



# Parametric study of electro-Fenton treatment for real textile wastewater, disposal study and its cost analysis

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## Abstract

Treatment of real textile wastewater by electro-Fenton method was investigated using Ti/RuO<sub>2</sub> electrodes. The performance of the treatment process was evaluated in terms of %chemical oxidation demand removal; %color removal; and energy consumed, at three electro-Fenton process parameters: current, electrolysis time and ferrous sulfate concentration. To determine the optimum operating conditions, multiple responses optimization based on Box–Behnken design with desirability function was used. The optimum value of parameters were found to be current=0.32 A, time=90 min and ferrous sulfate concentration=0.53 mM. Box–Behnken design suggested the %chemical oxidation demand removal; %color removal; and energy consumed were 100%, 90.30% and 1.27 Wh, respectively at optimized process parameters. The predicted performance parameters agree well with the experimental data. Second-order kinetic model was fitted to the experimental data, at optimum conditions. GC–MS analysis confirmed that dye components were totally eliminated after electro-Fenton treatment of textile effluent. To determine the toxicity of the treated textile effluent bioassay analysis was performed. It was identified that the generated by-products were non-toxic in nature. The total cost to treat the 1 m<sup>3</sup> of real textile wastewater by electro-Fenton at optimum conditions was \$ 3.13.

**Keywords** Real textile wastewater · Electro-Fenton · Chemical oxygen demand removal · Color removal · Response surface methodology · Energy consumed

## Introduction

Global industrialization and urbanization has attained high pace leading to enormous generation of wastewater. Textile industries require large amount of freshwater for textile processing and generate huge amount of wastewater (Gregory 1986; Phalakornkule et al. 2010). To improve the performance of finished textile products, textile industries use dyes, which are recalcitrant in nature and varieties of chemicals (bleaching agents, salts, acids, alkalis, etc.), which

are lost/remaining in processing water during the processing and goes with discharged wastewater. Therefore, the high-strength wastewater is produced having burly color, high suspended particles, high pH and chemical oxygen demand (COD) (Olmez et al. 2007; Vlyssides et al. 1999). Furthermore, the composition of textile effluent is altered depending on different types of dyestuff and auxiliary chemicals used. This wastewater if discharged without treatment may pose problem to the environment. Moreover, environmental regulatory agencies have set the discharge standards for release of the wastewater in to the environment.

Treatment of real textile wastewater is tedious task to meet the discharge standards. Various physical and chemical treatment methods like chemical coagulation, adsorption processes and membrane filtration are not preferred for the treatment of such type of effluents because of their unsuitability due to expensive chemical coagulants, adsorbents, membranes and membrane cleaning and production of large volume of secondary pollutants (Georgiou et al. 2002; Cañizares et al. 2006). The conventional treatment technology used in the textile industries employs activated

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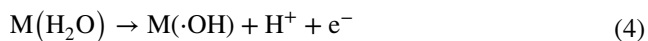
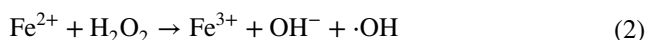
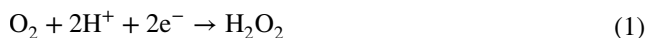
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sludge process (ASP) as a secondary treatment facility. ASP is prone to bulking of sludge and is very sensitive toward variation in COD and BOD loadings, as happens in case of textile industries wastewater. ASP also requires large area for its installation and high level of controlling. Except these, non-biodegradability of dyes limits the use of biological methods for the treatment of textile wastewater (Chen and Liu 2012; Bansal et al. 2013). Anaerobic processes are also not suitable for wastewater containing dyes, because the dyes degradation under anaerobic conditions leads to the formation of toxic organic compounds (Meric et al. 2004).

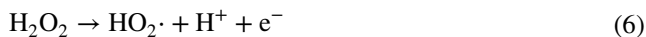
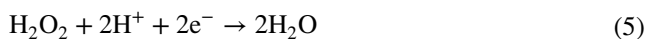
The inefficiency of the traditional treatment methods has motivated researchers to explore other techniques like electrochemical advanced oxidation processes (EAOPs). These methods are based on the in situ generation of  $\cdot\text{OH}$  radicals and the degradation of pollutants. Among the different EAOPs, several researches have demonstrated that the electro-Fenton (EF) process is a promising technology to be more efficient and environmental friendly to remove organic matter (Brillas et al. 2009; Sandhwar and Prasad 2017).

In classical Fenton process,  $\text{H}_2\text{O}_2$  is added with Fenton reagent to generate  $\cdot\text{OH}$  radicals. EF process allows better control of the process and avoids the storing and transport of the highly reactive  $\text{H}_2\text{O}_2$ . Moreover, EF process does not produce secondary pollutants. In the EF process, organics are eliminated by the action of both Fenton's reaction (Eq. 2) in the bulk and anodic oxidation at the anode surface (Eq. 4). The oxidation of pollutants is achieved by anodic oxidation by using high-oxygen-overvoltage anodes (such as dimensionally stable anode (DSA), Pt and BDD (boron-doped diamond) anode (Lin et al. 2014; Nidheesh and Gandhimathi 2014).  $\text{H}_2\text{O}_2$  is continuously generated in the solution during electrolysis in EF process due to two-electron oxygen reduction at cathode (Brillas et al. 2009; Sirés and Brillas 2012) in an acidic medium (Eq. 1), and ferrous ion added into the system analogously generates the  $\cdot\text{OH}$  radicals in the classical Fenton's reaction (Eq. 2). Due to high standard redox potential ( $E^\circ(\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$ ) of  $\cdot\text{OH}$  radicals, organics present in the effluent are oxidized to  $\text{CO}_2$ , water and inorganic ions. At the same time, in this process, the ferrous ion is regenerated at the cathode (Eq. 3), reducing its further addition.



