

Decolourization of Textile Dyebath Chloride Rich Wastewater by Electrolytic Processes

Harpreet Singh^{1,*}, Manpreet S. Bhatti², Akepati S. Reddy¹

¹School of Energy and Environment, Thapar University, Patiala-147004, Punjab, India

²Department of Botanical and Environmental sciences, Guru Nanak Dev University, Amritsar-143001, Punjab, India

*E-mail: Harryenv@gmail.com

Received: 26 January 2017 / Accepted: 19 March 2017 / Published: 12 April 2017

The potential of electrolytic process was studied for the treatment of textile dyebath dump chloride (Cl⁻ concentration ~8250 ppm) rich wastewater. The effluent used in the experiments was obtained from the cotton dyeing industry in Ludhiana/India. The performances of four electrode combinations (stainless steel-stainless steel, iron-iron, aluminium-aluminium and iron-aluminium) were investigated to remove color and COD concentration. In addition, best removal efficiency and minimum power consumption along with sludge generation rate was estimated. The coefficient of determination value (R^2) of Color removal % was 0.984 as determined from Analysis of variance (ANOVA). Response surface methodology was followed for optimizing the voltage and treatment time. ANOVA model seems significant with Fe-Fe electrodes for CRWW and optimized process conditions were 1V and 8.2 min. to achieve 96% color removal efficiency. The study indicated that the dye bath dump wastewaters from cotton fabric dyeing can be consistently treated by electrolytic processes using iron electrodes.

Keywords: Electrocoagulation, Electrodes, Response Surface Methodology (RSM), Optimization, Chloride wastewater

1. INTRODUCTION

Colored wastewater is mainly an aesthetic problem and the downstream use is discouraged. The color has to be removed before discharging the wastewater into water sources. Textile industries employ dyeing operations and washing/rinsing steps in the textile processing. These use large amounts of water and generate equivalent amount of colored dyebath wastewater. These wastewaters contain exhausted dyes, residues of dyeing auxiliaries (leveling agents, wetting agents, anti-creasing agents and stabilizing agents etc), chemical residues (sodium sulfate/sodium chloride, sodium hydroxide,

sodium carbonate, sodium sulfite, sodium hydrosulfite, acetic acid and hydrogen peroxide etc). The wastewater has higher levels of total dissolved solids as well as organic contents.

Various conventional (chemical coagulation, biological, anaerobic-aerobic, adsorption etc) as well as advanced treatment techniques (membranes- RO, UF, MF, NF, photo-oxidation-UV, Ozone, Photo-fenton processes- H_2O_2 etc) have been tried on the textile wastewater [1-10]. Most of these have not proved cost effective and have not been very effective in the removal of the colour, COD and other dissolved ions.

Electrocoagulation (EC) is an alternative technique which is effective in removal of organic and inorganic pollutants. The electrolytic process involves the in-situ generation of coagulants by oxidation of specific electrodes (anode) and the dosing depends upon the applied voltage and current density. It does not require addition of chemicals hence have advantage of low sludge generation as well as the evolution of hydrogen at cathode helps the agglomeration of small particles to become flocs which constitutes the sludge [11]. Distinguished types of electrodes (Fe, Al, Steel, Graphite, Platinum etc) and there combinations [12-15] are generally used to treat various wastewaters in recent studies- Galvanic rinsing wastewater [16], Beer brewery wastewater [17], Dairy wastewater [18], Cattle abattoir wastewater [19], Metal plating wastewater [20], Baker's yeast wastewater [21], Potato chips manufacturing wastewater [22], Pulp and paper industry wastewater [23], Oil drilling mud leachate [24] and Fertilizer production wastewater [25] etc. EC was also successfully applied for the treatment of textile wastewater and the dyes containing effluents by various investigators [26-29]. Removal of phosphates from industrial effluents was investigated using continuous recirculation EC reactor [30].

Various types of response designs and removal models were used for optimization of process parameters for getting maximum pollutant removal efficiencies. Response Surface Methodology (RSM) was used to optimize the process parameters in various studies [31-33]. Box–Behnken response design was employed to optimize and investigate the effect of process variables on total solids and COD removal to treat grey wastewater using Fe electrodes [34]. In another study, Removal of As (V) from groundwater by a new air-injected EC reactor using Fe ball anodes was investigated and the operating conditions were optimized with a three-level factorial design viz. Box–Behnken statistical experiment design [35]. Taguchi method was also applied in a study to determine the optimum operating conditions for textile wastewater treatment by EC with Fe electrodes [36]. Reduced quadratic multiple regression model (SMLR) and artificial neural network (ANN) was also employed for color removal efficiency and energy consumption by EC using synthetic wastewater, containing disperse orange 25 dye [37].

Most of the investigations in literature have been carried out at the laboratory scale using the synthetic solutions [38]. In this context, decolourization of the real industrial textile chloride rich wastewater (CRWW) has been tried by electrolytic processes. The treatment was carried out in a batch system. The study was focused on finding out the best sacrificial electrode material for the CRWW by using Stainless steel, iron, aluminium and iron-aluminium combination electrodes. Voltage and treatment time was used as process variables and COD removal efficiency and Color removal efficiency were taken as responses as per IV-optimal design of RSM. Energy consumptions as well as sludge generation were also studied accordingly. TOC and SEM analysis with best sacrificial electrode was also carried out.

