

Electrolyte Assisted Sono-Electrochemical Decomposition of Reactive Red 195

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Summary: Untreated textile wastewater causes serious environmental impacts due to the presence of unfixed dyes. A commonly used Reactive Red (RR) 195 dye is significantly discharged in textile effluents thus enhancing water pollution. Therefore, the current research was conducted for the treatment of reactive dye RR 195 by electrolyte assisted electrochemical process at various process conditions i.e. initial dye concentrations, pH, and concentration of supporting electrolyte (NaCl). The decomposition of dye and color removal was analyzed using UV-Vis spectrophotometer. The results indicated that pH and NaCl were playing an important role in the degradation of RR 195. It was observed that 95.4% of dye was decomposed using 1.5g/L NaCl at pH 3 after 25 min. Kinetics studies showed that degradation of RR195 apparently followed second order reaction. The electrical energy consumption was found to be 6.11 Whm³ for dye effluent at 100 Am² current density. For the justification of findings in experimental results Bayesian regression analysis was used to determine the effect of NaCl, pH and dye concentration on degeneration of RR195. It was observed that NaCl had positive impact whereas pH and dye concentration had negative impact on degeneration of RR195.

Keywords: Electrochemical degradation, Sono-electrochemical decomposition, RR195 dye, Electrolyte assisted electrolysis, Treatment of textile dye, Bayesian regression for electrochemical process.

Introduction

The effluent discharged from textile and dyestuff industries contain significant amounts of reactive compounds. These compounds are generally released into streams and thus are resulted the severe contaminations of surface and ground waters [1]

Reactive dyes have been widely used in textile industries due to their excellent fastness properties and presences of reactive groups which bind on fibers through covalent bonds. However, the affinity of reactive dyes for fabrics is low resulting the discharge of high dye concentrations in textile wastewaters [2]. These unfixed dyestuffs in wastewater pose serious environmental problems as they are highly toxic and carcinogenic in natural environment. Therefore, it is necessary to remove the pollutants from the wastewater before their final discharge in the environment [3].

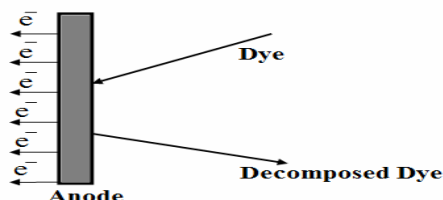
Different processes have been used to remove dyes from textile wastewater. These can be classified in four main groups; physical (membranes filtration, nano-filtration, adsorption, etc.), chemical (oxidation, hydrolysis, electrolysis, ozonolysis, photocatalysis, etc.), physicochemical (ion exchange,

coagulation, flocculation, reverse osmosis, etc.) and biological (aerobic and anaerobic decomposition, enzymatic decolourization, etc.) [4]. The physicochemical processes used for the purification of dyeing wastewater are effective for decolourization, but their use is limited due to the problems associated with sludge generation and disposal. The other chemical methods such as ozonolysis and photocatalysis also give rapid decolourization, along with degradation of dyes but these methods are quite expensive and have operational difficulties [5-9]. Although biological methods are cheap and simple to apply but the pollutants caused by textiles industries cannot easily be degraded by traditional biological process and remain in the effluent and stay in the environment.

The electrochemical oxidation process is a promising method and has been applied successfully for the degradation of reactive dyes. This method is cost effective with little or no chemical consumption, and reduced problem of sludge generation [10]. Electrochemical processes are of two types, direct and indirect oxidation. Former takes place directly on the electrode surface, while later takes place

indirectly at anode surface due to the presence of some electrolyte in bulk solution. During indirect oxidation, while using NaCl as an electrolyte the most common oxidants chlorine and hypochlorite radicals are formed, which react with the organic matter present in bulk solution (Fig. 1) [11].

Direct Oxidation Mechanism



Indirect Oxidation Mechanism

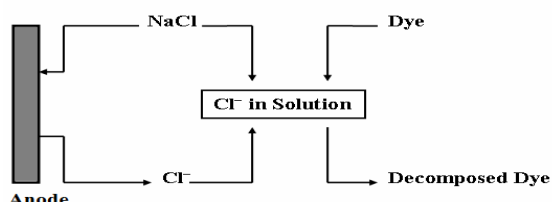


Fig. 1: The Scheme of Pollutant (Dye) removal pathway in electrochemical Oxidation.