Rate of Fenton's reaction in EF process is predominantly controlled by the  $\text{H}_2\text{O}_2$  production rate, which depends on factors such as  $\text{O}_2$  solubility, temperature, pH, cathode type

and current density. Current controls not only the  $\text{H}_2\text{O}_2$  generation rate (Eq. 1), but also regeneration rate of  $\text{Fe}^{2+}$  (Eq. 3). At the same time, high current density supports other side reactions leading to reduction in the  $\text{H}_2\text{O}_2$  production (Eqs. 5–7) and production of  $\text{H}_2$  at cathode (Eq. 8).



Nature and concentration of catalyst used significantly affect the process efficiency. Usually,  $\text{Fe}^{2+}$  has been reported the best catalyst in the EF process due to its efficient activity even at lower concentrations (Sirés et al. 2014).

In the literature, various authors reported the EF treatment performance for textile wastewater using different types of electrodes (Brillas and Casado 2002; Nasr et al. 2005; Wang et al. 2005; Zhou and He 2007; Martinez-Huitle and Brillas 2009; Salazar et al. 2012; Oturan et al. 2012; Pajootan et al. 2014; Ghanbari and Moradi 2015; Asghar et al. 2015; Garcia-Segura and Brillas 2016). In the reported literature, investigators discussed about the treatment of simulated/dye textile wastewater only, by using EF process (Lin et al. 2014, Nidheesh and Gandhimathi 2014). Some investigators perform EF with the combination of other processes for the treatment of real textile wastewater (Santos et al. 2010). The treatment performance of EF for real textile wastewater is not investigated in the reported literature. Real textile wastewater contains number of components, which can promote or hinder the treatment process like chloride content, TS, composition of different types of dyes. Therefore, performance investigation and applicability of EF process require more study on real industrial textile wastewater.

Real textile wastewater contains high chloride; however, dimensionally stable active electrodes may be suitable for the textile wastewater treatment. Textile wastewater electro-oxidation has been reported by various dimensionally stable electrodes like Pt, BDD and metal oxide-coated anodes such as  $\text{Ti}/\text{IrO}_2$ ,  $\text{Ti}/\text{PbO}_2$  and  $\text{Ti}/\text{RuO}_2$  (Kaur et al. 2015, 2017).  $\text{Ti}/\text{RuO}_2$  has been reported dimensionally stable active electrode with high electrode potential (Santos et al. 2010).  $\text{Ti}/\text{RuO}_2$  anodes generate various chlorine products such as  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{ClO}^-$  in solutions containing high chloride. These chlorine products additionally oxidize the pollutants by mediated oxidation method in association with direct oxidation by  $\cdot\text{OH}$  radicals. But, in the presence of Fenton reagent the generation of  $\cdot\text{OH}$  radicals increases which leads to the  $\cdot\text{OH}$  radicals-mediated organics oxidation of pollutants. Therefore, during the textile wastewater treatment,  $\text{Ti}/\text{RuO}_2$  anode is capable of delivering high degradation of pollutants



by both electro-oxidation and Fenton ·OH radicals-mediated organics oxidation. However, degradation mediated by chlorine products yields suspicion of carcinogenic/toxic chlorinated organic compounds generation. Therefore, there is a need to explore the true efficiency of EF process with Ti/RuO<sub>2</sub> electrodes and its applicability for the treatment of real textile wastewater.

The purpose of the present study is to investigate EF treatment of actual textile wastewater using Ti/RuO<sub>2</sub> electrodes. Effects of various EF process parameters are as follows: current (*i*), time (*t*) and concentration of ferrous sulfate (*C*<sub>Fe</sub>) (Fenton reagent) on %chemical oxidation demand (COD) removal (*M*<sub>1</sub>), %color removal (*M*<sub>2</sub>) and energy consumed (*M*<sub>3</sub>). GC–MS at optimum conditions was performed for safe disposal point of view. Moreover, COD removal and color removal kinetics were investigated. To determine the economic feasibility of EF process to treat the textile wastewater, operating cost exploration was executed.

This study was performed in Industrial Pollution Abatement Laboratory, Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala, Punjab, India (April 2015–February 2016).