2. MATERIALS AND METHODS

2.1. Materials

A batch of exhausted dyebath was collected from a cotton textile processing industrial unit located in Ludhiana, Punjab, India. The cotton textile dyeing process included use of common salt (NaCl) as a dye auxiliary to facilitate the dyeing reaction to increase the dye diffusion onto fabric and to maximize the exhaustion of the dyes. About 200 kg/Batch of cotton fabric was dyed in soft flow machine of 300 kg/Batch capacity. Fabric to water ratio employed was 1:8. Dyes, dye auxiliaries and other chemicals were used in the dyeing process. After the dyeing, the dyebath contents (liquid) were drained as dyebath dump wastewater. Initial characteristics of this cotton textile dyebath dump wastewater are presented in Table-1.

Table 1. Characterization of the cotton textile dyebath dump wastewater

S.No.	Parameter with units	Value	Methods
1	Color (Pt Co units)	2135	APHA 22 nd Edn. 2120-C
2	COD (mg/L)	756	APHA 22 nd Edn. 5220-B
3	TOC (mg/L)	45.72	APHA 22 nd Edn. 5310-B
4	Turbidity (NTU)	385	APHA 22 nd Edn. 2130-B
5	Conductivity (mS/cm)	32	APHA 22 nd Edn. 2510-B
6	pH	9.53	APHA 22 nd Edn. 4500-H ⁺ B
7	TDS (mg/L)	12820	APHA 22 nd Edn. 2540-C
8	TSS (mg/L)	138	APHA 22 nd Edn. 2540-D
9	Sulphate (mg/L)	255.13	APHA 22 nd Edn. 4500 SO ₄ ²⁻ C
10	Total Alkalinity (mg/L)	130.06	APHA 22 nd Edn. 2320-B
11	Sodium (mg/L)	4360	APHA 22 nd Edn. 3500 Na-B
12	Chloride (mg/L)	8249.86	APHA 22 nd Edn. 4500 Cl ⁻ B
13	Surfactants (ppm)	Nil	APHA 22 nd Edn. 5540-C
14	Phenols (ppm)	<0.1	APHA 22 nd Edn. 5530-D
15	Sulfide (mg/L)	<1	APHA 22 nd Edn. 4500 S ²⁻ D
16	Sulfite (mg/L)	<2	APHA 22 nd Edn. 4500 SO ₃ ²⁻ B
17	Calcium (mg/L)	79.5	APHA 22 nd Edn. 3500 Ca-B
18	Magnesium (mg/L)	23.3	APHA 22 nd Edn. 3500 Mg-B

2.2. Electrolytic unit

The experimental setup used in the study is shown in Figure-1. It includes a reactor, a digital DC power system, electrodes, connecting wires, magnetic bit and a magnetic stirrer. The reactor was constructed from acrylic sheet (6mm) and has working volume of 415 mL. Its dimensions are 6.1 cm

length, 4.7 cm width and 33.3 cm height. Two electrodes each of 4.9 cm width, 20 cm length and 3mm thickness with an effective electrode area of 0.0098m^2 , were used as anode and cathode inside the reactor. Four different pairs of sacrificial electrodes (Al-Al, Fe-Fe, SS-SS and Fe-Al) were used in the present study. Gap between the two electrodes was maintained at 10 mm. A magnetic bit of 2.3 cm length was used for mixing the reactor contents. The reactor was placed over a magnetic stirrer and used. A DC power supply system (ELNOVA Pvt. Ltd, Model No. 664300300D with input voltage 230V/AC+10%/50Hz/Single phase) having 483mm x 285mm x 435mm dimensions was used. This system is capable of producing a maximum voltage of 30 volts. Supplies of either voltage or current are regulated. The output voltage and current are monitored by separate front panel meters. Output voltage and current load were noted continuously from the panel meters during experiments. The reactor was operated in a batch mode.

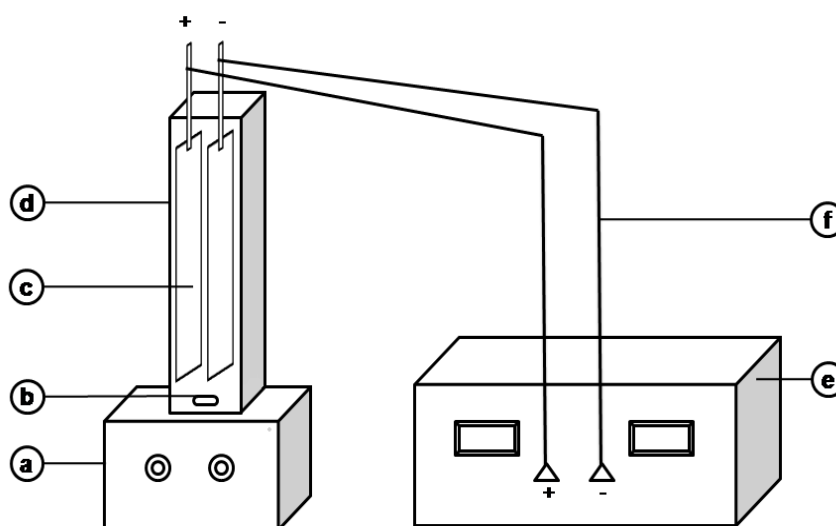


Figure 1. Schematic diagram of electrocoagulation unit (a) Magnetic stirrer (b) Magnetic bit (c) Electrode (d) Reactor (e) DC power supply (f) Inter-connecting wires