In both type of electrochemical oxidation processes, the simultaneous oxidation of pollutants and water takes place at anode when applied cell voltage is high. At low cell voltage O₂ evolution does not take place because of the formation of some side products by direct oxidation. These by-products adsorb on surface of anode and hence decrease its efficiency. Therefore, low voltage is not utilized for the current study [12]. The current study focused on the degradation and decolouration of reactive red 195 (Table-1) by indirect electrochemical method

Table-1: General Characteristics of RR195.

Chemical Structure	
CAS	93053-79-4
Molecular formula	C ₃₁ H ₁₉ ClN ₇ O ₁₉ S ₆ .5Na
Molecular mass (g/mol)	1136.31
λ _{max} (nm)	542
Natural pH	5.6

The objective of the current study was to investigate the effect of electrolyte assisted electrochemical oxidation process on the decolourization and degradation of RR195 at different experimental conditions such as initial concentration of dye, pH and concentration of

electrolyte for the efficient removal of azo dye in aqueous solution. During electrolyte assisted electrochemical degradation of RR195, the rate and kinetics of reaction and energy consumptions were determined and experimental conditions were optimized. Further, Bayesian regression model is used to support the results obtained from experiments.

Table-2: Second order rate constant k_{obs}, half-life t_{1/2}, and regression coefficients R² for degradation of RR195 at different initial concentration.

Dye concentration (ppm)	k _{obs} (L mg ⁻¹ min ⁻¹)	t _{1/2} (min)	R ²
60	0.57774	0.02958	0.9887
80	0.65469	0.01979	0.9883
100	0.83996	0.012916	0.9717

Results and Discussion

Effect of NaCl Concentration on the Degradation of RR195

The effect of chloride ions on during decolourization of model dye solution at different concentrations of NaCl was studied. The addition of supporting electrolyte (NaCl) increases the conductivity and thus, decreases the energy cost of the process. Fig. 2 shows that at 0.5 g/L of NaCl, the degradation rate of RR195 was as low as 49%. By increasing its concentration to 7 g/L, maximum degradation occurs after 5 min. However at 1.5 g/L of NaCl, the rate of decolourization was increased to 95.4% in 25minutes. By increasing the concentration of chloride ion, the decomposition rate was also increased. This improvement in decolourization process can be explained by the reaction taking place at anode (equation 1).

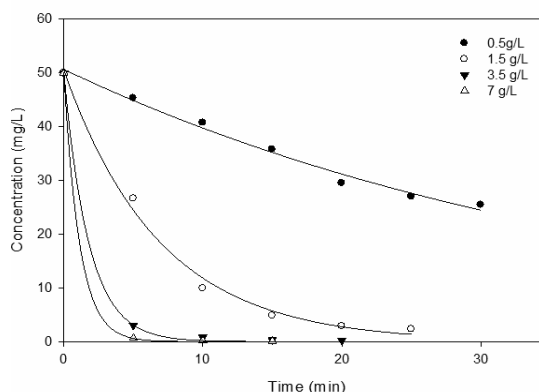
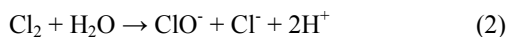


Fig. 2: Effect of NaCl concentration on the degradation of RR 195 (conditions: pH 3, current density = 100 Am⁻², dye concentration = 50 mg/L).

The generated chlorine can be converted quickly into hypochlorite in solution:



The generated hypochlorite in equation 2 can enhance the decolourization of RR195, while the chloride ion can be recycled and used as the reactant [13].

The further experiments were conducted at 1.5 g/L of sodium chloride concentration, in order to keep total dissolved solid (TDS) concentration low in treated water. Although the chloride concentration is high (5000–10000 mg/L) in real textile processing wastewater [14].

Effect of pH on Degradation of RR 195

The RR195 dye solution was adjusted to the different pH values (3, 5.6, 7, 9 and 11) using NaOH and HCl to determine its effect on its decolourization during the electrochemical degradation. During this processes NaCl (1.5g/L) was also used as a supporting electrolyte. The results showed (Fig. 3) that by increasing the pH of solution, the percent decomposition of dye was decreased. At pH 3 maximum degradation efficiency was 95.4% in 25 minutes. The higher rate of decolourization in acidic medium is because of the formation of hypochlorous acid since at basic pH production of chlorine/hypochlorite is decreased (equations 3 and 4) [15].