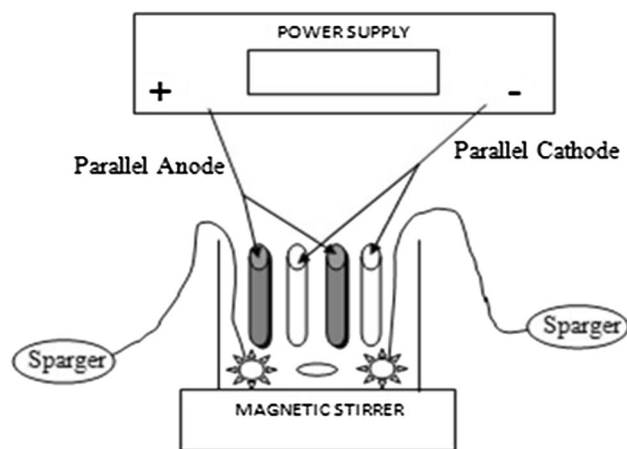
## Materials and methods

### Wastewater sampling, characterization and experimental setup

Real textile wastewater was provided by a mink blanket industry (Ludhiana, Punjab, India). Textile wastewater contains most of the basic dyes that are used in mink blanket industry. The physicochemical characterization of textile wastewater for water quality parameters is given in Table 1. A cubical shaped EF batch reactor made from plexi glass sheet of 1.5 L working volume was used (Fig. 1). Ti/RuO<sub>2</sub> electrodes of dimensions 100 mm × 85 mm × 1.5 mm were supplied by Titanium Tantalum Products Limited, Chennai, India, and were used as anode, whereas cathode was of aluminum (Al) plate of same dimensions. A digital power supply provided by DIGITECH, Roorkee, India (Model:

**Table 1** Physicochemical characterization of textile wastewater (all the values are in mg/l, except pH)

Parameters	Before EF treatment	After EF treatment
pH	9.84	3.86
BOD	200	35
COD	544	55
TDS	50,800	800
TSS	59,400	360



**Fig. 1** Schematic diagram of experimental setup of EF

4818A10; 0–20 V, 0–5 A), was used to supply the DC during experiments. A pump with air sparger was used for continuous supply of air to the real textile wastewater sample in the reactor. To adjust the pH of textile wastewater for a particular run with 0.1 N HCl solution was used. Magnetic stirrer was used to agitate the real textile wastewater sample in the reactor.

### Experimental design, mathematical modeling and optimization

The EF process was modeled and analyzed using Box–Behnken design (BBD) under response surface methodology (RSM). RSM facilitates in designing experiments, modeling, process parameter effects assessment and identifying optimum conditions for responses (Sangal et al. 2013). BBD under RSM allows the identification and quantification of interactive effects of various parameters. Equation 9 shows the relationship between the response and the process parameters as the surface of the  $x_1, x_2, \dots, x_k$  coordinated in the graphical sense.

$$M = f(x_1, x_2, \dots, x_k) \pm \delta_r \quad (9)$$

where *M* is the response,  $x_1, x_2, \dots, x_k$  are quantitative factors, *f* is the response function and  $\delta_r$  is the statistical error

In the present study, predicted response (*M*) refers to the %COD removal, %color removal and energy consumed. A second-order polynomial equation (Eq. 10) was used to determine the relevant model terms where  $\omega_0$  is the model constant;  $\omega_i$  represents the linear coefficient;  $\omega_{ii}$  and  $\omega_{ij}$  are the interaction coefficients; *k* is the number of the factors or variables; and  $\delta_r$  is the statistical error. The interaction between the process variables and the responses was analyzed from an analysis of variance (ANOVA).



$$M = \omega_0 + \sum_{i=1}^k \omega_i x_i + \sum_{i=1}^k \omega_{ii} x_i^2 + \sum_{i < j} \omega_{ij} x_i x_j + \delta_r \quad (10)$$

The statistical Design-Expert software version 6.06 (STAT-EASE Inc., Minneapolis, USA) was used for designing the experiments by BBD. The process parameters: current (0.25–3 A), time (10–90 min) and ferrous sulfate concentration (0.20–1.0 mM), were selected from preliminary experiments. Multi-response optimization with desirability function was applied for maximizing the %COD removal and %color removal and minimizing the energy consumption simultaneously. The electro-Fenton responses, i.e., %COD removal, %color removal, energy consumption of textile effluent, were measured according to the design matrix (Table 2) to optimize the EF process.

### Operational details of experimental system and data analysis

Experiments were conducted, as per the design matrix shown in Table 2. The pH of textile wastewater collected was found to be 9.84. It has been reported that the best working pH for EF processes is pH = 3 (Sun and Pignatello 1993). Therefore, before conducting the EF experiments, the pH of textile wastewater was altered to pH = 3. The EF treatment time ( $t$ ) measured from the moment of power supply button was switched on. During the EF treatment, the supplied current intensity ( $i$ ) was kept constant. In EF process, oxygen is

required for generation of  $\text{H}_2\text{O}_2$  (Eq. 1), and hence,  $\cdot\text{OH}$  radicals are generated (Eq. 2). In the present study, oxygen was supplied in the form of air with the help of air diffuser at the bottom (Fig. 1). Further, the supplied air/oxygen should be distributed evenly in the reactor and its concentration and mass transfer rate should be high in order to generate high concentration of oxidants ( $\text{H}_2\text{O}_2$  and  $\cdot\text{OH}$ ). To ensure this, magnetic stirrer was used to stir the content of the reactor, and high flow rate of air was maintained. After the desired treatment time ( $t$ ), the power supply was switched off, and samples were collected from the reactor for further analysis.

The samples were then analyzed for color and COD with double-beam UV visible spectrophotometer (HACH, DR 5000, USA) and COD digestion unit (Spectra lab, 2015D, India). Energy consumed ( $E$ ) during the EF process was assessed by Eq. 11:

$$E = \left[ \frac{\{(Vit)/Z\}/10^3}{\text{COD}_r/10^6} \right] \quad (11)$$

where  $i$  = current (A);  $V$  = voltage (volt);  $t$  = treatment time (h);  $Z$  = sample volume (L);  $\text{COD}_r$  = COD removed (mg/L).

