Treatment of Reactive Red 195 Textile Dye Solution by Electrocoagulation Process

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Abstract

Textile and dyeing sectors are highly water intensive sectors. Typically, untreated dye wastewaters are intensely coloured and highly resistant to biodegradation due to their complex chemical structures.In the present work, the decolorization and removal of Reactive Red 195 (RR-195) textile dye in aqueous medium by employing electrocoagulation technique using aluminium (Al) and iron (Fe) sacrificial anodes has been investigated. The treatment efficiency is analysed in terms of percentage decolorization of 25 mg/L of RR-195 dye solution at an initial pH of 7.7 and a current density of 6 mA/cm2 in 2 g/L NaCl electrolyte medium for an electrolysis duration of 30 min. The present study proves the efficacy of electrocoagulation, with Fe-Fe electrode pair resulting in a higher RR-195 dye decolorization efficiency of 96.4% as compared to 84.7% for Al-Al electrode pair.Pseudo-first order kinetic constant (k) values were observed to be 0.0618 min-1 and 0.1258 min-1 for Al-Al and Fe-Fe electrode pairs respectively implying higher dye decolourization and removal rates exhibited by Fe-Fe electrode pair.

Keywords: *- Electrocoagulation (EC),Reactive textile dye, Reactive Red 195, Aluminium (Al) electrode, Iron (Fe) electrode, Electrolysis, Decolourization, Kinetics*

INTRODUCTION

Wastewater generated as a result of anthropogenic activities resulting from domestic, commercial and industrial sources not only impact the quality of the water negatively but also pose significant threats to biotic and abiotic components of ecosystem [1].

Availability of clean water to a vast majority of the global population has emerged as one of the major challenges of the 21st century [2]. Textile sector is one of the highest consumers of water [3]. There is a huge market for reactive dyes in textile industry attributed to their bright colour ranges and high affinity for the fibers [4].

It has been reported that globally 8000 tons/annum of reactive dyes are released into the aqueous environment [4]. Textile industry wastewaters represent a substantial source of environmental degradation due to presence of high concentrations of refractory organic compounds that can have serious implications on the aqueous ecosystems [5]. Wastewaters generated from textile, dyeing and finishing industries are characterized by very high total dissolved solids (TDS), intense colour, chemical oxygen demand (COD) and much fluctuating pH levels [6].

Technologies conventionally employed to treat such harsh wastewaters fall under various biological, chemical and physical categories that include chemical precipitation, adsorption, chemical coagulation, photo-oxidation, and biodegradation [3].

Since these methods involve high investment and operating costs in addition to lower treatment performance, there emerges an urgency to investigate more inexpensive and robust methods that need least chemical and energy utilization along with reasonable footprints [7].

Electrochemical techniques offer various merits in terms of no chemical consumption, no sludge generation, least footprint requirement low capital costs and ease of process control [8]. In recent times, studies have focused on application of electrocoagulation (EC) technology for treating difficult effluents that has proven to be a potential tool offering high pollutant removal efficiencies [6,7].

Electrocoagulation is a process of creating flocs of metallic hydroxides within the effluents by electro-dissolution of soluble sacrificial anodes, typically consisting of aluminium (Al) and iron (Fe) [7]. In electrocoagulation, direct current is passed between sacrificial metal anodes like Fe and Al immersed in wastewater that causes dissolution of these metal anodes generating metal ions [3]. The process is pH driven and at optimum pH, these ions form diverse ranges of in-situ metal hydroxides and coagulated species that cause destabilization and aggregation of suspended solids and even precipitation and adsorption of dissolved organic pollutants [8,9].

Electrocoagulation has been applied with appreciable success for treating various urban, industrial and domestic wastewaters that include a variety of pollutants such as anions, suspended oil droplets, dyes as well as heavy metals [2,8,9]. EC has also proven to substantially reduce the sludge generation in comparison to conventional chemical coagulation because of production of hydrogen (H_2) microbubbles at the cathodic sites [8].