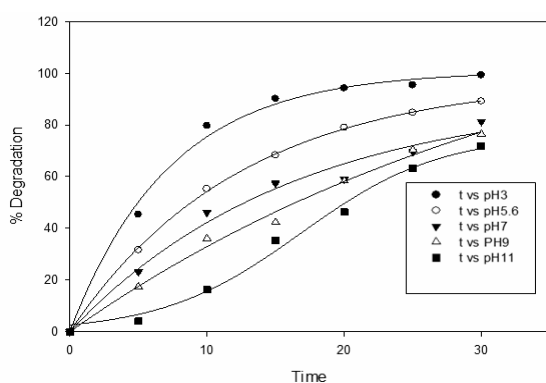
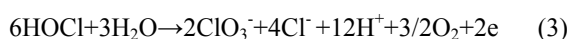


Fig. 3: Effect of pH on the electrochemical degradation of Reactive Red 195 (conditions: current density = 100A/cm², sodium chloride = 1.5 g/L, Reactive Red concentration = 50mg/L, reactor volume = 1 L).

The increase in rate of decolorization by higher production of hypochlorous acid is also explained by oxidation potential values.. Hypochlorous acid has higher oxidation potential than hypochlorite [17]. The mediated oxidation of dyes with these species is then expected to be faster in acidic than in alkaline media because of the higher standard potential of Cl₂ (aq) (E° = 1.36 V vs. SHE) and HClO₃⁻ (E° = 1.47 V vs. SHE) than ClO⁻ (E° = 0.89 V vs. SHE). However, the rates of electrode reactions are a function of the electrocatalytic activity of the anode, chloride concentration and current density [16].

Effect of Initial Concentration of RR195

The influence of initial dye concentration by electrolyte assisted electrochemical process was studied in the range from 20 to 100 mg/L while the other conditions were remained constant. It was observed that the net amount of color removal decreased with increase in the concentration (Fig. 4). The concentration of dye was found to be inversely proportional to dye degradation. The increase of RR 195 dye concentration from 20 to 100 mg L⁻¹ decreased the decolourization from 98.07% to 47.82%. As the initial dye concentration increased, the rate of RR 195 decomposition decreased. This may be explained by the fact that, the production rate of chlorine/hypochlorous acid is constant and the increased amount of dye may require to increase the concentration of hypochlorous acid.

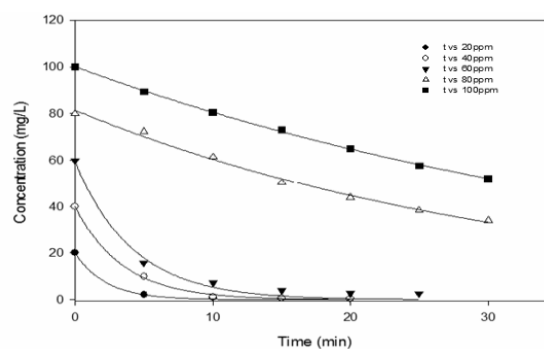


Fig. 4: Effect of initial dye concentration on the degradation of RR195 Note: Dye concentration 20mg/L to 100mg/L, Current density 100Am⁻²; initial pH 3; concentration of supporting electrolyte (NaCl) 1.5g/L.

Energy Consumption for the Degradation of RR195

The energy consumption for the degradation of RR195 by electrochemical degradation process is

calculated by using equation 3. As per the results the minimum electrical energy consumption was 6.11 Whm^{-3} for dye effluent at 100 Am^{-2} current density.

UV-visible Spectral Changes During the Degradation of RR-195

The UV-visible spectrum of RR195 at 50 mg/L , pH 3 and amount of NaCl 1.5 g/L by using electrochemical method is shown in Fig. 5. An absorption band from 200 nm to 800 nm was observed. The maximum absorbance ($\lambda \text{ max}$) of RR195 was found to be at 542 nm in the visible region because of the chromophore (color producing -N=N-) group. During electrochemical degradation process sample was analyzed at different interval of time. The maximum decolouration of RR195 was observed in 25 min of electrolysis at pH 3. At this pH active chlorine species hypochlorous acid, generated has oxidized the effluent effectively. During electrochemical degradation, the cleavage of chromophoric groups present in the reactive red has occurred, which resulted in the decrease of absorbance at 542 nm.