GC–MS of treated textile wastewater (at optimum conditions) and untreated textile wastewater was carried out to identify various transformation products formed during EF degradation and for disposal study. The sample for GC–MS (Perkin-Elmer Clarus 500 MS) analysis was prepared by solvent extraction method. The Fused silica capillary columns coated with a 5% diphenyl/95% dimethyl polysiloxane of

**Table 2** Box–Behnken design for the electro-Fenton process

Std	Run	$i$ (A)	$t$ (min)	$C_{\text{Fe}}$ (mM)	% COD removal, $M_1$	% Color removal, $M_2$	Energy consumed (Wh), $M_3$
14	1	0.63	50	0.60	87.7	100.0	2.594
15	2	0.63	50	0.60	87.7	100.0	2.594
10	3	0.63	90	0.20	94.7	100.0	2.532
12	4	0.63	90	1.00	94.0	100.0	2.568
17	5	0.63	50	0.60	87.7	100.0	2.594
8	6	1.00	50	1.00	64.3	96.0	4.21
6	7	1.00	50	0.20	62.1	87.3	4.12
4	8	1.00	90	0.60	97.2	98.5	4.2
9	9	0.63	10	0.20	39.3	70.9	2.407
1	10	0.25	10	0.60	27.7	66.4	0.827
3	11	0.25	90	0.60	82.9	98.8	0.935
13	12	0.63	50	0.60	87.7	100.0	2.594
2	13	1.00	10	0.60	36.3	66.2	4.15
7	14	0.25	50	1.00	58.3	96.5	0.815
16	15	0.63	50	0.60	87.7	100.0	2.594
11	16	0.63	10	1.00	49.8	76.3	2.48
5	17	0.25	50	0.20	61.5	94.7	0.855



25 m length and 0.20  $\mu\text{m}$  internal diameter were used at injector temperature of 300  $^{\circ}\text{C}$ . The helium (carrier gas) with a flow rate of 1 ml/min was used. The temperatures of the inlet line and ion source were set at 250 and 280  $^{\circ}\text{C}$ , respectively. The run time for the samples was 26 min.

## Results and discussion

### Model fitting and statistical analysis

The responses %COD removal,  $M_1$ ; %color removal,  $M_2$ ; and energy consumed,  $M_3$ , for the EF were measured after conducting experiments as per design matrix listed in Table 2. Quadratic model was found to be best fitted to the experimental responses. Quadratic model also supported by ANOVA with  $F$ -values of 77.47, 72.1 and  $1.1 \times 10^4$  for the responses  $M_1$ ,  $M_2$  and  $M_3$ , respectively, shown in Table 3. Adequate precision ratio above 4, in the present study, shows that model is efficient in navigating the design space. The statistical regression coefficient values  $R^2$ , adjusted  $R^2$  and predicted  $R^2$  for responses  $M_1$ ,  $M_2$  and  $M_3$  found to be 0.99, 0.98 and 0.84; 0.99, 0.98 and 0.83; and 0.99, 0.99 and 0.99, respectively, which shows a good relation between predicted and experimentally observed values. The values of “Prob >  $F$ ” smaller than 0.05 show that model terms are significant with 95% confidence level. ANOVA indicated that  $i$ ,  $t$ ,  $i^2$ ,  $C_{\text{Fe}}^2$  are highly significant model terms for  $M_1$ ;  $t$ ,  $i^2$ ,  $t^2$ ,  $C_{\text{Fe}}$  are highly significant model terms for  $M_2$ , while  $i$ ,  $t$ ,  $C_{\text{Fe}}$ ,  $i^2$ ,  $t^2$ ,  $C_{\text{Fe}}$ ,  $i * C_{\text{Fe}}$  are highly significant for  $M_3$  (Table 3). The quadratic equations for  $M_1$ ,  $M_2$  and  $M_3$  in terms of coded variables after the elimination of insignificant terms are given below:

$$M_1 = 87.70 + (3.69 * i) + (26.97 * t) - (17.29 * i^2) - (9.39 * t^2) - (8.87 * C_{\text{Fe}}^2) \quad (12)$$

$$M_2 = 100 + (14.68 * t) + (1.97 * C_{\text{Fe}}) - (5.36 * i^2) - (12.19 * t^2) \quad (13)$$

$$M_3 = 2.59 + (1.66 * i) + (0.046 * t) + (0.020 * C_{\text{Fe}}) - (0.031 * i^2) - (0.035 * t^2) - (0.063 * C_{\text{Fe}}^2) - (0.014 * i * C_{\text{Fe}}) - (9.25 * 10^{-3}) \quad (14)$$

Normal probability, outlier- $t$ -residual plots and studentized residuals explained that the quadratic model will satisfy the ANOVA.

