment systems [6]. Precisely, the biological methods are limited due to the following drawbacks i) requirement of large area, ii) generation of voluminous sludge and iii) incomplete organic removal.

In recent years, electrochemical techniques are being tried both for the removal of effluents containing dyes and for the treatment of tannery effluents. The degradation of organic dyes in the presence of various metals and metal-oxide coated electrodes was studied by various researchers [7-11]. The effluent containing different dyes was successfully treated with 100% decolorization and 70% COD removal using carbon based electrode material [12]. Electrooxidation was observed to be very effective for the removal of Procion black 5B [13] whereas electrocoagulation process was observed to be effective for the decolorization of acid orange II [14] and purification of textile wastewater [15]. The COD was totally removed by adopting combination of electrocoagulation and electro-oxidation processes wherein granulated activated carbon packed between stainless steel electrodes was used as electrodes [16]. The activated carbon fiber electrode was tried to remove different dyes [17-18]. Roessler et al., [19] have tried granulated graphite as cathode for the reduction of vat dyes. Though the carbon electrodes are proved to be effective, their utility in industrial practice was poor due to low mechanical strength. Alternatively, boron doped diamond electrodes were tried [20-21] and found to be very effective. However, their usage at an industrial scale is yet to be ascertained. The life of the electrodes was improved by incorporating surface modifications [22].

The present work deals with the removal of pollutants from tannery and textile effluents by electro-coagulation/flotation and electro-oxidation techniques. Also the mineralization of CI acid orange 10, CI reactive blue 221 and tannin related molecules such as resorcinol, pyrogallol, catechol and phloroglucinol was discussed.

DEGRADATION OF CI REACTIVE BLUE 221

### 1. Effect of supporting electrolyte and electrode material

The effect of electrolytes viz. NaCl, Na_2SO_4 and $NaNO_3$ on the oxidation of CI Reactive Blue 221 was studied in the presence of both $IrO_2/TaO_2/RuO_2$ coated titanium and graphite electrodes. The initial concentration of the dye and electrolyte were maintained at 200 mg L^{-1} and 0.01M respectively. The results shown in Fig. 1 indicate that the graphite electrode is very effective. The COD removal of 98 % was achieved using graphite where as it is hardly 44 % with $IrO_2/TaO_2/RuO_2$ coated titanium. The results also indicate that the COD removal is better in the presence of NaCl compared to Na_2SO_4 and $NaNO_3$. This may be attributed to the catalytic action of chloride ion [23]. During the electrolysis, evolution of Cl_2 in the presence of NaCl and $S_2O_8^{2-}$ in the presence of Na_2SO_4 is expected as a secondary electrochemical reaction. The anodic discharge of chlorine and peroxodisulfate can be represented as

$$2Cl^- \longrightarrow Cl_2 + 2e^- \tag{1}$$
$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^- \tag{2}$$
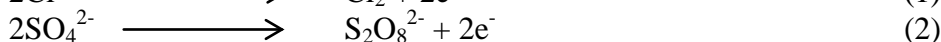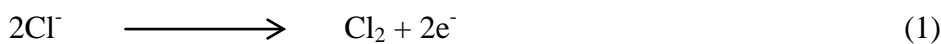
The simultaneous Cl- measurements revealed the depletion of chloride ion to the extent of 60% and 25% in the presence of graphite and $IrO_2/TaO_2/RuO_2$ coated titanium electrode respectively. This clearly suggests the liberation of Cl_2 during the electrolysis. At 25 °C and normal atmospheric pressure, the chlorine gas thus liberated from anode can dissolve in water to the extent of 6.413 g L^{-1}[25]. If its solubility exceeds locally on the surface of the electrode, then the chlorine bubbles may form and escape from aqueous phase. Since the experiments were conducted around neutral pH, entire chlorine will be in the form of HOCl and OCl^- species. The evolution of oxygen from anode can be represented as

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{3}$$
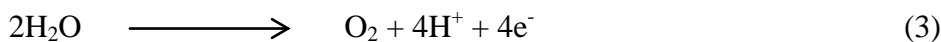
The cathodic conversion of molecular oxygen to H_2O_2 can also be expected which can be represented as

$$4H_2O + 2O_2 + 4e^- \longrightarrow 2H_2O_2 + 4OH^- \tag{4}$$
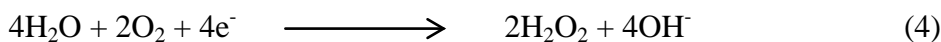
Production of ozone also is expected when the anode potential exceeds beyond 1.51V

$$H_2O + O_2 \longrightarrow O_3 + 2H^+ + 2e^- \qquad (5)$$
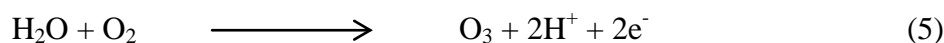
Lidia et al., [11] suggested that various oxidants such as O_2, O_3, H_2O_2 and Cl_2 and free radicals such as $Cl^\cdot$, $ClO^\cdot$ and $OH^\cdot$ are generated during electrolysis. Thus, the aqueous solution contains a cocktail of oxidants.
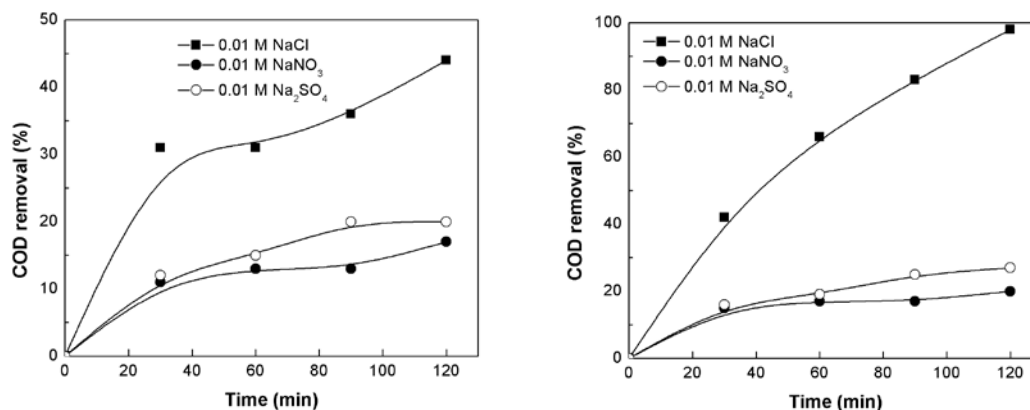

Fig. 1 Effect of electrolyte and electrode material on COD removal. Current density: 15.76 mA cm^{-2}; Initial dye concentration: 200 mg L^{-1}. Left: IrO$_2$/TaO$_2$/RuO$_2$ coated titanium, right: graphite. Reproduced from Ref. [**].