2.3. Design of experiments

Electrocoagulation treatment of cotton textile dyebath dump CRWW was studied using four electrode combinations: Al-Al, Fe-Fe, SS-SS and Fe-Al. The operating parameters and their ranges were selected initially through preliminary study and from the understanding of the EC process. Voltage and time were used as operating parameters and Color, COD, power consumption and sludge generation were recorded as responses.

IV-optimal design strategy of RSM with Design Expert Software (trial version 8.0- Stat-Ease, Inc), was used for the design of experiments [39]. Total 19 experiments, as presented in Table 2, including six model points, five replicates at center point and additional three center runs and five runs for estimating the *Lack of fit*, were designed and run for obtaining the needed data.

The Experiments were conducted batch-wise while continuously stirring the reactor contents. The sacrificial electrodes were positioned in the grooves of the reactor wall and the reactor was filled with the wastewater of determined quantity. Voltage was adjusted with 'coarse and fine controls' on the front panel of DC power supply system. The current (Amperes) was monitored at regular intervals (0.5 or 1 min). Surface of the electrodes was rinsed with distilled water after each experiment prior to the start of next experiment. Polarity of the electrodes was interchanged intermittently at regular intervals to improve the performance and to inhibit the passivation process. For supporting the electrolysis no chemicals were added as effluent contains NaCl as major constituent.

After the experimental run, the treated wastewater was filtered through whatman filter paper No. 1 of 11 μ m pore size. The sludge retained on the filter paper was measured gravimetrically for knowing the sludge generation rate. The filtrate was analyzed for Chemical Oxygen Demand (COD), Color, Conductivity and pH. Current density and power consumptions were also estimated for each of the experiment. The APHA methods were followed for the analysis of the untreated and treated wastewater for characterization [40].

2.4. SEM for best sacrificial electrode combinations

SEM (Scanning Electron Microscope) analysis was carried out for best sacrificial electrode combination using Jeol, JSM-6510LV Scanning Electron Microscope. SEM analysis was taken before and after EC treatment for comparison of texture of surfaces and to study the morphology of electrodes.

3. RESULTS AND DISCUSSION

From the 19 experiments conducted on the chloride rich wastewater with Fe-Al, Al-Al, Fe-Fe and SS-SS electrode combinations are presented in Table 2(a) to 2(d).

Table 2(a). Results of experimentation on chloride rich wastewater with Al-Al electrodes

Voltage (V)	Time (min)	Current density (A/m ²)	Color (Pt Co Units)	COD (mg/L)	Conductivity (mS/cm)	pH	Power consumption (KWh/m ³)	Sludge generation rate (g/L)
12	15	2041.84	451	303	33.8	9.4	162.24	34.2
4	15	386.73	2110	735	32.4	9.4	10.24	7.2
12	15	2248.98	461	307	33.7	9.6	178.70	37.2
4	15	445.92	2260	726	32.5	9.3	11.81	14.3
4	3	493.88	2750	466	31.6	9.5	2.62	3.6
12	3	2469.39	1130	449	31.7	9.7	39.24	7.9
12	3	2588.78	1150	458	32.7	9.9	41.14	9.7
10	6	2326.53	800	693	32.3	9.7	61.62	12.8
6.6	12.9	1171.43	910	346	32.2	9.5	44.03	15.8
5.8	5.7	783.67	1300	111	32.8	9.7	11.44	8.6
9.6	12.6	1952.04	830	228	33.5	9.4	104.23	26.2

8	9	866.33	1260	553	30.8	9.6	27.53	10.2
8	9	1231.63	1000	537	31.3	9.7	39.14	8.1
8	9	1530.61	910	569	31.2	9.6	48.65	15.8
12	9.6	2353.06	390	268	33.3	9.5	119.66	18.0
7.6	3	1425.51	2130	651	31.2	9.3	14.35	8.2
4	8.4	387.76	2560	594	31.4	9.3	5.75	7.8
4	8.4	443.88	2060	570	30.8	9.3	6.58	7.3
7.6	3	1258.16	2320	668	30.8	9.6	12.66	9.4

Table 2(b). Results of experimentation on chloride rich wastewater with Fe-Al electrodes