### Parametric study, optimization and disposal study

To explore the effects of EF parameters and their interactions, 3D response surface graph was drawn. Figure 2a and b shows the interaction of  $C_{\text{Fe}}$  and  $i$  on the  $M_1$  and  $M_2$  with

time,  $t$ , respectively. The 3D plot showed that  $M_1$  decreases at higher and lower  $C_{\text{Fe}}$  at all the  $i$  values. However,  $M_1$  increases with the increase in  $i$  from 0.25 to  $\approx 0.81$  A, after it starts decreasing.  $M_1$  also increases with the increase in  $C_{\text{Fe}}$  from 0.20 to  $\approx 0.53$  mM. This trend was also observed for  $M_1$ . On the other side, with increasing  $C_{\text{Fe}}$  along with the increase in  $i$  value from 0.30 to  $\approx 0.81$  A, increases  $M_2$ . 100%  $M_2$  was observed, when  $C_{\text{Fe}}$  was up to 0.53 mM at  $i = 0.32$  A.

Figure 2c, d shows that  $M_1$  and  $M_2$  increases with the increase in  $t$  for all  $i$  value. However, increase in  $t$  at particular  $i$  between 0.50 and  $\approx 0.81$  A showed 100%  $M_1$  and  $M_2$ .  $M_3$  value increases with the increase in  $C_{\text{Fe}}$ ,  $t$  and  $i$ .

It is asserted that electro-oxidation (EO) and Fenton  $\cdot\text{OH}$  radicals-mediated organics oxidation are responsible for the removal of COD and color from the real textile wastewater. It was well known that Fenton's reaction can be applied in acidic pH (Sun and Pignatello 1993) to efficiently produce  $\cdot\text{OH}$  radicals, but EO, at acidic pH, generates oxidants such as  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\cdot\text{OH}$ . It has been reported that chloro-oxidants have lower oxidation potential and are toxic/carcinogenic in nature (Deborde and Von Gunten 2008). However, oxidation of pollutant particles occurs at the surface of Ti/RuO<sub>2</sub> electrodes due to chloro-oxidants and  $\cdot\text{OH}$  radicals. Due to lower oxidation potential, chloro-oxidants transform pollutants into chloro-compounds. Furthermore, these chloro-compounds are mineralizing by Fenton  $\cdot\text{OH}$  radicals-mediated oxidation. Therefore,  $M_1$  and  $M_2$  are increased with the increase in  $C_{\text{Fe}}$  at all  $i$  values. But, it has been also seen that after  $C_{\text{Fe}} = 0.53$  mM, there is a sharp decrease in  $M_1$  and  $M_2$  along with electrolysis time ( $t$ ) at particular  $i$  value. Due to the high generation of  $\cdot\text{OH}$  radicals at the higher concentration of Fenton reagent, a competitive reaction occurs between the  $\text{Fe}^{2+}$  and hydroxyl radicals. It could reduce the concentration of hydroxyl radicals to the pollutant particles (Bouafia-Chergui et al. 2010). Therefore, above  $C_{\text{Fe}} = 0.53$  mM, there is a sharp decrease in  $M_1$  and  $M_2$ .

Optimum operating conditions were derived for simultaneous optimization of the multiple responses. For this purpose, the process parameters ( $i$ ,  $t$  and  $C_{\text{Fe}}$ ) were selected within whole range of study and responses ( $M_1$  and  $M_2$ ) maintained as maximum; however, response ( $M_3$ ) maintained as minimum. Using minimum and maximum acceptability of the responses, individual and simultaneous desirability was calculated. The one-sided desirability for all the responses was 1.0, and overall desirability was 0.92. The optimum values of parameters were found to be  $i = 0.32$  A,  $t = 90$  min and  $C_{\text{Fe}} = 0.53$  mM with corresponding desirability value 0.920 for simultaneous optimization. At optimum conditions, the  $M_1$ ,  $M_2$  and  $M_3$  suggested by BBD were found to be 90.30, 100% and 1.27 Wh, respectively. At optimum values of parameters, experiments were performed in duplicate and average values of responses were found to be





**Table 3** ANOVA for the responses (%COD removal, %color removal and energy consumption)

Source	% COD degradation				%Color removal				Energy consumption						
	Sum of Squares	DF	Mean square	F-value	Prob>F	Sum of squares	DF	Mean square	F-value	Prob>F	Sum of squares	DF	Mean square	F-value	Prob>F
Model	8144.2	9	904.9	77.47	< 0.0001	2578.15	9	286.4	72.1	< 0.0001	21.9	9	2.4	1.1 × 10 <sup>4</sup>	< 0.0001
<i>i</i>	109.1	1	109.1	9.344	0.0184	8.79	1	8.7	2.2	< 0.0001	21.9	1	21.9	10.5 × 10 <sup>4</sup>	< 0.0001
<i>t</i>	5817.9	1	5817.9	498.09	< 0.0001	1724.9	1	1724.9	434.4	0.0002	0.017	1	0.01	82.4	< 0.0001
<i>C<sub>Fe</sub></i>	9.7	1	9.73	0.83	0.3904	30.96	1	30.96	7.7	0.0207	0.003	1	3 × 10 <sup>-3</sup>	15.1	0.0060
<i>i<sup>2</sup></i>	1258.1	1	1258.1	107.7	< 0.0001	121.02	1	121.02	30.4	< 0.0001	0.004	1	4 × 10 <sup>-3</sup>	19.8	0.0030
<i>t<sup>2</sup></i>	371.5	1	371.5	31.80	0.0008	625.79	1	625.7	157.6	0.0001	0.005	1	5 × 10 <sup>-3</sup>	24.1	0.0017
<i>C<sub>Fe</sub><sup>2</sup></i>	331.3	1	331.3	28.36	0.0011	4.24	1	4.2	1.06	0.0594	0.016	1	0.01	79.1	< 0.0001
<i>t × i</i>	8.1	1	8.1	0.70	0.4303	2.2 × 10 <sup>-4</sup>	1	2 × 10 <sup>-4</sup>	5.67 × 10 <sup>-7</sup>	0.0323	0.0008	1	8 × 10 <sup>-4</sup>	4.02	0.0847
<i>t × C<sub>Fe</sub></i>	7.3	1	7.3	0.63	0.4530	11.83	1	11.8	2.980222	0.8844	0.004	1	4 × 10 <sup>-3</sup>	20.2	0.0028
<i>t × C<sub>Fe</sub><sup>2</sup></i>	31.3	1	31.3	2.68	0.1453	7.12	1	7.1	1.795371	0.0207	0.0003	1	3 × 10 <sup>-4</sup>	1.6	0.2412
Residual	81.7	7	11.6			27.78	7	3.9			0.001	7	2 × 10 <sup>-4</sup>		
Lack of fit	81.7	3	27.25			27.7	3	9.2			0.001	3	4 × 10 <sup>-4</sup>		
Pure error	0	4	0			0	4	0			0	4	0		
Cor total	8225.9	16				2605.9	16				21.9	16			