2. Effect of electrolyte concentration and electrode material
Since the degradation of CI Reactive Blue 221 was found to be effective in the presence of NaCl, further experiments were conducted at various NaCl concentrations using graphite and IrO$_2$/TaO$_2$/RuO$_2$ coated titanium anode at constant applied current densities 15.76 mA cm^{-2} and 16.20 mA cm^{-2}, respectively and the results are presented in Fig. 2. It clearly indicates that the dye degradation is enhanced by increasing the NaCl concentration and the complete removal of TOC was achieved using graphite anode at higher NaCl concentration of 0.1 M. By increasing the NaCl concentration, the degradation rate of CI Reactive Blue 221 was found to increase. This could be explained due to increased generation of active chlorine at higher NaCl concentrations. The degradation results of of CI reactive Blue 221 using IrO$_2$/TaO$_2$/RuO$_2$ coated titanium anode showed that the mineralization of the dye is lower compared to graphite electrode. The low degradation of organics in the presence of IrO$_2$/TaO$_2$/RuO$_2$ electrodes may be ascribed to the competition between the oxidation of organics and oxygen evolution reaction at the anode surface.
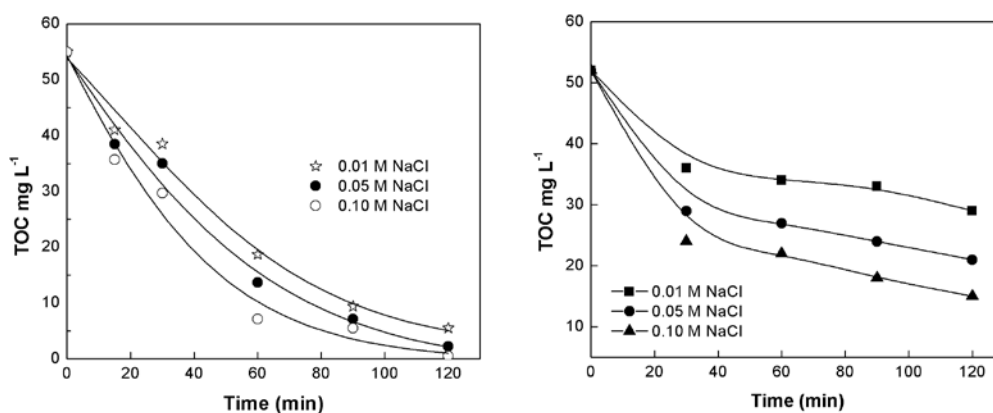
Fig. 2 Effect of electrolyte concentrations on TOC. Current density: 15.76 mA cm^{-2} for graphite and 16.20 mA cm^{-2} for IrO$_2$/TaO$_2$/RuO$_2$ coated Ti; Initial dye concentration: 200 mg L^{-1}. Left: IrO$_2$/TaO$_2$/RuO$_2$ coated titanium, right: graphite. Reproduced from Ref. [**].
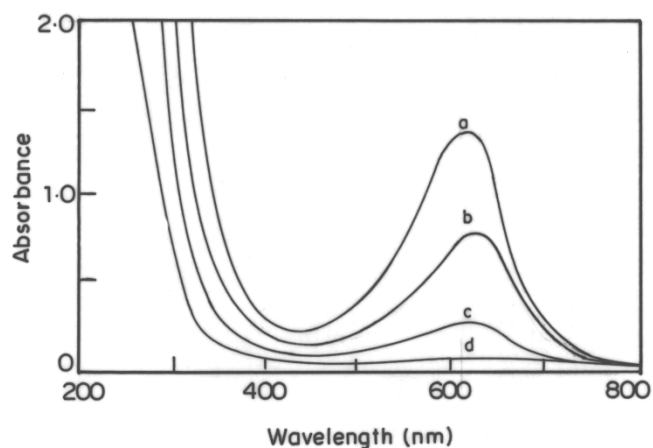

Fig. 3 Changes in UV-Visible spectra of CI Reactive Blue 221 during electrooxidation. Electrode: IrO$_2$/TaO$_2$/RuO$_2$ coated titanium; current density: 8.10 mA cm^{-2}; curve: a) 0 min; b) 5 min; c) 10 min; d) 15 min. Reproduced from Ref. [**].

The decolorization of the CI Reactive Blue 221 in the presence of both IrO$_2$/TaO$_2$/RuO$_2$ coated Ti and graphite was followed using UV-Visible spectrophotometer and the results are shown in Fig. 3. From the results it is
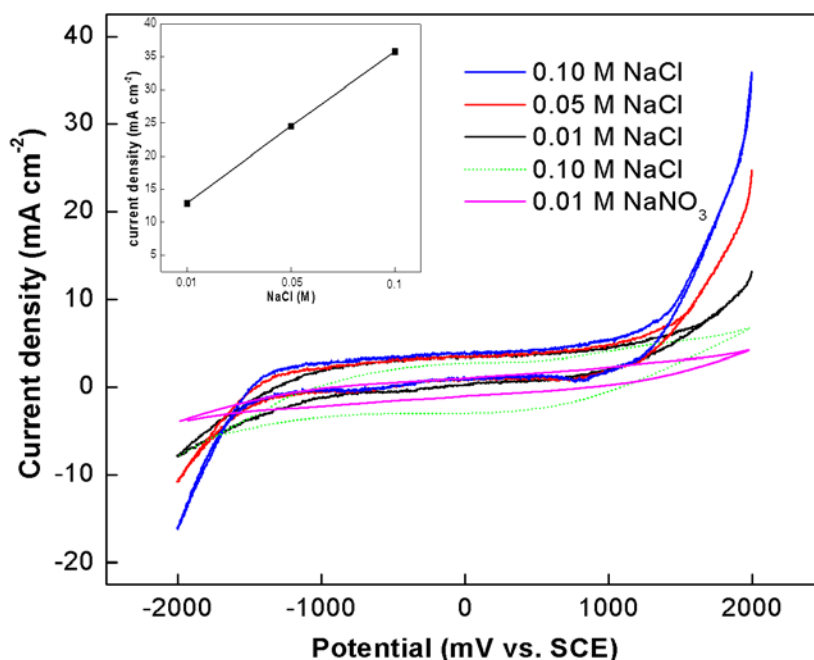
Fig. 4 Cyclic voltammograms recorded on graphite (continuous line) and $IrO_2/TaO_2/RuO_2$ coated Ti (dotted line) working electrodes at neutral pH; initial concentration of the dye: 200 mg L^{-1} (scan rate = 50 mV s^{-1}). Inset: maximum anodic peak current with varying NaCl concentrations in graphite electrode system. Reproduced from Ref. [**].

apparent that the total decolorization of CI Reactive Blue 221 was occurred after 2 hours of electrolysis in the presence of graphite electrode where as it happened within 15 minutes in the presence of $IrO_2/TaO_2/RuO_2$ coated Ti anode. In the latter case, though the aqueous solution was totally decolorized with in a shorter duration of 15 minutes, the decrease in TOC was very marginal. Thus it is evident that only the chromophoric structure of dye molecule was destroyed while using $IrO_2/TaO_2/RuO_2$ coated titanium. However, the decolorization and degradation was observed to be simultaneous in the case of graphite electrode. From the above, it is apparent that the electrode material strongly influences both the selectivity and the efficiency of the oxidation process. In the case of non-active electrodes like graphite, the complete degradation of organics is mediated by hydroxyl/oxy chlorides radicals where as oxidative reaction via the surface redox couple (MO_{x+1}/MO_x) is more selective than the reactions involving hydroxyl radicals on the surface of $IrO_2/TaO_2/RuO_2$ coated titanium electrode.
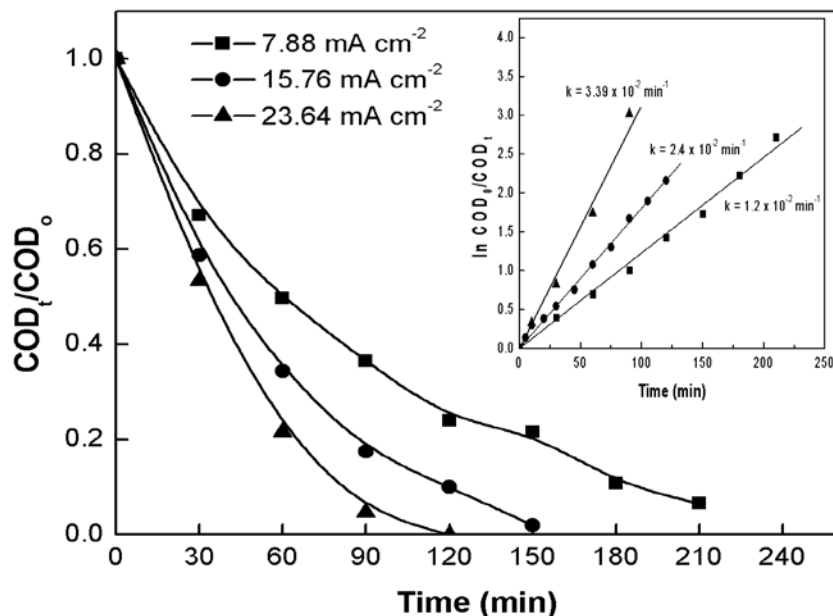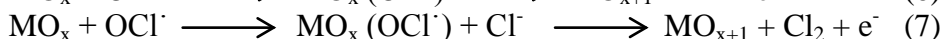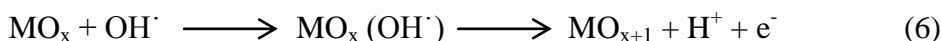
Fig. 5 Kinetics of degradation of CI Reactive Blue 221 in the presence of graphite anode. Initial concentration: 200 mg L^{-1}; electrolyte: 0.01 M NaCl. Reproduced from Ref. [**].