Kinetic Studies

During the electrochemical process, the elimination of colour occurs due the breakage of azo bond (-N=N-) [6]. In order to determine the the

number of chemical species involved in electrochemical degradation of RR195, its kinetic studies were undertaken at different dye concentrations by keeping all parameter constant. The electrochemical degradation of RR195 apparently followed second order reaction. The second order reaction was further supported by plotting the graph between $1/C$ and time at different initial concentrations. The half-life $t_{1/2}$ and regression coefficient R^2 obtained for second order reaction at different concentrations of RR195 was shown in (Fig. 6). These values range from 0.99 to 0.97 confirming that electrochemical degradation of RR 195 followed the second order reaction.

Statistical Analysis

In present study, the percentage color removal is considered as response variable whereas pH, NaCl and dye concentration are considered as independent variable. The 1000 observations for each regression coefficient are simulated by using Learn Bayes statistical package [17]. The distribution for each regression coefficient and standard error are shown in Fig. 7. The resulting fitted regression model can be written in the form of following equation

$$\text{RR195} = 129.98 + 8.58\text{NaCl} - 0.74\text{Dye.Concentration} - 6.90\text{Ph} \quad (5)$$

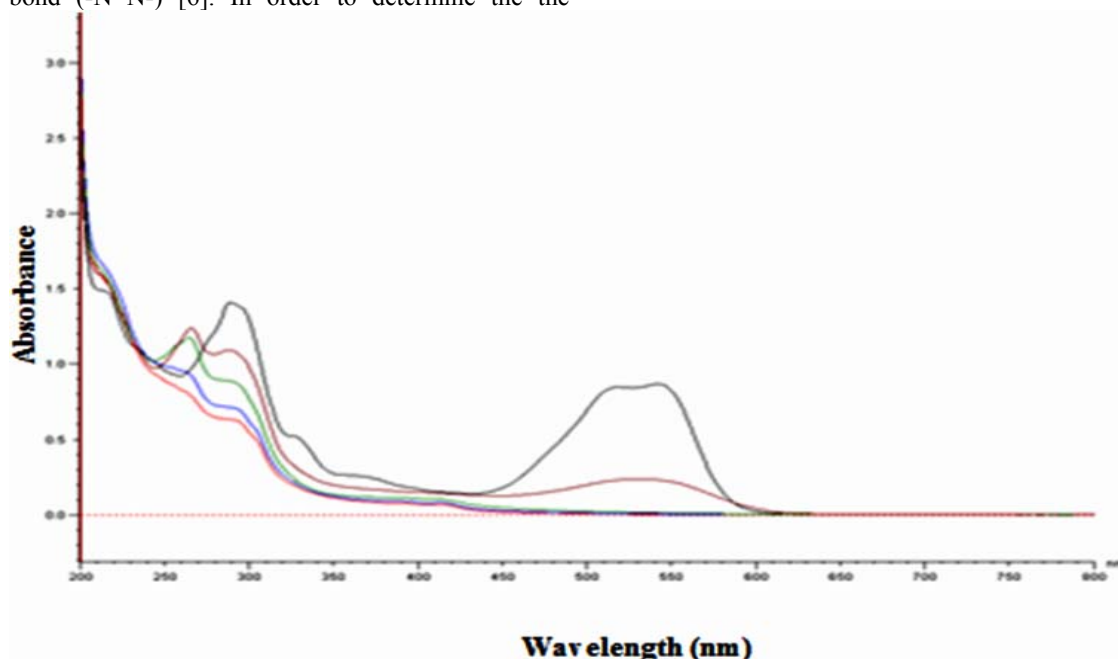


Fig. 5: UV-visible spectra during electrochemical degradation of RR 195 dye. Reaction conditions: initial pH = 3, dye concentration = 50 mg L^{-1} , temperature = 25°C , reactor volume = 1 L, NaCl concentration = 1.5 g/L .