89.75, 99.49 and 1.067 Wh, for *M*<sub>1</sub>, *M*<sub>2</sub> and *M*<sub>3</sub>, respectively. This validation explains good correlation between the values of experimental and predicted responses and the reliability of modeling by RSM.

At optimum conditions, both EO and Fenton ·OH radicals-mediated oxidation are participating in the oxidation of pollutant species of actual textile wastewater, which can be confirmed by GC–MS analysis of both the untreated and treated real textile wastewater (at optimum conditions). The intermediate/transformation products from GC–MS analysis of untreated and treated real textile wastewater are shown in Tables 4 and 5, respectively. There is no chlorinated compound identified, so it shows that chloro-compounds are mineralizing by Fenton ·OH radicals-mediated oxidation. GC–MS analysis also shows that dye components are totally eliminated after treatment by EF. After treatment, there was no component observed that was previously present in real textile wastewater. Butyl phthalate was found in treated sample with highest matching % as shown in Table 5. It is non-toxic and biodegradable component. It is observe from GCMS analysis that there is no toxic component present in treated real textile wastewater. To confirm this, the bioassay analysis was performed. The toxicity analysis of untreated and treated wastewater was carried out using E coli DH-α strain with standard Kirby–Bauer method. The result of bioassay analysis shows a zone of inhibition with less number of bacterial colonies in case of untreated, and there is no zone of inhibition in case of treated wastewater. There is a heavy count of bacterial colonies around the puncher well for treated wastewater (Fig. 3).

**Reaction kinetics**

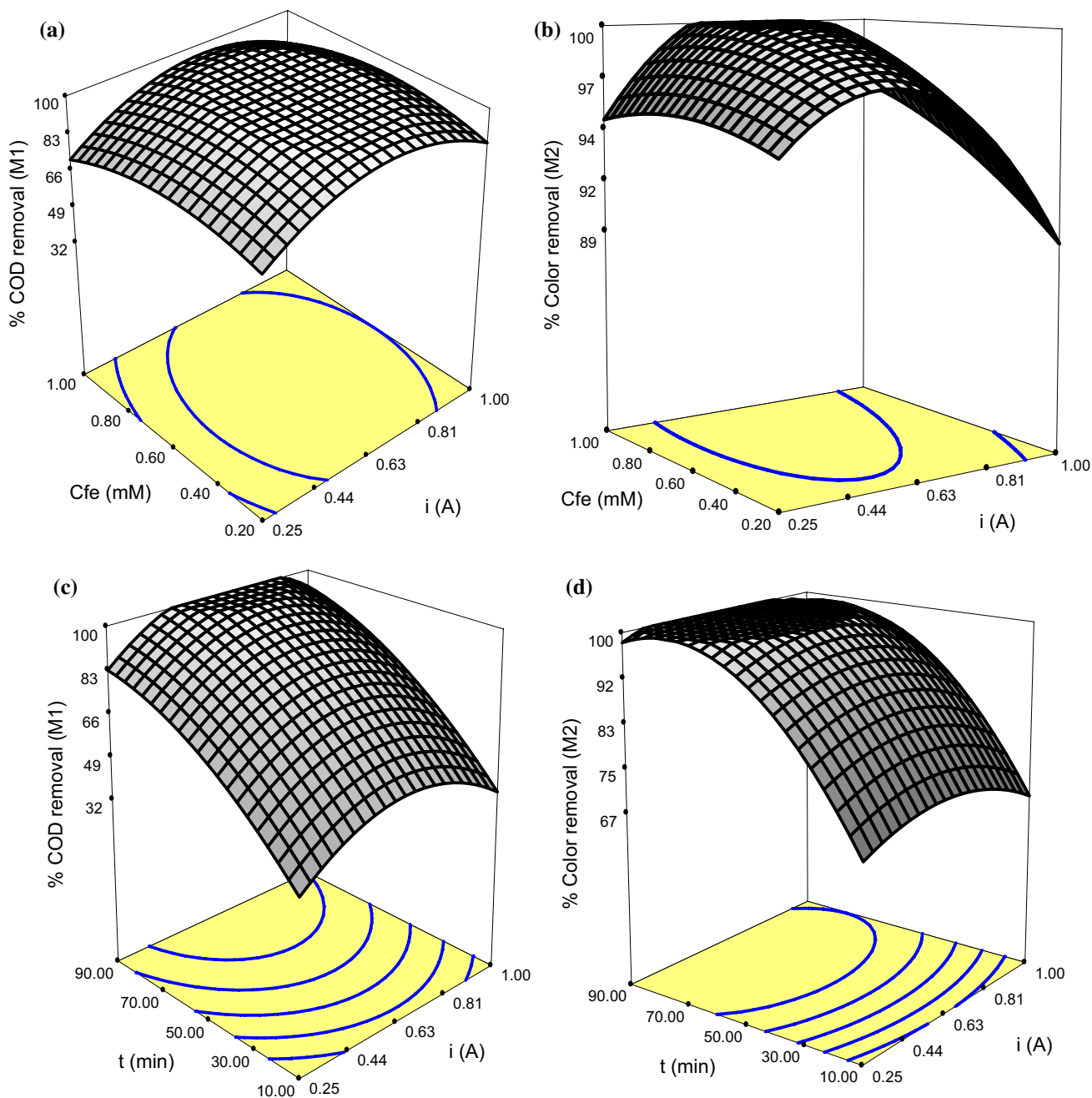
At optimum parameters of the EF process, kinetics of COD and color removal was studied. Second-order model was fitted to the experimental data at optimum conditions (*i* = 0.32 and *C<sub>Fe</sub>* = 0.53 mM) for COD removal and color removal according to the rate equation.