As EC requires low power, it has been recommended to power these installations from renewable energy sources [4]. Especially EC treatment of industrial effluents from oil refineries, slaughterhouses, tanneries, pulpand paper mills, laundries, paints, yeast, pharmaceuticals, polymers and landfill leachates have drawn significant attention in present times [2]. Table 1 compiles works on application of electrocoagulation for removal of various contaminants in aqueous medium reported in literature.

Important operating factors affecting performance of electrocoagulation are typeand choice of electrolyte type and concentration [2]. These factors together determine the overall electrocoagulation performance.

Table 1- Reported studies on electrocoagulation

Pollutant treated	Initial concentration (Co)	Anode-Cathode /Arrangement	pH	Current density (j)	Supporting electrolyte	Treatment time	Removal Efficiency (%)	Reference
Textile wastewater	COD = 3422 mg/L TOC = 900 mg/L	Al-Fe / Monopolar	Acidic (Al), weakly alkaline (Fe)	80–100 A/m^2	Conductivity = 3990 μS/cm	10 min	Turbidity - 98% COD – 61-65%	6
Levafix orange textile dye	100 mg/L	Al / Monopolar	6.4	100 A/m^2	NaCl	12 min	Decolorization = 95%	7
Acid green dye 50	100 mg/L	Graphite – Stainless steel mesh	6.9-11	3.51 mA/cm^2	NaCl	21 min	COD – 87% Decolorization = 97%	3
Acid Orange 7	50 mg/L	Al-Fe	7.1	15.5 mA/cm^2	NaCl, Conductivity = 7.5 mS/cm	5 min	Decolorization = 98%	8
Textile industrial wastewater	COD = 478 – 800 mg/L	Steel-Al	6-9	5-11mA/cm^2	Conductivity = 668.8-51200 μS/cm	5-15 min	Turbidity - 82% COD – 59% Decolorization = 86%	12
Reactive Black 5	50 mg/L	Al-Fe/ Monopolar	6.03-7.76	1.04–8.33 A/m^2	KNO_3, Na_2SO_4, NaCl, $NaNO_3$, NH_4Cl, K_2SO_4, KCl	10 min	RB5 Removal - 45-98% Decolorization = 98%	4
DanixMarinho S-2G 200 %	50 mg/L	Al	7	6 A	NaCl	10 min	Decolorization = 99.86%	5
Remazol Brilliant Blue R	50 mg/L	Al	9	8 A	NaCl	40 min	Decolorization = 99.65%	5

Based on reported literature, not enough work has been undertaken on electrocoagulation of Reactive Red 195 (RR-195) dye, hence it was chosen as model pollutant for the present work [13].The present study is aimed at investigating the performance of electrocoagulation technology in terms of percentage decolorization and removal of recalcitrant RR-195 dye in aqueous medium using Al and Fe anodes that are easily available, characterized by least toxicity and rapid electro-dissolution.

ELECTROCOAGULATION (EC) MECHANISM

Following reactions occur during the electrocoagulation process at the anode and cathode [2]. Metal anode generates cat ions by reaction (1). These highly charged positive ions destabilize colloids by developing polyvalent hydroxide complex that tend to exhibit good adsorption properties, forming pollutant agglomerates. Hydrogen and oxygen gases evolve during the process that help in mixing and further flocculation.