Voltage (V)	Time (min)	Current density (A/m ²)	Color (Pt Co Units)	COD (mg/L)	Conductivity (mS/cm)	pH	Power consumption (KWh/m ³)	Sludge generation rate (g/L)
12	15	2009.18	94	866	33.4	11.1	155.45	29.1
4	15	459.18	72	874	33.1	11.5	11.84	8.0
12	15	1871.43	98	850	33.2	11.4	144.79	24.1
4	15	381.63	198	819	32.0	10.9	9.84	8.6
4	3	467.35	278	820	32.1	9.9	2.41	3.3
12	3	2023.47	32	529	32.0	11.1	31.31	9.6
12	3	2425.51	32	498	31.3	10.1	37.53	11.7
10	6	1635.71	76	717	33.4	10.3	42.18	12.5
6.6	12.9	774.49	141	702	31.3	11.9	28.34	10.3
5.8	5.7	603.06	280	717	33.2	10.3	8.57	6.3
9.6	12.6	1363.27	86	717	33.4	11.3	70.88	15.7
8	9	1158.16	73	411	33.1	10.8	35.84	13.8
8	9	1419.39	49	378	32.9	11.2	43.93	14.2
8	9	1063.27	142	396	31.7	10.4	32.90	10.9
12	9.6	2288.78	58	835	31.8	10.5	113.33	15.7
7.6	3	1293.88	55	655	31.3	10.4	12.68	7.2
4	8.4	385.71	57	906	31.8	10.5	5.57	5.4
4	8.4	356.12	69	976	31.4	10.2	5.14	4.6
7.6	3	1405.10	38	678	32.3	10.6	13.77	6.4

Table 2(c). Results of experimentation on chloride rich wastewater with SS-SS electrodes

Voltage (V)	Time (min)	Current density (A/m ²)	Color (Pt Co Units)	COD (mg/L)	Conductivity (mS/cm)	pH	Power consumption (KWh/m ³)	Sludge generation rate (g/L)
12	15	2528.57	12	63	35.9	11.9	206.5	24.4
4	15	547.96	30	674	32.1	10.9	14.92	9.7
12	15	2501.02	10	72	36.4	11.6	204.25	25.0
4	15	393.88	47	690	33.2	10.5	10.72	8.4
4	3	225.51	1950	771	31.8	10.2	1.23	3.6
12	3	2618.37	80	594	32.1	10.2	42.77	9.2
12	3	2591.84	83	567	31.8	10.2	42.33	10.3
10	6	2011.22	38	616	32.5	10.9	54.75	12.8
6.6	12.9	876.53	44	412	32.1	10.9	33.86	12.7
5.8	5.7	524.49	274	728	31.9	10.0	7.87	5.1

9.6	12.6	2120.41	41	132	32.6	11.6	116.37	21.4
8	9	1389.80	44	242	33.3	11.2	45.40	15.0
8	9	1286.73	57	228	31.7	10.3	42.03	13.9
8	9	1576.53	53	268	32.1	11.1	51.5	14.1
12	9.6	2839.80	11	268	33.2	11.4	148.43	23.3
7.6	3	800.00	650	190	31.1	9.7	8.27	4.0
4	8.4	175.51	970	632	31.4	9.6	2.67	4.2
4	8.4	169.39	1160	672	31.6	9.7	2.58	5.0
7.6	3	919.39	478	133	31.7	9.5	9.51	4.6

Table 2(d). Results of experimentation on chloride rich wastewater with Fe-Fe electrodes

Voltage (V)	Time (min)	Current density (A/m ²)	Color (Pt Co Units)	COD (mg/L)	Conductivity (mS/cm)	pH	Power consumption (KWh/m ³)	Sludge generation rate (g/L)
12	15	2530.61	32	428	35.3	11.5	190.77	17.3
4	15	484.69	63	242	33.3	12.1	12.18	9.3
12	15	2598.98	26	405	34.9	11.4	195.92	22.7
4	15	604.08	43	230	31.9	11.5	15.18	9.8
4	3	492.86	375	441	31.9	10.1	2.48	3.2
12	3	2528.57	87	381	31.9	10.4	38.12	8.7
12	3	2191.84	89	405	31.7	10.4	33.05	7.9
10	6	1863.27	84	204	32.2	10.3	46.82	10.1
6.6	12.9	935.71	92	242	31.9	10.6	33.36	9.1
5.8	5.7	792.86	133	149	31.7	10.3	10.98	5.7
9.6	12.6	1997.96	42	767	32.2	11.1	101.21	19.0
8	9	1307.14	46	532	31.2	11.2	39.41	12.4
8	9	1322.45	53	502	31.7	11.0	39.88	12.1
8	9	1623.47	45	516	31.5	11.0	48.95	13.5
12	9.6	2826.53	43	527	33.3	11.5	136.37	22.2
7.6	3	1077.55	130	510	31.8	10.6	10.29	5.8
4	8.4	574.49	98	553	32.1	10.5	8.08	6.4
4	8.4	580.61	99	467	31.5	10.8	8.17	6.3
7.6	3	1184.69	138	406	31.3	10.6	11.31	6.1