To investigate the evolution of chlorine during the electrooxidation process, a series of cyclic voltammetric experiments were carried out using graphite as well as IrO$_2$/TaO$_2$/RuO$_2$ coated titanium. Fig. 4 shows typical cyclic voltammograms obtained in aqueous solutions of the dye with supporting electrolytes of NaCl and NaNO$_3$. It is apparent that the anodic peak current for graphite electrode (continious line) increases to 0.873 A from 0.311 A and shifts (0.80 V) toward less positive by increasing the concentration of NaCl. The prominent peak before 1.5 V is due to the chlorine evolution. No such evolution peak was seen while using NaNO$_3$ as supporting electrolyte. This confirms the evolution of chlorine in chloride medium. The inset of Fig. 4 clearly shows the linear increase of anodic peak current with concentration of NaCl. This observation is consistent with the earlier reports [26]. It is noteworthy that the reverse peak corresponding to the reduction of Cl$_2$ produced during the oxidation sweep was not observed. This confirms that the chlorine might have been diffused into the bulk solution rather than reducing to Cl$^-$. In the case of IrO$_2$/TaO$_2$/RuO$_2$ coated titanium electrode system (dotted line), chlorine evolution even at a higher concentration of 0.1 M NaCl is comparatively insignificant. Conclusively, the effective degradation of

dye molecules could be attributed to chlorine-based oxidants.

3. Effect of applied current density

Effect of applied current density on the oxidation of CI Reactive Blue 221 was investigated by varying the current density from 7.88 mA cm^{-2} to 23.64 mA cm^{-2}. Working solution containing 200 mg L^{-1} of dye and 0.01M NaCl as supporting electrolyte at neutral pH was taken and subjected to electrooxidation using graphite electrode. The results are shown in Fig. 5. It could be seen that the rate of COD removal increases with applied current density and the complete degradation was achieved at higher applied current density of 23.64 mA cm^{-2} within 120 minutes of electrolysis time, whereas it takes more than 210 minutes to reach the 100 % degradation at lower applied current density value of 7.88 mA cm^{-2}. It could be attributed to the increased rate of oxidants generation with current density. The experimental results were evaluated to obtain the order of the reaction. The results presented in Fig. 5 were found to fit in pseudo-first order rate equation with R^2 values of above 0.98. The rate constants calculated from linear regression are 3.39×10^{-2}, 2.4×10^{-2} and 1.2×10^{-2} min^{-1} for 23.64, 15.76 and 7.88 mA cm^{-2}, respectively. It may be noted that by increasing the current density from 7.88 to 15.76 mA cm^{-2}, the rate of organics degradation was doubled. The oxidation of organics in the presence of "active" electrodes like IrO$_2$/TaO$_2$/RuO$_2$ coated titanium was attributed to the formation of "higher oxides" [27] via adsorption of hydroxyl/oxy chloride radical which can be represented as

$$MO_x + OH^{\cdot} \longrightarrow MO_x(OH^{\cdot}) \longrightarrow MO_{x+1} + H^+ + e^- \qquad (6)$$
$$MO_x + OCl^- \longrightarrow MO_x(OCl^-) + Cl^- \longrightarrow MO_{x+1} + Cl_2 + e^- \quad (7)$$

The organics are selectively oxidized in the presence of chemisorbed active oxygen whereas they will be completely mineralized to CO$_2$ and H$_2$O in the presence of physisorbed active oxygen [28]. The efficient removal of organics in the presence of graphite electrode may be attributed to its non-active nature and effective generation of HOCl which is stronger oxidant compared to oxygen. Serikava et al [23] have observed strong catalytic effect of chloride ion in the conversion of organic pollutants to innocuous CO$_2$ and H$_2$O. The instantaneous current efficiency (ICE), electrochemical oxidisability index (EOI) and the specific energy consumption (E*) were calculated using the following relationships [29].

$$ICE(\%) = \frac{COD_t - COD_{t+\Delta t}}{8I\Delta t} FV \times 100 \qquad (8)$$

where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demands at times t and $t+\Delta t$ (in g O2 L^{-1}), respectively, I is current (A), F is Faraday constant (96,487 C mol^{-1}), V denotes the volume of electrolyte (L) and 8 is the oxygen equivalent mass (g eq^{-1}), Δt is change in time seconds.

$$EOI = \frac{\int_0^\tau (ICE)dt}{\tau} \qquad (9)$$

where τ is electrolysis time when the ICE is zero.

$$E^* = \frac{IV_A t}{V(\Delta COD)3600} \quad \text{kWh g}^{-1}\text{COD} \qquad (10)$$

V_A is voltage in V, I is applied current in A, ΔCOD is difference in COD values in g L^{-1} between the time interval and t is the electrooxidation time in seconds.

Table 1. The ICE, EOI and power consumption in the presence of different electrodes and current densities.

Anode material	C.D. (mA cm^{-2})	Electrolyte NaCl concentration (M)	ICE[a] (%)	EOI	E*[a] (K Wh g^{-1} COD)
Titanium	8.10	0.01	4.0	0.0591	0.715
	16.20	0.01	5.6	0.0529	1.120
	24.31	0.01	6.5	0.0513	1.924
Graphite	7.88	0.01	8.5	0.0761	0.3622
	15.76	0.01	9.9	0.1633	0.4105
	23.64	0.01	10.09	0.1550	0.5214

[a] Values at time 120 minutes of electrooxidation. Reproduced from Ref. [**].

The ICE, EOI and E* were calculated and the results were shown in Table 1. Among the two electrode materials, graphite has exhibited slightly better current efficiency compared to IrO$_2$/TaO$_2$/RuO$_2$ coated titanium electrode. Depending on the current density, The ICE values were observed to vary from 4.0-6.5% and 8.5-10.5% with IrO$_2$/TaO$_2$/RuO$_2$ coated titanium and graphite electrodes, respectively. It is apparent that the electrooxidation at lower current density is advantageous due to less power consumption.
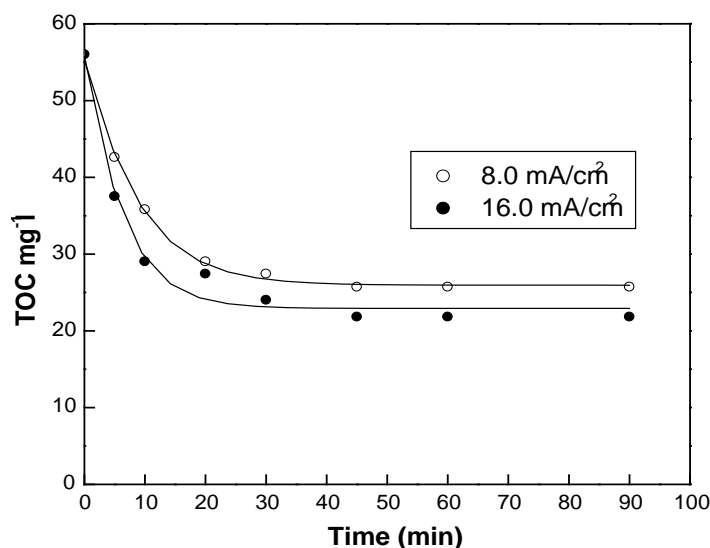
Fig. 6 Effect of current density on TOC reduction with time during electrocoagulation. Initial concentration of dye 100 mg L^{-1}; electrolyte 0.017 M NaCl. Reproduced from Ref. [**].