Anode: $M_s \rightarrow M^{n+}_{(aq)} + ne^-$ (1)

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2g} + 4e^- \quad (2)$$

Cathode: $M^{n+}_{(aq)} + ne^- \rightarrow M_s$ (3)

$$2H_2O_{(l)} + 2e^- \rightarrow H_2 + 2OH^-_{(aq)} \quad (4)$$

Main reactions at anode and cathode considering aluminium (Al) anode are [6,8,10]:

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (5)

Cathode:

$$3H_2O_{(l)} + 3e^- \rightarrow 1.5H_2 + 3OH^-_{(aq)} \quad (6)$$

Reactions (5) and (6) produce Al^{3+} and OH^- ions that react to form diverse monomeric species like $Al(OH)^{2+}$, $Al_2(OH)^{2+}$, $Al(OH)_4$ and polymeric species like $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$ and $Al_{13}(OH)_{34}^{5+}$ that finally get transformed into Al(OH)$_{3(s)}$ as per the following reaction:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (7)$$

Amorphous Al(OH)$_{3(s)}$ also referred to as sweep flocs possess large surface area that rapidly adsorb soluble organic contaminants and trap colloids. These flocs can be further removed from aqueous solution by H_2 flotation or settling.

Main reactions at anode and cathode considering iron (Fe) anode are [6,8,10,12]:

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (8)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (9)$$

Cathode:

$$2H_2O_{(l)} + 2e^- \rightarrow H_2 + 2OH^-_{(aq)} \quad (10)$$

Overall:

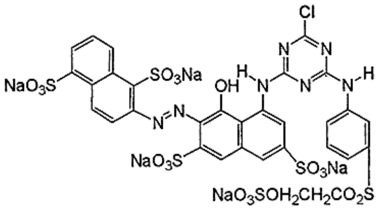
$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 (11)$$

MATERIALS AND METHODS

I. Materials

Commercially available reactive azo dye, Reactive Red 195 (RR-195),was procured from a local vendor and its characteristics are shownin Table 2.

Table 2- Characteristics of RR-195 dye

Structure	
CAS number	93050-79-4
Molecular formula	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$
Molar mass	1136.32
λ_{max} (nm)	543 nm

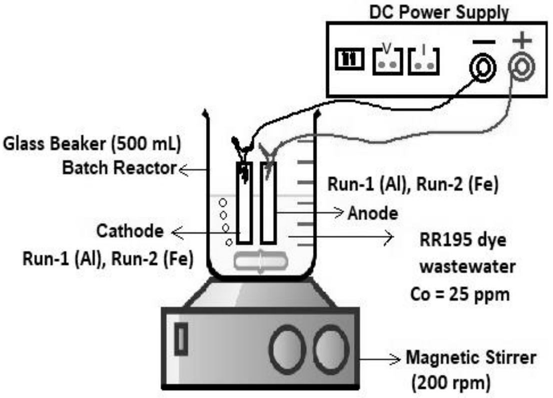


Figure 1 Experimental apparatus

Two electrodes (5cm x 7cm x 0.3cm), acting as anode and cathode, with an inter-electrode distance of 1 cm and an effective area of 25 cm2were immersed in the dye solution. The electrodes were connected to a digital D.C. power supply (Aplab India, LD-3205).

EXPERIMENTAL PROCEDURE

Two experimental runs were conducted in batch mode at room temperature of 30^{0}C under atmospheric pressure. In Run-1, Al plates of similar dimensions were used as both anode and cathode and in Run-2, Fe plates of same sizes were employed as anode and cathode each. Stirring was advantageous for efficient dye removal which was maintained constant at 200 rpm. Before each run, the electrodes were washed with acetone and further etched in 35% HCl solutionto remove surface impurities. For each experimental run, 500 mL of 25 ppm RR-195 dye solution was prepared in tap water. NaCl was selected as electrolyte for present work as it gives best colour removal for RR-195 dye amongst different studied electrolytes such as NaCl, KCl, Na2SO4 and Na2CO3 due to generation of hypochlorite ions (OCl□) that offer higher oxidation potential [14]. NaCl concentration of 2 g/L was used for each run. It is reported that operational pH range of 4-9 produces various polymeric species of metals that further precipitate as metal hydroxides [13]. Based on work reported on electrocoagulation for RR-195, final dye removal efficiency is least affected by initial acidic or basic pH and hence in the present work, no initial pH setting is done and work is carried out at an initial pH of 7.7 which is in the range of 4-9 [13].Current density of 6 mA/cm^2 was employed to conduct electrolysis.Electrolysis was carried out for 30 minutes and treated samples were withdrawn every 15 minutes for analysis.