The first set of experimental runs with Al-Al electrodes were analyzed and maximum COD removal efficiency of 85.3 % at 5.8 V and 5.7 min. treatment time was observed. Sludge generation was 8.6 g/L at 783.67 A/m² current density. Power consumption was 11.44 KWh/m³. The maximum color removal efficiency (81.7 %) was observed at 12V and 9.6 min. treatment time. Current density was 2353.06 A/m². Power consumption and sludge generation were 119.66 KWh/m³ and 18.0 g/L respectively. In the experiments, power consumption and sludge generation were found positively related (3.6 g/L at 2.62 KWh/m³ and 37.2 g/L at 178.7 KWh/m³). At higher power consumption levels, more of the sacrificial electrode (Al) must be getting dissolved and generating more sludge. The Al ions dissolved from the Al anode undergo hydrolysis in the wastewater and form various monomeric and polymeric aluminium hydroxides (Al(OH)₂⁺, Al(OH)₂²⁺, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₁₃(OH)₃₄⁵⁺ etc). At pH ≥ 7 (between 9.3-9.9 pH) these hydroxides undergo polymerization and

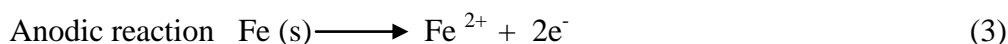
Al(OH)_3 converts into amorphous Al(OH)_4^- through consuming OH^- ions. The amorphous Al(OH)_4^- in turn helps in the coagulation process.

Maximum COD removal efficiency of 50 % at 8 V and 9 min. treatment time was observed with Fe-Al electrode combination. Sludge generation was 14.2 g/L at the current density of 1419.39 A/m^2 and power consumption was 43.93 KWh/m^3 . More than 90 % of color removal efficiency was observed in most of experimental runs. The maximum removal (98 %) was observed at 12 V and 3 min. treatment time and at 2425.51 A/m^2 current density. Power consumption was 37.53 KWh/m^3 and sludge generation rate was 11.7 g/L. Here also power consumption and sludge generation rates in these experimental runs were positively related (3.3 g/L was sludge generation at 2.41 KWh/m^3 power consumption and 29.1 g/L sludge generation at 155.45 KWh/m^3 power consumption). In some of the experimental runs (4 V- 3 min, 8.4 min, 15 min and 12 V- 9.6 min, 15 min) COD was found increasing with the treatment, from the original COD (756 mg/L) to 820 mg/L, 976 mg/L, 819 mg/L, 835 mg/L, 866 mg/L respectively. The increase in COD was also reported in a study [41]. The increase in COD occurs due to leaching of organic matter from the sludge generated during experimental run. Even some compounds form stable products with Fe^{2+} and remain in solution which directly contributes in enhancing the COD [42].

The SS-SS electrode combination gave maximum of 91.7 % COD removal and 99.5 % Color removal at 12 V and 15 min. at 2528.57 A/m^2 current density. Power consumption was 206.5 KWh/m^3 and sludge generation was 24.4 g/L for this experimental run. With increase in current density, dissolution rate of anode also increases. This enhances the metal hydroxides flocs formation and this in turn increased the color and COD removal rates.

The Fe-Fe electrode combination gave 80.3% maximum COD removal efficiency at 5.8V and 5.7 min. treatment time. Sludge generation rate for this experimental run was 5.7 g/L at 792.86 A/m^2 current density. Power consumption was 10.98 KWh/m^3 . At 12 V and 15 min. treatment time the maximum color removal efficiency (98.8 %) was observed with 22.7 g/L sludge generation rate and 2598.98 A/m^2 current density. Power consumption was 195.92 KWh/m^3 . In all the experimental runs with Fe-Fe electrode combination, formation of brown color flocs was observed. Oxidation of ferrous iron into ferric iron could be responsible for this.

SEM of electrodes before performing various EC experiments (Figure 2a) was taken which depicts the plain and uniform surface of Fe electrode. Figure 2b shows the rough surface and presence of troughs and dents of various sizes on its surface resulting due to release of Fe ions (Eq. 3) during dissolution of electrodes [43].



No significant change was observed in pH and conductivity (σ) with the electro-flocculation of CRWW with all the four electrode combinations because ions after treatment is insignificant and hence conductivity is not rising and also in alkaline medium electrolytic processes contains little pH buffering capacity as founded in previous work [41] and it also shows that some of the chlorine derivatives were not produced during electrolytic process as supported by another research [26].