4. Reaction pathway of CI Reactive Blue 221 degradation

Among the two electrodes employed, only graphite electrode resulted with complete degradation of the dye. Hence, the dye metabolites during oxidation were identified using GC-MS. In the first step, –N=N–, C–N and O–Cu bonds are cleaved and the fragments are ultimately converted as CO_2 and water. The interesting point here is that triazine (atrazine) was completely mineralized without forming the refractory cyanuric acid. Also, it is noteworthy that formation of organic acids is consistent with the fact that the electrolyte pH was intended to shift towards slightly acidic region during the course of the reaction process. The organically bound nitrogen was measured as total kjeldahl nitrogen before and after the electrooxidation process by macro-kjeldal method (4500-N_{org}) as per the standard methods [30]. The kjeldahl nitrogen of 4.0 mg L^{-1} was found to be totally removed at the end of the process. This clearly indicates the complete mineralization of dye molecule.

DEGRADATION OF ACID ORANGE 10

1. Removal by Electrocoagulation

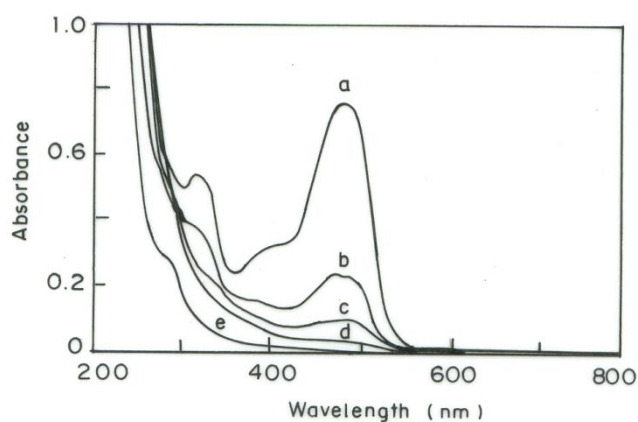Removal of CI acid orange 10 using steel as electrode material was studied at two
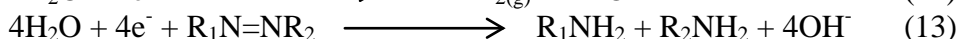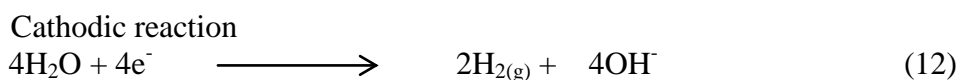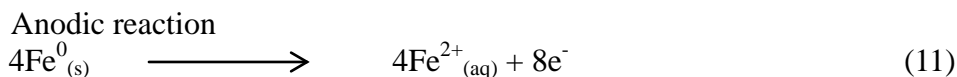
Fig. 7 UV–Vis spectra of CI Acid orange 10 during the process of electrocoagulation: (a) initial, (b) after 5 min, (c) after 10 min, (d) after 20 min and (e) after 60 min. Reproduced from Ref. [**].

different current densities (15 mA/cm^2, 30 mA/cm^2) and the results are presented in Fig. 6. The initial TOC was brought down to below 22 ppm from its initial value of 57 ppm. Around 60% of TOC removal was achieved within 20 minutes and there was no change thereafter. It may be noted that Fe^{2+} ions released from anode (anodic dissolution) in turn form iron oxy-hydroxide, which is a good adsorbent and coagulant. The TOC removal can be either due to the adsorption of dye molecules on iron oxy-hydroxide or due to interaction of Fe ions with dye molecule forming insoluble metal-dye complex. If the Acid orange10 as a molecule is adsorbing on the surface of iron oxy-hydroxide then the removal should be proportional to the amount of iron oxy-hydroxide produced.   In other words, dye could be totally removed by extending the duration of electrocoagulation. However the TOC measurements clearly indicate that part of the dye was left out in aqueous phase.

During the course of experimentation, the dye solutions were collected at different time intervals and their UV-Visible spectra were recorded. The UV-Visible spectra of the samples drawn at 300 s, 600 s, 1200 s and 3600 s along with original spectrum of acid orange10 were presented in Fig. 7. The acid orange10 exhibited two absorption bands at 485 nm and 325 nm. The characteristic band at 485 nm could be assigned to the n-π* transition of –N=N– group [32]. The weak band at 325nm could be attributed to the π-π* transition related to the aromatic ring bonded to the –N=N– group in the dye molecule. It is apparent that the intensity of characteristic band (485 nm) of acid orange 10 was found to diminish gradually

during the experiment and disappeared totally after 20 minutes. The disappearance of the bands indicates the effective destruction of the chromophore. From the UV-Visible spectra, it could be concluded that the dye molecule undergoes degradation in the presence of iron electrodes. The chromatogram of the degradation products indicated the presence of aniline and 1-amino-2-naphthol-6,8-disulphonic acid.

Nam et al [33] have studied the reduction of different azo dyes using iron granules and concluded that the decolorization of azo dyes was due to the reduction of the azo groups. Linear and cyclic sweep voltammetry studies [34] have also revealed that the reduction of azo group leads to cleavage of azo linkage to produce amino compounds as the final products without stopping at hydrazo stage (–NH–NH–). The electrons generated as a result of Fe oxidation are utilized for the reduction of Acid orange 10. Four electrons are required per azo group for the complete reduction to the corresponding amine. It is well known that the electron withdrawing nature of the azo linkages obstructs the susceptibility of the dye molecules to oxidative reactions.   In contrast reductive cleavage of azo linkages is favoured under anaerobic conditions or reducing environment. Thus in the presence of iron electrodes, the azo dyes are converted to usually colorless but potentially harmful aromatic amines. These amines are generally not amenable to degradation under anaerobic or reducing conditions. It was established that the cathodic de-colorization of azo dyes lowers the absorbance of highly colored effluents of textile industry. In fact, some researchers [35] have suggested two-stage treatment wherein azo dyes are anaerobically degraded to corresponding amines in the first stage and the amines thus produced are further degraded by aerobic treatment in the second stage. The incomplete removal of COD even under extended duration of electrocoagulation can be interpreted due to the poor interaction of aniline with iron oxy-hydroxide. Whereas 1-amino-2-naphthol-6,8-disulfonic acid is precipitated from the aqueous phase as insoluble metal complex. The following electrochemical reactions are proposed to describe the decolorization and reductive cleavage of Acid orange10.