ANALYTICAL METHODS

UV/Vis spectrophotometer (Shimadzu, Japan, UV-1800) was used to record the maximum wavelength of RR-195 dye (λ_{max}= 543 nm) samples which was further employed to estimate the dye concentration by means of a pre-generatedcalibration plot. The percentage decolourization was calculated using equation (12) [12]:

$$Decolourization(\%) = \frac{Abs_0 - Abs_t}{Abs_0} \times 100 \quad (12)$$

where Abs_0 and Abs_t are absorbances before and after electrolysis time *t*, respectively, at the maximum wavelength (λ_{max}) of the dye. Calibration plot was generated for RR-195 dye solutions in the concentration range of 5 – 50 mg/L with an interval of 5 mg/L as shown in Figure-2.

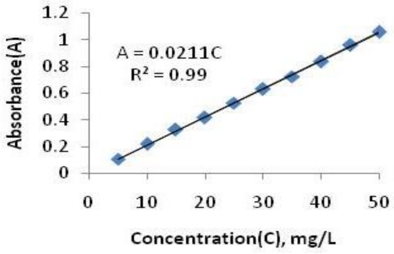


Figure 2 Calibration plot for RR-195

RESULTS AND DISCUSSION

Table 3 shows Absorbance recorded for electrode pairs Al-Al (run-1) and Fe-Fe (run-2) using UV-VIS spectrophotometer at λ_{max} = 543 nm for RR-195.Using equation (12), variation in percentage decolorization with respect to electrolysis time were estimated for both the electrode pairs, Al-Al (run-1) and Fe-Fe (run-2) for an electrolysis duration of 30 minutes. Figure-3 shows the percentage decolourization plotted as a function of electrolysis time for run-1 and run-2.

Table 3- Absorbance recorded for electrode pairs Al-Al (run-1) and Fe-Fe (run-2)

Time (minutes)	Run-1: Al-Al	Run-2: Fe-Fe
	Absorbance (A)	Absorbance (A)
0	0.486	0.501
15	0.203	0.031
30	0.074	0.018

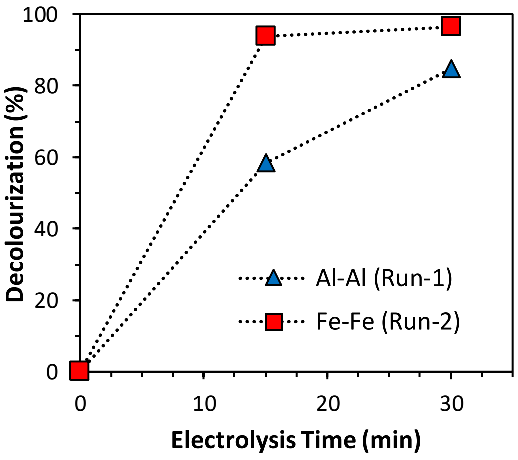


Figure 3 Decolourization (%) as function ofelectrolysis time for Al-Al and Fe-Fe electrode pairs

As seen from the figure, after 30 minutes of electrocoagulation, Fe-Fe electrode pair resulted in a higher decolorization efficiency of 96.4% compared to 84.7 % for Al-Al electrode pair at operational pH of 7.7.

The mechanism of RR-195 dye decolourization may involve the dye molecules being adsorbed by both electrostatic attraction and physical entrapment by metal hydroxide flocs. Further these flocs being insoluble can eliminate dye by surface complexation since the dye molecule can exhibit a ligand character that binds hydrous moiety with both adsorption as well as precipitation [13]. Electrostatic attraction involves metal species binding to the anionic organic (dye) molecule sites thereby causing charge neutralization and reducing their solubility. This further causes adsorption of organic pollutants on metal hydroxide precipitates that are typically amorphous in nature [15].