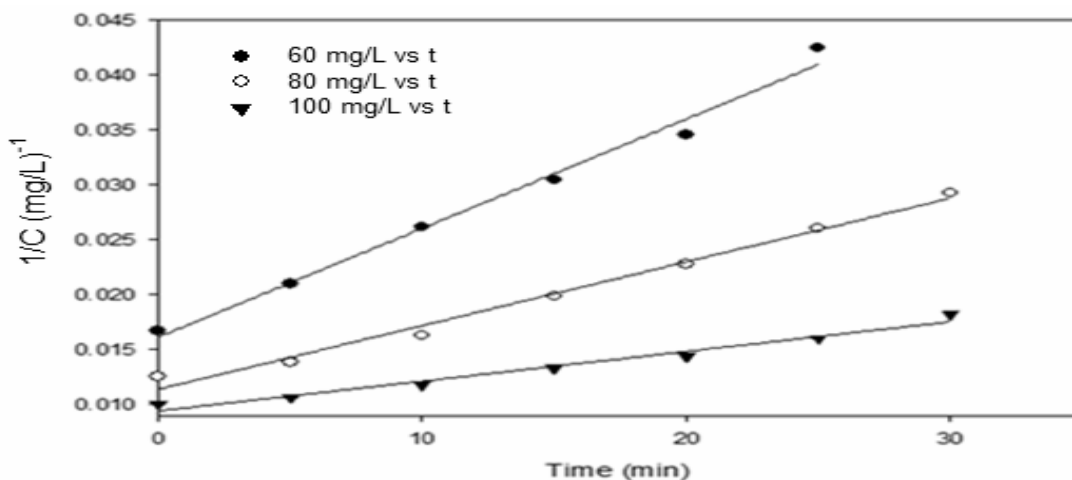


Fig. 6: Second order kinetic plot of RR195 degradation by electrochemical process Note: pH = 3, current = 1 Ampere, Temperature = 25°C, Reactor Volume = 1L.

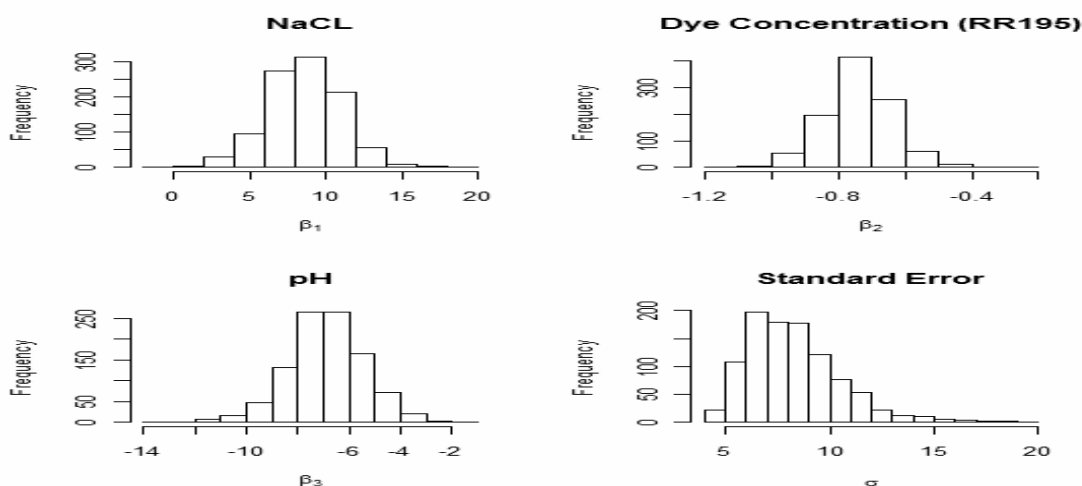


Fig. 7: The histograms for simulated regression coefficients and standard error.

In above equation it could be observed that NaCl has positive effect on RR195 whereas dye concentration and pH have negative effect on percentage removal. If we increase one unit of NaCl it causes to increase 8.58 unit of RR195 degradation. The one unit increase of pH level will cause 6.9 unit decreases in RR195 degradation. The dye concentration has very less negative effect on its degradation; one unit increase of Dye concentration level will cause 0.74 unit decrease in RR195. The estimated $R^2 = 91\%$ which means 91% variation of response variable is explained by independent variables used in fitted regression model and suggests that fitted regression model is reliable for reaction prediction.