Anodic reaction

$$4Fe^0_{(s)} \longrightarrow 4Fe^{2+}_{(aq)} + 8e^- \qquad (11)$$

Cathodic reaction

$$4H_2O + 4e^- \longrightarrow 2H_{2(g)} + 4OH^- \qquad (12)$$
$$4H_2O + 4e^- + R_1N{=}NR_2 \longrightarrow R_1NH_2 + R_2NH_2 + 4OH^- \qquad (13)$$

Overall reaction

$$4Fe^0_{(s)} \ + \ 8H_2O \ + \ R_1N{=}NR_2 \ \longrightarrow$$
$$R_1NH_2 \ + \ R_2NH_2 \ + \ 4Fe(OH)_{2(s)} \ + \ 2H_{2(g)} \qquad (14)$$
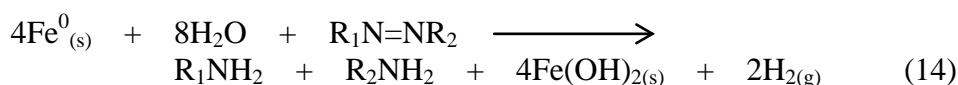
The Acid orange 10 is expected to reduce further in the presence of $Fe(OH)_2$ according to the following equation

$$4Fe(OH)_2 \ + \ 4H_2O \ + \ R_1N{=}NR_2 \ \longrightarrow$$
$$R_1NH_2 \ + \ R_2NH_2 \ + \ 4Fe(OH)_{3(s)} \qquad (15)$$
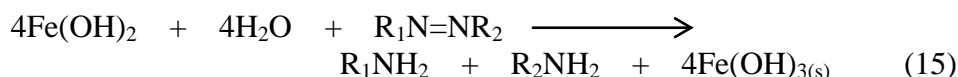
Where $R_1N{=}NR_2$ is Acid orange 10, R_1 is benzene and R_2 is 2-naphthol-6,8-disulfonic acid.

Solution pH is one of the important factors that affect the performance of electrochemical process. Hence experiments were conducted to study the effect of pH on the removal of CI Acid orange 10. Since pH was found to increase during electrocoagulation, dilute acid was used to adjust the pH. The experiment was stopped for every 60 s and the pH of the solution was adjusted to its initial pH. From the results presented in Fig. 8, it is apparent the TOC removal was optimum around pH 9.0. The results published by earlier workers [14,15] on the removal of Acid orange II and on textile wastewater were also incorporated in Fig. 8. In general it is evident that better removal of dyes was observed between pH 6.0 and 9.0. The Fe ions released from anode form respective oxy-hydroxy species such as $FeOH^+$, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4^-$ and $FeO(OH)$. The activity of $Fe(OH)_2$, $Fe(OH)_3$ species will be predominant between pH 7.0 and 8.5. The metal hydroxy species have pronounced tendency to interact with hydroxyl groups of adjacent molecules and forms coagulum. Thus the maximum removal of TOC between pH 6 and 9 could be attributed to the interaction of 1-amino-2-naphthol-6,8-disulfonic acid which resulted from the cleavage of azo link of CI Acid orange 10 with iron oxy-hydroxide and $Fe(OH)_2$ precipitate. The interaction between 1-amino-2-naphthol-6,8-disulfonic acid and iron oxy-hydroxide could be represented as

$$={Fe(OH)} \ + \ HO\text{-}L \ \longrightarrow \ FeOL \ + \ H_2O \qquad (16)$$
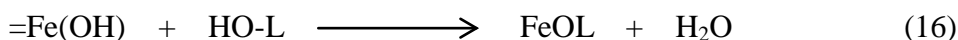
The interaction between dye molecule and iron oxy hydroxide could be due to the formation of inner sphere complex between metal ion and O and N atoms of the molecule. However the interaction of aniline that resulted from the cleavage of CI Acid orange 10 with oxy-hydroxide of iron was observed to be poor.

In spite of prolonged duration of experimentation, the complete removal of dye

could not be achieved. Generally, O, N and S attached to adjacent carbon atoms of organic molecules are known to facilitate co-ordinate covalent bond with transitional metal ions. In the case of 1-amino-2-naphthol-6,8-disulfonic acid, O and N atoms attached to adjacent carbon atoms can facilitate co-ordinate covalent bond with Fe ions to form insoluble organo-metal complex. The precipitate formed during electrocoagulation was further analyzed by FT-IR spectroscopic technique and zeta potential measurement (Data not included) [31]. The data clearly indicates interaction between the OH groups of iron oxy-hydroxide and 1-amino-2-naphthol-6,8-disulphonic acid.
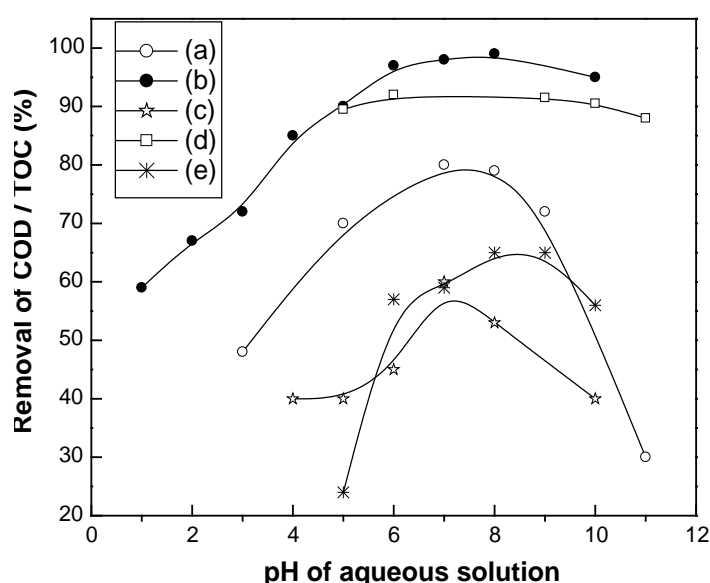

Fig. 8 Effect of pH on the removal of dyes from wastewater. (a) Mixture of dye solutions (Kobya et al. 2003), (b) Acid orange II (Daneshvar et al. 2003), (c) Mixture of textile wastewater (Lin et al. 1996), (d) Acid orange II (Mollah et al. 2004), (e) C.I. Acid orange 10 (removal of TOC %). Reproduced from Ref. [**].

2. Removal by Electro-oxidation Method

Oxidation of Acid orange10 was studied separately by using graphite and triple oxide coated titanium electrodes and the results are presented in Fig. 9. From the results, it is apparent that the COD removal was better with graphite electrode compared to triple oxide coated titanium electrode. The TOC was removed to the extent of 96% in the presence of graphite electrode whereas it is only 60% in the presence of triple oxide coated titanium electrode. During electro-oxidation, the
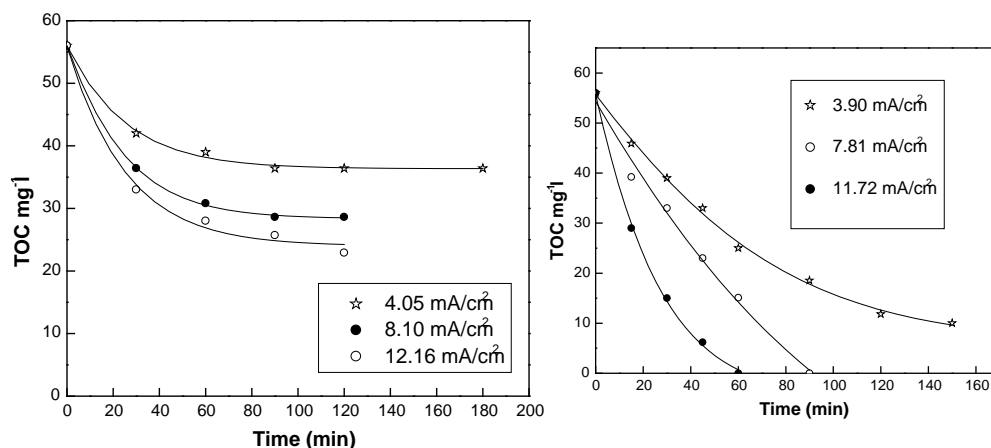
Fig. 9 Kinetics of TOC removal at different current densities during electrooxidation with electrolyte 0.017 M NaCl using (a) $IrO_2/TaO_2/RuO_2$ coated Ti, initial concentration of dye 100 mg L^{-1}; (b) graphite electrode, initial concentration of dye 100 mg L^{-1}. Reproduced from Ref. [**].

concentration of chloride ion was decreased to 367 ppm from its initial value of 554 ppm. Depending on the pH, the active chlorine formed can form hypochlorous acid hypochlorite ion and chlorate. Also, different oxidizing radicals involving chlorine and oxygen are formed during electro-oxidation. Though these radicals are short lived, they can oxidize even refractive organic molecules. The anode type and its potential, govern the formation of different oxidizing species. The oxidizing agent generated in-situ are responsible for the complete oxidation of dye molecules.