Figure-4 shows the variation of RR-195 dye concentration plotted as a function of electrolysis time for run-1 and run-2.After 30 minutes of electrocoagulation, Fe-Fe electrode pair resulted in a higher RR-195 dye removalwith its concentration dropping from 25 mg/L to 0.853 mg/L compared to 3.507 mg/Lby Al-Al electrode pair at pH of 7.7.Figure-5 shows visual change in colour intensity of the reaction contents after electrocoagulation conducted for 30 min using Fe-Fe and Al-Al electrode pairs.

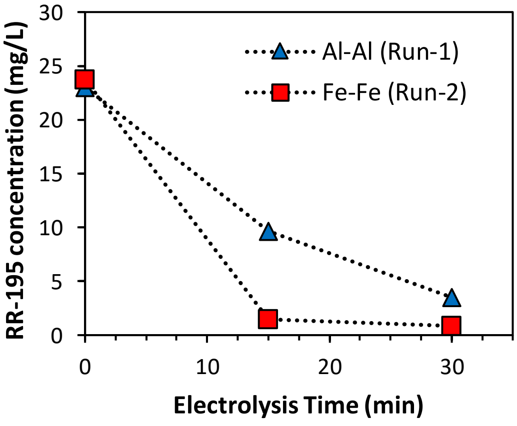


Figure 4RR-195 dye concentration as function ofelectrolysis time for Al-Al and Fe-Fe electrode pairs

Al and Fe coagulants are widely applicable coagulants due to their multivalent features [11]. Based on inference made from present study, Fe-Fe electrode pair is observed to perform better in terms of colour and dye removal compared to that by Al-Al electrode pair in presence of NaCl electrolyte which is also reported in literature [4]. Fe electrodes are a better choice over Al electrodes due to formation of metal hydroxide precipitates in a wider pH range [4,9].

Moreover, it is also reported that Fe electrodes produce more coagulants than Al electrodes at the same current density as per Faraday's law [4] which highlights superior performance of Fe over Al.

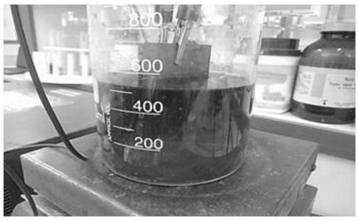


Figure 5 (a) Colour before electrolysis

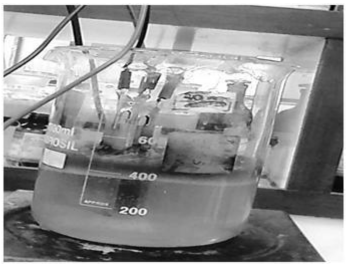


Figure 5 (b) Change in colour with Al-Al pair after 30 min electrocoagulation

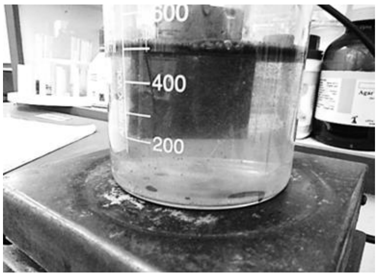


Figure 5 (c) Change in colour with Fe-Fe pair after 30 min electrocoagulation

Addition of NaCl as electrolyte enhances solution conductivitythat reduces its ohmic resistance thereby reducing the electrical energy consumption [4,11]. Voltage requirement for electrodissolution also diminishes appreciably in presence of chloride-based supporting electrolytes [9,11].Physicochemical properties of coagulants such as solubility and electrical conductivity of metal hydroxides as well as size of colloidal coagulant complexes are regulated by operating pH. Neutral and alkaline pH are beneficial for efficient coagulation [9,11]. It has been confirmed by various authors that in the pH range of 5.5 – 8.5, most of electrogenerated Fe^{3+} ions form $Fe(OH)_3$ flocs that can rapidly remove dye molecules by electrostatic attraction or complexation, further followed by coagulation [2,9,11,12]. Moreover, comparing Figures–5(b) and 5(c), it is evident that considerable sludge generation was observed for Al-Al electrode pair compared to that by Fe-Fe electrode pair.