Further, 1000 samples for each value of response variable are simulated their mean value are compared with actual value of response variable (Table-3). In Fig. 9, 80 percent and 95 percent credible intervals (C.I) from the simulated values are estimated and then actual values of response variables are plotted in that interval. It could be observed (Fig. 8) that actual data set lies in credible interval even though we decrease the credible interval limit into 80% which suggests that our fitted Bayesian linear regression model is reliable for reaction prediction. The amount of percentage removal for 36 new combinations of independent variables is predicted and the distribution of 4 out of 36 combinations is presented in Fig. 9.

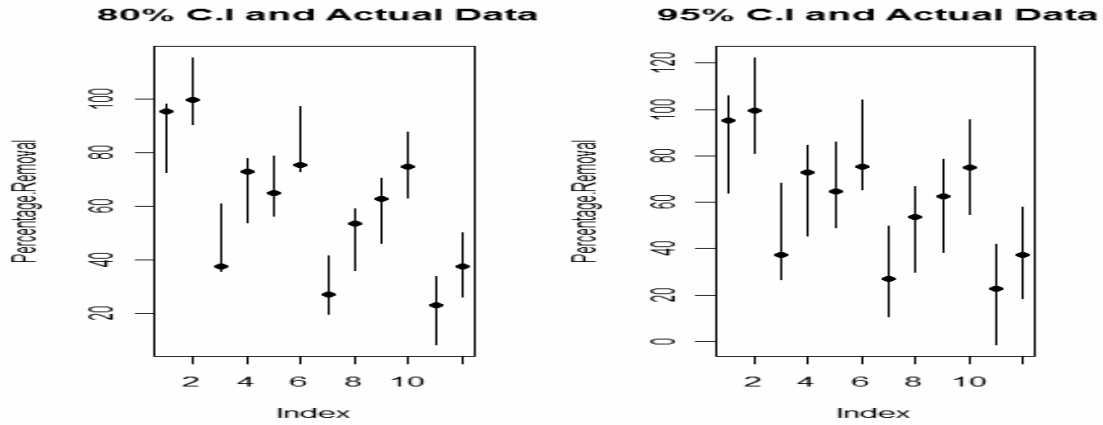


Fig. 8: Comparison of 80% and 95% credible interval and the actual data.

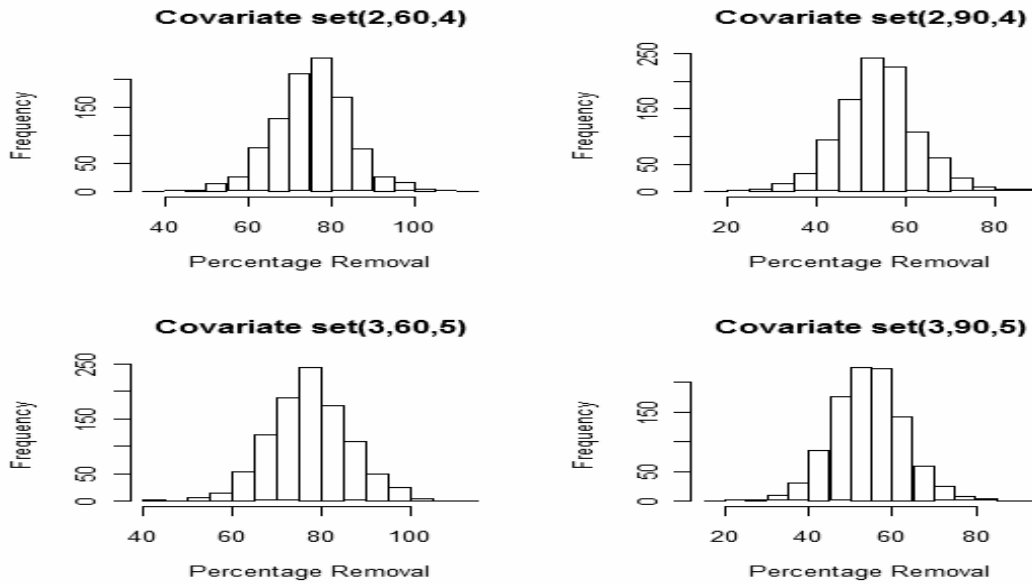


Fig. 9: The predictive distribution of selected 4 combinations of independent variables to predict the unknown percentage removal.