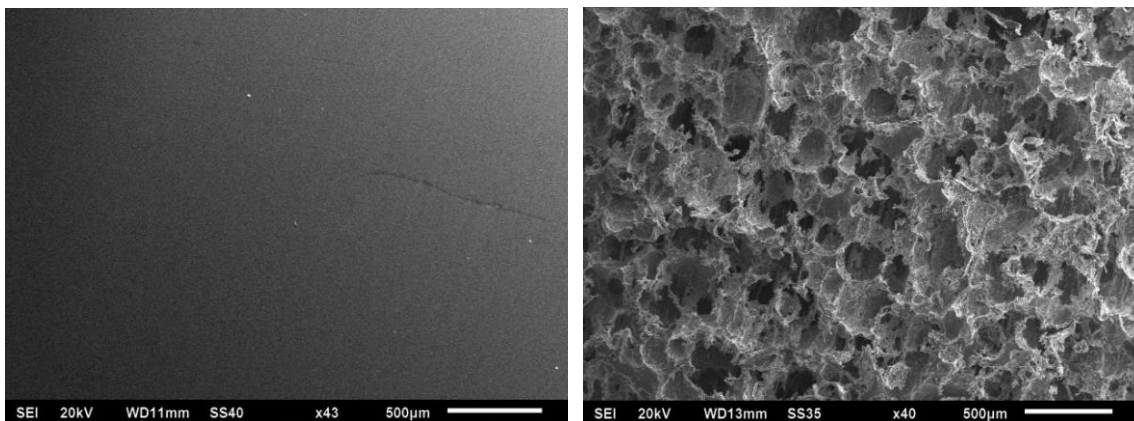


Figure 2. (a) SEM image of Fe Electrode before EC (b) SEM image of Fe Electrode after EC

pH was not adjusted by adding any acid or basic solutions to maintain stability of active intermediates participating in electrolytic process in real time treatment. Due to higher concentration of NaCl in CRWW the chlorine gas evolves at anode which destroys the passive oxide film and forms hypochlorite and OCl^- species during EC. At higher pH (as in our case its 9.53), OCl^- species of chlorine which is strong oxidant, dominates which enhances the COD removal efficiency [44]. As concluded from the experiments the color removal efficiencies with Al-Al electrodes were lower, hence the Al-Al electrodes appeared to be less efficient than SS-SS and Fe-Fe electrodes. For Fe and SS electrodes the phase transfer as well as redox reactions helps in color removal as compared to Al electrodes in which only phase transfer exists as reported previously [45].

3.1. Statistical modeling for Color removal efficiency with Fe-Fe electrodes for CRWW

From the experimental runs, Fe-Fe electrodes are giving promising results, thus it is used for statistical modeling and RSM. The model is significant but *Lack of fit* is not significant. This indicated that model cannot be navigated in the design space (higher noise than signal S/N ratio). The ratio of max to min color removal is only 1.05, for good model which should be more than 1.5. Under these circumstances, it was concluded that the color will be removed also efficiently at low voltage at less treatment time. In an investigation [14] the 8 g/L of NaCl (19.13 mS/cm of conductivity) increase the color removal efficiency by 83% at 2.9 V and 127.8 A/m^2 whereas in our research also with CRWW having high conductivity (32 mS/cm), with Fe electrode 98.8 % color removal efficiency was achieved at 12 V and at current density of 2598.98 A/m^2 , thus it needs low voltage for efficient electroflocculation. Therefore, IV-optimal design strategy of RSM with Design Expert Software was used again for the design of experiments. The 7 experiments were designed and conducted for CRWW with Fe-Fe electrode combination for color removal model. The color removal efficiency, current density, power consumption and sludge generation rate were estimated as shown in Table 3.

Table 3. Set of experimental design as per IV optimal design and results of experimentation on CRWW with Fe-Fe electrodes

S.No.	Voltage (V)	Time (min.)	Current density (A/m ²)	Color (Pt. Co. Unit)	Color removal (%)	Power consumption (KWh/m ³)	Sludge generation rate (g/L)
1	1	1	57.14	1440	32.6	0.02	0.0182
2	1	1	52.04	1569	26.5	0.02	0.0163
3	1	3.25	42.86	940	56.0	0.06	0.1062
4	1	7.75	36.73	126	94.1	0.12	0.3462
5	1	10	38.78	79	96.3	0.16	0.6456
6	1	10	42.86	106	95.0	0.18	0.6310
7	1	5.5	43.88	209	90.2	0.10	0.2626

The original dyebath wastewater was dark red colored, which became pigment red at 1V and 3.25 min. treatment time. The sample looks alike coral pink at 1V 5.5 min. treatment time. After 1V and 10 min. treatment time, the color was almost clear and the sample was representing aesthetically suitable.

The results of ANOVA statistics for color removal are given in Table 4.

Table 4. Results for ANOVA statistics for Color removal for CRWW

Source	Sum of Squares	dF	Mean Square	F Value	Prob>F	
Model	5699	2	2849	121	0.0003	significant
A-Time	5084	1	5084	217	0.0001	
A ²	615	1	615	26	0.0069	
Residual	94	4	23			
Lack of fit	74	2	37	4	0.2071	not significant
Std. Dev.		4.845	R ²	0.984		
Mean		70.100	Adjusted R ²	0.976		
C.V. %		6.912	Predicted R ²	0.951		
PRESS		283.609	Adeq Precision	21.192		

The CV of 6.91 % and predicted R²=0.951 was closed to adjusted R² of 0.976. Also, S/N ratio of 21.2 indicated that model noise is not significant as compared to signal. Thus, model could be navigated in the design space. The unit-less regression equation in terms of coded factors is given in Eq. (1) and in terms of actual factors in Eq. (2).

$$\text{Color removal efficiency (\%)} = +84.46 + 33.61 \times A - 22.34 \times A^2 \quad (1)$$

Where, A: Voltage are in coded units.

$$\text{Color removal efficiency (\%)} = +10 + 19.604 \times \text{min} - 1.103 \times \text{min}^2 \quad (2)$$

Where, min: are in actual units.