TREATMENT OF TEXTILE EFFLUENT BY ELECTROCHEMICAL TECHNIQUES

The raw wastewater collected from Tirupur textile cluster was analyzed and its characteristics were shown in Table 2. The textile wastewater was initially treated by electrocoagulation to remove the suspended solids. After the electrocoagulation, the wastewater was further treated by electrooxidation for COD removal. Mild steel as anode was found to be effective for coagulation of suspended solids. For electrooxidation, graphite and $IrO_2/TaO_2/RuO_2$ coated titanium were used as electrodes. The efficiency of these electrode materials was evaluated in terms of chemical oxygen demand (COD) removal. From the data (Table 4.1) it is evident

that the wastewater contains 1500 mg L^{-1} of suspended solids with a mean size of 6.21 μm and 530 mg L^{-1} of COD.

Table 2. Physico-chemical characteristics of the raw effluent and electrochemically processed samples.

Parameter	Raw effluent	After electrocoagulation[*]	After electrooxidation[**]
Colour	Dirty Green	Pale yellow	Colourless
pH	8.04	8.64	7.91
Conductivity (μmhos cm^{-1})	16300	15890	15270
BOD_5 (mg L^{-1})	175	80	5.0
COD (mg L^{-1})	530.7	246.1	22.3
Total Solids (g L^{-1})	10.75	9.52	9.44
Total Dissolved Solids (g L^{-1})	9.19	9.08	9.01
Suspended solids (SS) (g L^{-1})	1.5	0.04	0.03
Total Hardness as $CaCO_3$ (mg L^{-1})	640	420	320
Ca^{2+} (mg L^{-1})	40	40	40
Mg^{2+} (mg L^{-1})	131	78	53
Total alkalinity as $CaCO_3$ (mg L^{-1})	12450	920	885
Chloride (mg L^{-1})	5317	5069	4431
Sulphate (mg L^{-1})	360	360	416
TKN (mg L^{-1})	11	BDL	BDL
Mean size of SS (μm)	6.21	-	-

[*] electrocoagulation time: 10 min, current density: 25 mA cm^{-2} and electrode: mild steel.
[**] electrooxidation time: 150 min, current density: 5.446 mA cm^{-2} and electrode: graphite rod. Reproduced from Ref. [**].

1. Electrocoagulation
The wastewater was initially subjected to electrocoagulation using mild steel and aluminum as electrodes separately to remove the suspended solids. The results incorporated in Table 2 indicate that around 97% of suspended solids and 54% of COD were eliminated during electrocoagulation. The removal of COD is observed to be slightly better in the presence of mild steel (54%) compared to aluminum electrodes (51%). It is well known that the oxy-hydroxides of Al^{3+}/ Fe^{2+} ions formed during the process act as coagulant. Sufficient quantity of effluent was processed by electrocoagulation using steel electrode and the sample was subjected to filtration. The filtrate was used for further electrooxidation studies.

2. Electro-oxidation
The degradation of organics in the presence of different anode materials and

current densities was studied and the results were presented in Fig. 10. During the process, the concentration of Cl⁻ was decreased from 5069 mg L^{-1} to 4395 mg L^{-1} indicating the discharge of chlorine at the anode. The COD removal in the presence of graphite sheet, graphite rod and $RuO_2/IrO_2/TaO_2$ coated titanium were found to be 93.3%, 90.9% and 54.5% respectively. Though the extent of COD removal is different, complete decolorisation of effluent was achieved within 5 minutes irrespective of electrode material. During the process, oxidants like hydrogen peroxide and hypochlorite are generated and their concentration will be gradually built-up with time. While simple organic molecules can degrade under mild oxidizing environment, stable and refractory molecules need high concentration of oxidant.
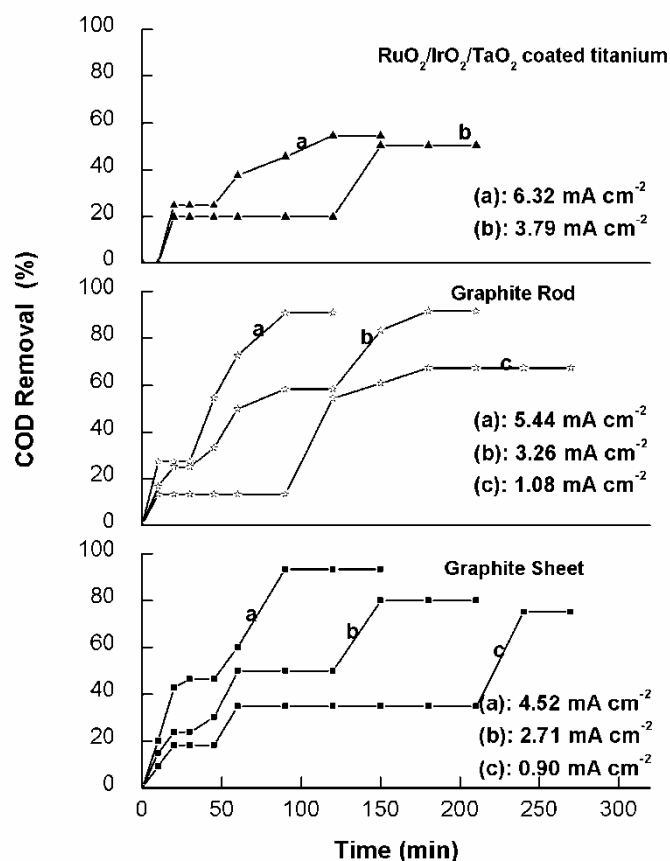

Fig. 10 Effects of current density and electrode material on COD removal. Reproduced from Ref. [**].

Two different mechanisms that are direct oxidation on the surface of the electrode and indirect oxidation mediated by the oxidizing agent generated in situ were suggested for electrochemical oxidation of organic molecules. Though the hydroxyl radicals act as mediated oxidants [35], they are highly reactive and oxidation of organics is expected close to the anode surface. These hydroxyl radicals are generated according to the following reactions

$$2H_2O \longrightarrow 2OH^{\cdot} + 2H^{+} + 2e^{-} \qquad (17)$$
$$OH^{-} \longrightarrow OH^{\cdot} + e^{-} \qquad (18)$$
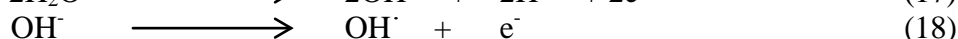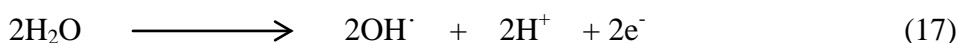
The oxygen evolution from physically adsorbed OH• could be represented as

$$M(OH^{\cdot}) \longrightarrow 0.5O_2 + M + H^{+} + e^{-} \qquad (19)$$

In the presence of noble oxide catalytic anode such as $RuO_2/IrO_2/TaO_2$ coated titanium, the oxidation of the pollutant was attributed to the formation of higher oxides [7] via adsorption of hydroxyl radical and its interaction with the oxygen already present in the oxide lattice with the possible transition to higher oxide.

$$MO_x + OH^{\cdot} \longrightarrow MO_x(OH^{\cdot})$$
$$\longrightarrow MO_{x+1} + H^{+} + e^{-} \qquad (20)$$
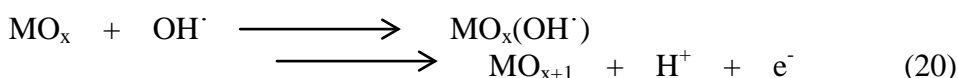
During the electrooxidation, the sulfate content was found to increase from its original value of 360 ppm to 416 ppm. It is known that most of the dyes are sulfonated to increase their solubility in water. During the oxidation process, the sulfonate groups attached to the dyes will be released as a result of oxidation of dyes. The sulfonates are further oxidized to sulfates during electrooxidation. Thus the excess sulfate in aqueous solution originates actually from the breakdown of dye molecules during oxidation.