$$-\frac{dC_s}{dt} = k[C_s]^2 \tag{15}$$

On integrating between known limits and rearranging, the above model becomes

$$\frac{1}{[C_s]} = \frac{1}{[C_0]} + Kt \tag{16}$$

where *C*<sub>0</sub> is initial color intensity or initial COD concentration, *C*<sub>*s*</sub> is final color intensity or final COD concentration, *t* is degradation time (min) and *k* is second-order rate constant (L/mg min). Figure 3a and b shows the fitting of second-order reaction kinetics to the %color removal and %COD removal for the treatment of textile effluent by EF



**Fig. 2** 3D response surface graph for the EF of real of real textile wastewater **a** %COD removal versus  $C_{Fe}$  and  $i$  **b** %color removal versus  $C_{Fe}$  and  $i$  **c** %COD removal versus  $i$  and  $t$  **d** %color removal versus  $i$  and  $t$

process. The kinetic raw data for the textile wastewater treatment by EF method has been shown in Table 6. The values of rate constant of second-order reaction kinetics are 0.001 and 2.756 L/mg min along with the  $R^2$  value 0.983 and 0.886 for  $M_1$  and  $M_2$ , respectively (Fig. 4).

### Cost analysis for EF process for the treatment of textile wastewater

The electrical energy and electrode cost required for the treatment of 1 m<sup>3</sup> and 1 kg of COD removal of textile wastewater by EF process were calculated at optimum conditions.

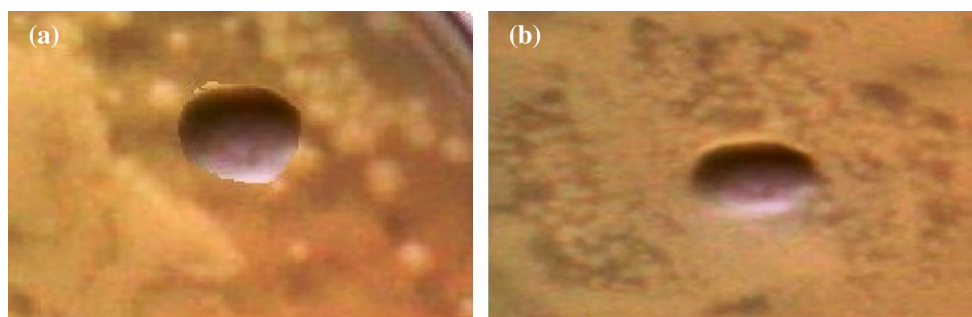
Electricity price in India = \$ 0.069 kWh

**Table 4** Untreated real textile wastewater analysis with GC–MS

S. No	Compound	Retention time	Molecular mass	Matching (%)
1.	Trimethyl-2-pentadecenyl	10.35	282	91
2.	3,5-Bis(ethoxycarbonyl) benzoic acid	10.35	266	90
3.	Dodecamethylcyclododecasiloxane	12.86	444	80.9
4.	3-Octanol 2-[(R)-(4-methylphenyl)sulfinyl]-1-(trimethylsilyl)	12.86	340	80.5
5.	5-Ethoxycarbonyl-2-phenyl-1,3-dioxane-5-carboxylic acid	15.11	280	80.2
6.	2,4,4-Trimethyl-3-(2-trimethylsilylethynyl)cyclohex-2-en-1-ol	18.8	236	95.6
7.	Dibutyl phthalate	20.01	278	90.5
8.	Tetracosamethyl-cyclododecasiloxane	22.27, 24.89 and 25.12	888	84.7/86.8/86.9
9.	Icosamethylcyclododecasiloxane	24.89	740	82.1
10.	Tetradecamethylhexasiloxane	24.89 and 25.12	458	80.7/80.7
11.	Tetrakis(trimethylsilyl) orthosilicate	24.89	384	79.4