ANOVA model was significant and the optimized process conditions are 1V and 8.2 min. to achieve 96.6 % color removal efficiency (Figure 3).

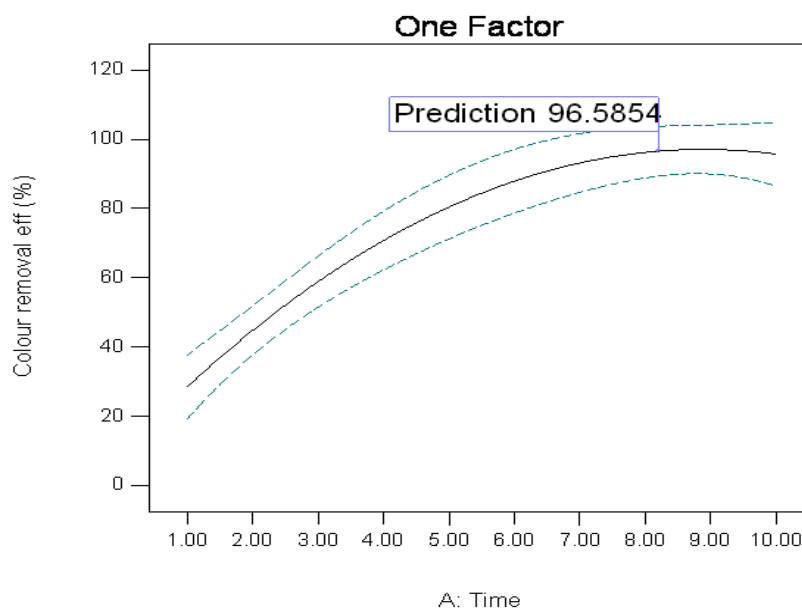


Figure 3. Predicted plot for color removal efficiency at 1V and 8.2 min

The results were verified by validation testing at new proposed conditions. The predicted color removal efficiency value was 96.6 % which was consistent with the practical color removal value of 94.4%. The Total Organic Carbon (TOC) was analysed (TOC-VCPH, Shimadzu, Japan) in lieu of COD for the optimum condition and it comes out to be 13.96 mg/L and indicates 69.5 % TOC removal with sludge generation of 0.46 g/L. The Na, Cl, Ca and Mg was 4010 mg/L, 8132.8 mg/L, 78.2 mg/L and 22.1 mg/L respectively for the treatment at optimum conditions.

4. CONCLUSIONS

The chloride rich textile dyebath wastewater was treated efficiently with iron electrodes. At 12 V and 15 min. treatment time the maximum removal efficiency of 98.8 % for color was observed with sludge generation rate of 22.7 g/L at current density of 2598.98 A/m² with power consumption of 195.92 KWh/m³. ANOVA model was significant with Fe-Fe electrodes and optimized process conditions are 1 V and 8.2 min. to achieve 96.6 % color removal efficiency with only 0.46 g/L of sludge generated. TOC removal efficiency was 69.5 %. The NaCl present in wastewater increases the performance of EC process with no additional electrolyte usage. This treated colourless textile dyebath CRWW may be reused for the reconstitution of dyebath without adding NaCl to dyeing recipe. Overall, the electrolytic processes have the potential to treat textile dyebath chloride rich wastewater which thus enhances the reuse potential of treated effluent.