REMOVAL OF TANNINS AND POLYHYDROXY PHENOL MOLECULES

1. Removal of commercial tannins

Aqueous solutions of six different synthetic tannins generally used in tanning of skins and hides were taken and subjected to electro-flotation and electro-oxidation. Three different materials viz aluminum, iron and triple oxide ($TaO_2/RuO_2/IrO_2$) coated titanium were used as anodes. Constant current of 7.5 A (47 mA cm^{-2}) was applied over a period of 900 seconds and the resultant aqueous solutions were analyzed for COD. The results thus obtained along with the initial COD of the respective solutions are shown in Table 3.

Table 3. Effect of anodic material on the removal of commercial tannins.

Tannin	Manufacturer	Initial COD (ppm)	COD removal (%) (after electrolytic treatment)		
			Al	Fe	Ti
Syntan GF	Bayer Chemicals AG	704	94.3	95.7	2.6
Syntan GDC	Bayer Chemicals AG	1055	75.7	90.0	2.3
Syntan RT	Bayer Chemicals AG	1339	74.7	88.3	0.4
Syntan Relugan RR	BASF AG	596	99.5	81.7	2.7
Syntan Relugan RE	BASF AG	763	74.3	96.5	0.5
Syntan Relugan RF	BASF AG	803	86.3	89.8	0.4

Conditions: current density: 47mA cm^{-2}, treatment duration: 900 s, tannin concentration: 2000 ppm, anode: Fe, cathode: Fe. Reproduced from Ref. [**].

From the results, it is evident that 75 to 99% of COD could be removed by using either aluminum or iron as anode. While the removal of COD was better by using iron and aluminum electrodes it is negligible in the presence of triple oxide ($TaO_2/RuO_2/IrO_2$) coated titanium electrodes. The poor removal of tannins by electro-oxidation may be attributed due to refractive nature of the molecules and insufficient oxidation time. The power consumption was calculated to be 1.9 wh.g-1 COD removal. Thus it is evident that the commercial tannins could be effectively removed from tannery wastewater by electroflotation using aluminum or iron as electrodes.

2. Removal of poly-hydroxy phenols
Since tannins are polymers of hydroxy phenols, pure compounds of resorcinol, catechol, pyrogallol and phloroglucinol were taken for further studies. Aqueous solutions of these compounds with known concentration were processed by using iron and triple oxide coated titanium electrodes. Fixed quantity of phenol solution was taken in to the electrochemical cell comprising iron electrodes. The pH of the solution was adjusted to a desired value using either HCl or NaOH. Fixed current density of 47 mA cm^{-2} was applied for a period of 900 seconds. Maximum removal of hydroxy phenols was observed in the pH range 8.0 to 9.0. The results presented in Fig. 11 show that the maximum removal of COD is taking place in the presence of $Fe(OH)_2$, $Fe(OH)_3$ precipitate.

Maximum adsorption observed around pH 9.0 was explained due to the formation of inner sphere complex between metal ion and hydroxy groups of the phenolic molecule. In all the cases, maximum removal of hydroxy phenol was observed at a point of maximum metal hyroxylation. Maximum removal of hydroxy phenols also coincides around the pKa values of hydroxy phenols. The respective pKa values for pyrogallol, phloroglucinol, catechol and resorcinol are 8.94, 8.45, 9.40
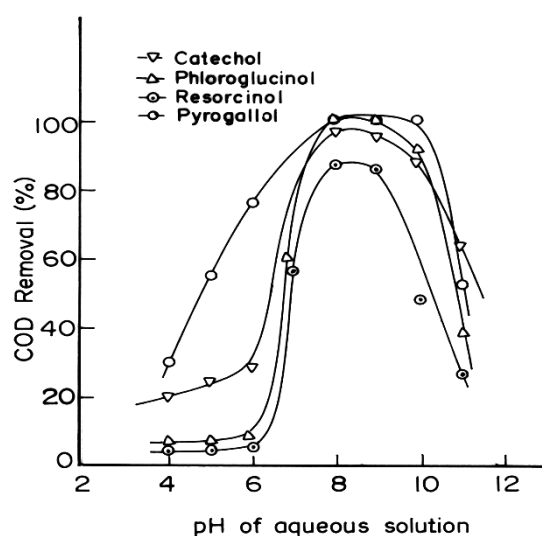
Fig. 11 Effect of pH on the removal of catechol, pyrogallol, phloroglucinol and resorcinol by electroflotation using iron electrodes. Reproduced from Ref. [**].

and 9.3. However, maximum adsorption of catechol on copper around pH 4.5 to 6.0 clearly illustrates the importance of metal hydroxy species in the adsorption process. If the pKa values influence the adsorption, maximum adsorption should take place at the pH where the proton attached to the reactive group of the ligand is dissociated. Thus the pKa values of the polyhydroxy phenols had little influence on the interaction process. The mechanism of interaction between iron hydroxide and the hydroxy phenols, both the supernatant solution and the precipitate analyzed by UV-Visible and FT-IR spectroscopic techniques (Data not included) suggest the metal-ligand complex as shown in the following figure [36].

Generally, molecules having oxygen atoms can share its lone pair of electrons with most of the d-block elements facilitating coordinate covalent bond. However the position of oxygen atoms in the organic molecule is paramount to achieve such chemical bonding. Hydroxyl groups in pyrogallol and catechol are situated in adjacent carbon atoms (para position) of the benzene ring where as in the case of resorcinol and phloroglucinol they are situated on alternate carbon atoms (meta position) of the ring. The chemical interaction is favorable only with the molecules having adjacent oxygen atoms. The driving force of the reaction is the confirmational stability of a five membered ring formed between Fe^{3+} and the hydroxy phenol. The possible reaction schemes of complex formation are given in

Fig. 12. The possibility of reaction schemes 2 and 4 were found to be remote, as the pH of the suspension remained intact.
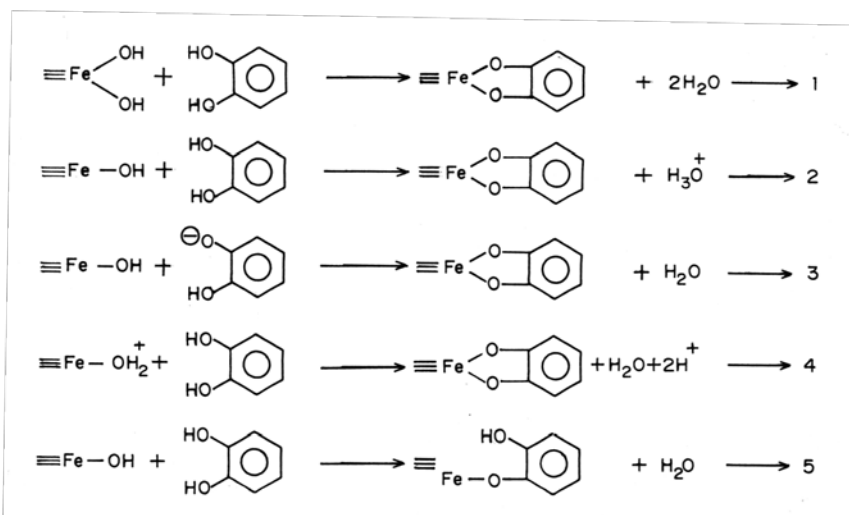