**Table 5** Treated real textile wastewater analysis with GC–MS by EF method

S. No	Compound	Retention time	Molecular mass	Matching (%)
1.	Butyl phthalate	20.02/21.51/21.16/21	278	95.2/81.3/92.9
2.	3,4-Dihydro-4-(1,3-dioxolan-2-yl)-5,7-dimethoxy-1(2H)-benzopyran-2-one	24.06/15.12	280	84
3.	1-Acetamidoadamantane	21.91	193	90.7

**Fig. 3** Bioassay testing **a** untreated test sample and **b** treated test sample

Electrical energy consumed = 0.789 kWh/m<sup>3</sup> of real textile wastewater or 1.306 kWh/kg of COD removal of real textile wastewater

Electrical energy consumption cost ( $C_E$ ) = \$ 0.054/m<sup>3</sup> of real textile wastewater

Electrical energy consumption cost ( $C_{E(\text{per Kg COD removed})}$ ) = \$ 0.10/kg of COD removed

Ti/RuO<sub>2</sub> electrodes price ( $C_{EL}$ ) = \$ 3.08/m<sup>3</sup> of textile effluent

Ti/RuO<sub>2</sub> electrodes price in India ( $C_{EL(\text{per Kg COD removed})}$ ) = \$ 5.66/kg of COD removed

Total cost ( $C_{T(\text{per Kg COD removed})}$ ) =  $C_{E(\text{per Kg COD removed})}$  +  $C_{EL(\text{per Kg COD removed})}$  = \$ 5.76/kg of COD removal

Total cost ( $C_T$ ) to treat one m<sup>3</sup> of textile wastewater =  $C_E + C_{EL}$  = \$ 3.13

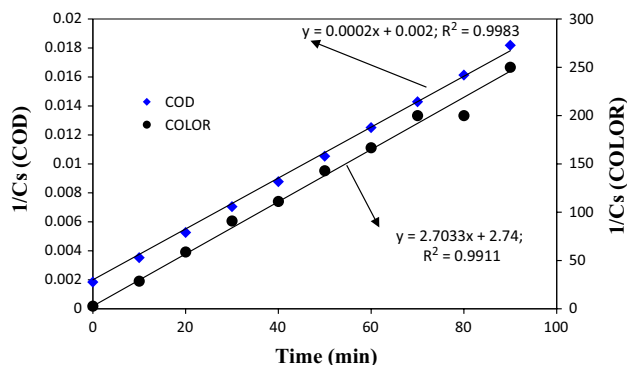
The total treatment cost of real textile wastewater by EF is \$ 5.76/kg of COD removal and \$ 3.13/m<sup>3</sup>. Cost of the treatment process can be reduced by avoiding the deterioration of catalytic electrodes. In electrochemical system, the major reason for the deterioration of catalytic electrode is generation of electric double layer, which affects the mechanism and kinetics of electrochemical reaction. In case of cathode, fermi level increases, electrons jump to unoccupied level to reduce the pollutant particles, but in case of anode fermi level goes on decreasing; then, electrons from bulk jump



**Table 6** Raw kinetic data for the textile wastewater treatment by EF method

Time (min)	COD	Color <sup>a</sup>
0	544	0.364
10	284	0.035
20	190	0.017
30	142	0.011
40	114	0.009
50	95	0.007
60	80	0.006
70	70	0.005
80	62	0.005
90	55	0.004

<sup>a</sup>Color was measured by UV-visible spectrophotometer by measuring absorbance at  $\lambda_{\max} = 614 \text{ nm}$

**Fig. 4** Fitting of second-order reaction kinetics to the COD removal and color removal for the treatment of textile wastewater by EF process at optimum conditions

to the electrode and participate in oxidation on the surface of anode (Newns 1969). Most of the catalyst atoms have  $d$  orbital. Bonding and antibonding levels affect the chemisorption bonds; however, filling of antibonding orbital will strengthen the chemisorption and weaken the intermolecular bond of adsorbed molecule. Filling of antibonding orbital also affects the catalyst bonding to the surface of a metal and leads to slowly deterioration of catalytic electrode (Anderson 1961).

## Conclusion

Electro-Fenton method was successfully performed in batch mode for real textile wastewater treatment. Statistical analysis advocated good correlation between the observed and predicted values. 3D response surface graph concluded that very high concentration of the Fenton reagent hinders the degradation process during electro-Fenton. The optimization

of process parameters was successfully performed. EO and Fenton  $\cdot\text{OH}$  radicals-mediated oxidation were responsible for %COD removal and %color removal in association with chloro-oxidant-mediated oxidation. Furthermore, chloro-compounds were mineralized by Fenton  $\cdot\text{OH}$  radicals-mediated oxidation. It was clear by GCMS analysis that there was no generation of chloro-compounds, and bioassay analysis confirmed that treated real textile wastewater was non-toxic. Therefore, textile wastewater after treatment by electro-Fenton method is safe to dispose in the environment. Therefore, no further treatment is required to dispose of the treated textile wastewater and it is found to be cost-effective than other electrochemical treatment methods.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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