References

1. I. K. Kapdan and S. Alparslan, *Enzyme Microb. Technol.*, 36 (2005) 273
2. A. Alinsafi, M. da Motta, S. Le Bonte, M. N. Pons and A. Benhammou, *Dyes Pigm.*, 69 (2006) 31
3. Y. K. Ong, F. Y. Li, S. Sun, B. Zhao, C. Liang and T. Chung, *Chem. Eng. Sci.*, 114 (2014) 51
4. J. Dasgupta, J. Sikder, S. Chakraborty, S. Curcio and E. Drioli, *J. Environ. Manage.*, 147 (2015) 55
5. M. Bauman, A. Lobnik, and A. Hribernik, *Ozone Sci. Eng.*, 33 (2011) 23
6. T. Turan-Ertas, *Ozone Sci. Eng.*, 23 (2001) 199
7. M. S. Lucas and J. A. Peres, *Dyes Pigm.*, 71 (2006) 236
8. A. K. Verma, R. R. Dash and P. Bhunia, *J. Environ. Manage.*, 93 (2012) 154
9. K. Sarayu and S. Sandhya, *Appl. Biochem. Biotechnol.*, 167 (2012) 645
10. F. Renault, B. Sancey, P. Badot and G. Crini, *Eur. Polym. J.*, 45 (2009) 1337
11. P. Canizares, F. Martinez, C. Jimenez, J. Lobato and M. A. Rodrigo, *Environ. Sci. Technol.*, 40 (2006) 6418
12. L. Szpyrkowicz, *Ind. Eng. Chem. Res.*, 44 (2005) 7844
13. M. Jovic, D. Stankovic, D. Manojlovic, I. Anđelkovic, A. Milic, B. Dojcinovic and G. Roglic, *Int. J. Electrochem. Sci.*, 8 (2013) 168
14. M. Kashefialasl, M. Khosravi, R. Marandi and K. Seyyedi, *Int. J. Environ. Sci. Tech.*, 2 (2006) 365
15. M. Rangel, J. L. Nava, J. M. Peralta-Hernandez, G. Carreno and R. J. Guerra-Sanchez, *Int. J. Electrochem. Sci.*, 8 (2013) 3310
16. M. Kobya, N. Erdem and E. Demirbas, *Desalin. Water Treat.*, 56 (2015) 1191
17. K. Vijayaraghavan, D. Ahmad and R. Lesa, *Ind. Eng. Chem. Res.*, 45 (2006) 6854
18. J. P. Kushwaha, V. C. Srivastava and I. D. Mall, *Sep. Purif. Technol.* 76 (2010) 198
19. K. Eryuruk, U. Tezcanun and U. Bakir Ogutveren, *Int. J. Environ. Res.* 8 (2014) 461
20. M. Al-shannag, Z. Al-qodah, K. Bani-melhem, M. R. Qtaishat and M. Alkasrawi, *Chem. Eng. J.* 260 (2015) 749
21. M. Kobya and S. Delipinar, *J. Hazard. Mater.* 154 (2008) 1133
22. M. Kobya, H. Hiz, E. Senturk, C. Aydiner and E. Demirbas, *Desalination*, 190 (2006) 201
23. R. Shanker, L. Singh, P. Mondal and S. Chand, *Desalin. Water Treat.*, 52 (2014) 7711
24. K. Ighilahriz, M. Taleb Ahmed, H. Djelal and R. Maachi, *Desalin. Water Treat.*, 52 (2014) 5833
25. O. T. Can, *Desalin. Water Treat.*, 53 (2015) 919
26. S. S. Vaghela, A. D. Jethva, B. B. Mehta, S. P. Dave, S. Adimurthy and G. Ramachandriah, *Environ. Sci. Technol.* 39 (2005) 2848
27. H. Singh, G. Singh, M. S. Bhatti and A. S. Reddy, *Desalin. Water Treat.*, 56 (2014) 665
28. I. Arslan-Alaton, I. Kabdasli, B. Vardar and O. Tunay, *J. Hazard. Mater.*, 164 (2009) 1586
29. M. A. Garcia-Morales, G. Roa-Morales, C. Barrera-Diaz, V. Martinez Miranda, P. Balderas Hernandez and T. B. Pavon Silva, *Int. J. Electrochem. Sci.*, 8 (2013) 8752
30. A. H. El-Shazly and M. A. Daous, *Int. J. Electrochem. Sci.*, 8 (2013) 184
31. K. Ulucan, H. A. Kabuk, F. Ilhan and U. Kurt, *Int. J. Electrochem. Sci.*, 9 (2014) 2316
32. N. Moulai-Mostefa, S. Ladjelat, H. Kermet-Said, M. Krea and M. Tir, *Desalin. Water Treat.*, 52 (2014) 2382
33. M. S. Bhatti, A. S. Reddy, R. K. Kalia and A. K. Thukral, *Desalination*, 269 (2011) 157
34. K. Thirugnanasambandham, V. Sivakumar and J. P. Maran, *Desalin. Water Treat.*, 55 (2015) 1703
35. E. Sik, M. Kobya, E. Demirbas, M. S. Oncel and A. Y. Goren, *Desalin. Water Treat.*, 56 (2015) 1177
36. F. Ozyonar, *Desalin. Water Treat.*, 57 (2016) 2389
37. A. Maleki, H. Daraei, B. Shahmoradi, S. Razee and N. Ghobadi, *Desalin. Water Treat.*, 52 (2014) 2400
38. V. Khandegar and A. K. Saroha, *J. Environ. Manage.*, 128 (2013) 949

39. R. H. Myers, D. C. Montgomery and C. M. Anderson-cook, *Response surface methodology: Process and product optimization using designed experiments*, Wiley, Hoboken, NJ (2009)
40. APHA, AWWA, WEF. *Standard Methods for the examination of water and wastewater*, 22nd ed., American Public Health Association, American Water Works Association and Water Environment Federation, Washington (2012)
41. Z. Zaroual, M. Azzi, N. Saib and E. Chainet, *J. Hazard. Mater. B*, 131 (2006) 73
42. H. A. Moreno-casillas, D. L. Cocke, J. A. G. Gomes, P. Morkovsky, J. R. Parga and E. Peterson, *Sep. Purif. Technol.*, 56 (2007) 204
43. V. S. Jagati, V. C. Srivastava and B. Prasad, *Sep. Purif. Technol.* 50 (2015) 181
44. M. Deborde and U. V. Gunten, *Water Res.* 42 (2008) 13
45. I. Kabdasli, B. Vardar, I. Arslan-Alaton and O. Tunay, *Chem. Eng. J.*, 148 (2009) 89

© 2017 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).