Fig. 12 Possible reaction schemes of interaction of hydroxy phenols with iron oxy-hydroxide. Reproduced from Ref. [**].
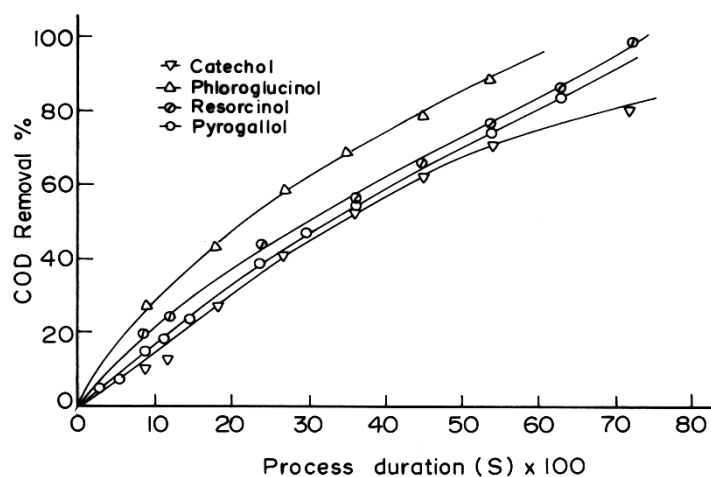

Fig. 13 Effect of electro-oxidation time on the removal of catechol, phloroglucinol, resorcinol and pyrogallol. Reproduced from Ref. [**].

3. Electro-oxidation of poly-hydroxy phenols

Removal of hydroxy phenols by electro-oxidation techniques was studied with reference to time and the results are plotted in Fig. 13. The removal rate of hydroxyl phenols by electro-oxidation process was observed to be very slow. It requires more than two and half-hours to achieve above 80% removal. Energy consumption for electro-oxidation process was estimated to be 555 wh.g^{-1}. The advantage of electro-oxidation is that the pollutants are converted to CO_2 and H_2O and the sludge generation could be totally avoided. It is also apparent that the degradation of resorcinol and phloroglucinol is better compared to catechol and pyrogallol by electro-oxidation.

Table 4. Effect of anodic materials on the treatment of tannery effluent (%).

Sl. No.	Parameter	Initial concentration (Mg/l)	Removal with different anode material			
			Graphite	Ti	Fe	Al
1	Suspended solids	3036	14.0	52.0	91.5	92.0
2	BOD	1750	6.0	37.0	53.0	51.0
3	COD	3092	12.0	31.0	52.0	52.0
4	Ca&Mg	464	0	27.0	81.0	75.0
5	Sulfate	2135	0	0.0	22.7	22.0
6	Sulfide	167	-	-	94.5	940
7	Chromium	2.5	-	-	99.0	N.A
8	Chloride	1850	N.A	1.6	1.54	1.35

Current density: 46 mA/cm^2, flotation time: 300 s and pH of the effluent 8.5. Reproduced from Ref. [**].

TREATMENT OF TANNERY EFFLUENT BY ELECTROCHEMICAL TECHNIQUES

Tannery effluent was collected from the equalization tank of Common Effluent Treatment Plant (CETP). Effluents from different tanneries of small and medium scale were generally collected in a sump and pumped to an equalization tank to homogenize the wastewater before subjecting to full-scale treatment. Samples were collected from such CETP unit situated in Tamilnadu, India. An hourly samples collected over a period of 24 h was thoroughly mixed in a drum to obtain a representative sample.

1. Suspended solids removal

Electroflotation tests were conducted varying the electrode materials and the results are presented in Table 4. The suspended solids were removed to the extent

of 92% that too within a short duration 300 seconds. From the results it is evident that the separation of suspended solids is near total in the presence of iron and aluminum and only partial in the presence of titanium electrode. Better separation of suspended solids could be attributed to coagulation of colloidal solids in the presence of soluble anodes. Since the poly-nuclear metal hydroxyl complexes with positive, negative and neutral charge are good coagulants, the suspended colloidal solids are adsorbed on highly active polymer molecules and form coagulum. The very fine suspended solids are coagulated in the presence of aluminum oxy-hydroxide polymer and these colloidal solids are picked up by hydrogen bubbles liberating from cathode. Thus the suspended solids could be effectively separated from wastewater by electroflotation.

2. Removal of COD, BOD and sulfide ions

The effect of electrode material for the removal of various pollutants was studied and the results are presented in Table 4. It was observed that the aluminum and iron electrodes are effective compared to graphite and titanium coated with oxides of Ir/Ta/Ru. It could be seen that the soluble electrodes are particularly effective in removing suspended solids, sulfide and chromium. These pollutants were removed to the extent of 90% during electroflotation. The removal of calcium, magnesium and chromium was also found be significant during electroflotation. The bubbles generated from electrolysis are quite capable to lift metal hydroxides and oxides that are highly hydrophilic. While using iron as anode, formation of black color precipitate typical to iron sulfides was observed in the flotation cell. This clearly indicates the reaction between Fe ions released from anode and sulphide ions present in the form of HS^-, S^{2-} and H_2S. Thus the sulphide content present in effluent can be effectively removed by converting to iron sulfide compounds that are less soluble and hydrophobic. The BOD and COD reduction around 50–70 % was achieved using Al and Fe as anode material. Major contribution towards COD and BOD is expected from dissolved organic substances. Generally strong oxidizing agents such as hydrogen peroxide are used to oxidize the dissolved organic molecules. The removal of COD and BOD by electroflotation could be attributed due to the removal of suspended solids and also due to precipitation of dissolved organic molecules as organo-metallic compounds. However, detailed studies on oxidation–reduction reactions on the surface of the electrodes and in bulk phase are essential to establish the electrochemical removal of COD content.

CONCLUSIONS

The removal of CI Reactive Blue 221 and CI Acid orange 10 dyes was studied by

electrocoagulation and electro-oxidation techniques using Fe, graphite and $IrO_2/TaO_2/RuO_2$ coated Ti anode materials. The dyes were effectively degraded using graphite material rather than metal oxide coated Ti. The rate of degradation was observed to increase by increasing the NaCl concentration. The formation of active chlorine was confirmed by cyclic voltammetric study and found to be better in the presence of graphite electrode. The CI Acid orange10 was removed only to the extent of 60 % using Fe as anode and it facilitated the reductive cleavage of azo linkage resulting in the formation of aniline and 1-amino-2-naphthol-6,8-disulfonic acid. 1-amino-2-naphthol-6,8-disulfonic acid could be removed during electrocoagulation whereas aniline continued to remain in aqueous phase. The mechanism of reductive cleavage of azo linkage and subsequent interaction of 1-amino-2-naphthol disulphonic acid on iron oxy-hydroxide was established. The combination of electrocoagulation and electro-oxidation technique was applied to the actual effluent from textile industry and found to be effective in eliminating COD up to 93%. The study was extended for the removal of tannins and poly-hydroxy phenols. The catechol and pyrogallol were observed to form metal complex with iron oxy-hydroxides by condensation mechanism. The chemical interaction of these compounds was substantiated by UV-Visible and FT-IR measurements. The removal rate of catechol and pyrogallol by electro-coagulation/flotation was better compared to phloroglucinol and resorcinol. However latter compounds are easily mineralized by electrooxidation. Tannery effluent was collected and subjected to electro-coagulation/flotation technique using Fe, Al, graphite and metal oxide coated Ti. Removal of pollutants such as COD, BOD, suspended solids, sulfides and chromium was achieved using Fe and Al.

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