Kinetics of RR-195 decolourization

Considering pseudo-first-order kinetics assumption, a simple kinetic analysis process was adopted as shown in equation (13) [16]:

$$\frac{-d[C]}{dt} = k[C] \quad (13)$$

The (ln) plot of the dye concentration (C) curve given by equation (13) represents the plot of the rate expression whose slope gives the value of rate constant k ($time^{-1}$).

$$\ln\frac{[C]_o}{[C]} = k\,t \quad (14)$$

Figure-6 shows the plot of dimensionless RR-195 dye concentration (ln(Co/C)) against electrolysis time (t) for Al-Al and Fe-Fe electrode pairs. From figure-6, the kinetic constant (*k*) values evaluated using equation (14)were found to be 0.0618min^{-1}(R^2 = 0.999) and 0.1258 min^{-1}(R^2 = 0.946) for Al-Al and Fe-Fe respectively which implied higher dye decolourization and removal rates exhibited by Fe-Fe electrode pair compared to Al-Al electrode pair.

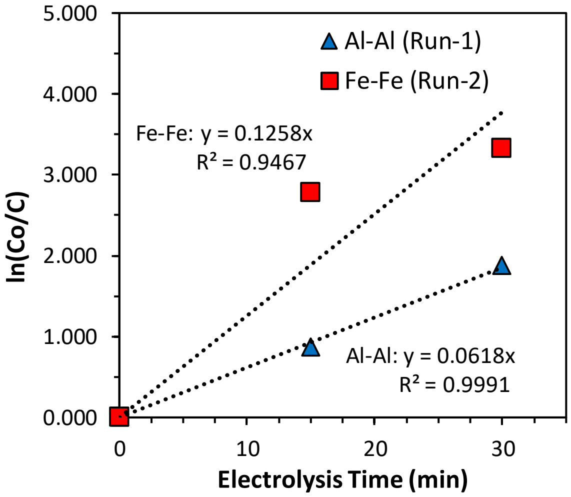


Figure 6Kinetic analysis of RR-195 decolorization

CONCLUSION

Electrocoagulation method is applied successfully to decolorize and reduce the concentration of reactive textile dye RR-195 (25 mg/L) from its aqueous solution using two different sacrificial electrode pairs Al-Al and Fe-Fe. Typical operating conditions for the experimental runs were 6 mA/cm2, 30 min electrocoagulation duration, initial pH 7.7 and 2 g/L NaCl. Fe-Fe electrode pair gave a superior performance compared to Al-Al electrode pair in terms of higher colour and dye removal by about 12% in presence of NaCl electrolyte medium attributed to production of more and robust in-situ coagulant species compared to Al at the same current density. Also, a more transparent solution with less sludge generation was observed using Fe-Fe electrode pair. The electrocoagulation set-up adopted in this work offers simplicity in construction, design and operation and can be employed as a suitable tool for removing textile dyes.Anode material plays a dominant role in releasing metallic ions to coagulate pollutants and thus, coagulants bearing higher charge valances are much preferable [4]. In addition to increase in solution conductivity, increase in current density is reported to enhance the rate of anode dissolution and thereby the generation of metal ions that results in increased metal hydroxide flocs thereby improving the pollutant removal efficiency [13].

Apart from achieving higher pollutant removal efficiencies, it is also needed to improvise the sludge handling aspect as it would lessen the burden of environmental disposal [7]. In addition, optimal design of reactors with minimum energy consumption for electrocoagulation employing renewable energy sources also need to be explored that would increase the economic viability of applying electrocoagulation technology at commercial scale of operation [7].

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