Table-3: The comparison of predicted response variables with actual response variables.

NaCl Concentration	Dye Concentration	pH	Actual RR195 Concentration	Predicted RR195 Concentration
1.5	50	3	95.28	85.25
3.5	50	3	99.60	102.41
1.5	100	3	37.41	48.19
3.5	100	3	73.01	65.23
1.5	50	5.6	64.78	66.68
3.5	50	5.6	75.36	84.50
1.5	100	5.6	26.90	30.06
3.5	100	5.6	53.56	48.03
1.5	50	7	62.58	57.92
3.5	50	7	74.87	74.55
1.5	50	5.6	75.36	84.50
1.5	100	5.6	26.90	30.06
3.5	100	5.6	53.56	48.03
1.5	50	7	62.58	57.92
3.5	50	7	74.87	74.55
1.5	100	7	22.88	21.29
3.5	100	7	37.35	37.84

Experimental

Textile mill (Arzoo) Faisalabad, Pakistan provided Reactive Red 195 (RR195) and was used without further purification. The pH of the dye solutions were adjusted by using NaOH and HCl. For supporting electrolyte, NaCl was used.

All experiments were performed in undivided electrolytic cell with a working volume of 1L. Graphite carbon electrodes were used as working and counter electrodes. The effective electrode surface area used was 75.9 cm². The working and counter electrodes were positioned vertically parallel to each other with an inner electrode distance of 2.0cm. The solution was constantly agitated by using a magnetic stirrer (Wise Stir MSH-30 03L-3) at 250 rpm. The experimental setup is shown in Fig. 10.

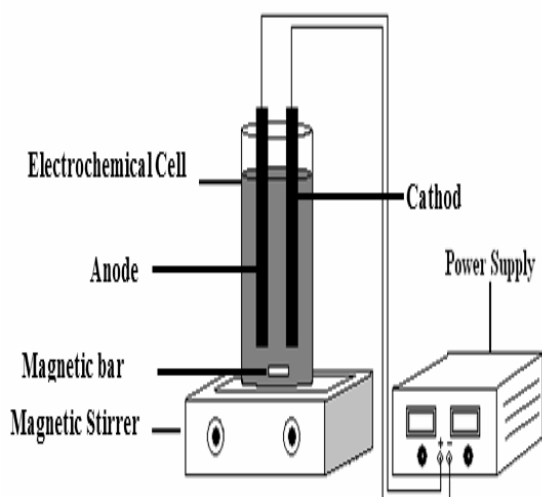


Fig. 10: Schematic diagram of the Electrochemical Cell.

The electrochemical degradation and decolouration was studied by using different concentrations (20, 40, 50, 60, 80, 100mg/L) of RR195. The effect of pH was studied by varying pH values at 3, 5.6, 7, 9, and 11. The concentration of supporting electrolyte was optimized after studying its different concentrations of 0.5, 1.5, 3.5 and 7g/L. The current density at electrodes was adjusted at 100 Am⁻².

Analytical Measurements

The initial dye concentration (C₀) and its concentrations at time t (C_t) in solutions were

scanned using UV-Vis spectrophotometer (UV-4000 spectrophotometer). The absorbance of RR195 was determined to calculate the percentage decolourization at wavelength of 542 nm. The percentage decolourization was calculated by using equation 6.

$$\text{Dye Decolourization (D\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (6)$$

Beer–Lambert law was used to calculate the concentration of dye in the solution [18].

The energy consumption was calculated for the decomposition of Reactive Red 195 (RR195) in model solutions by simple electrochemical process. The overall energy consumption inferred the power used to produce electrochemical reactions. Electrical energy consumption was calculated by using equation 7.

$$\text{EC(kWhL}^{-1}\text{)} = \frac{(P \times t)}{V \times 60 \times \log C_0 / C_t} \quad (7)$$

where P (W) is the power, V is the volume (L) of water treated, t is oxidation time (h), C₀ and C_t are the concentrations of dye in (mgL⁻¹) at reaction time 0 and t [19, 20].

Statistical Analysis and Graphical Work

All determinations were performed in duplicate and mean values were presented in the results. Statistical comparisons of the mean values were performed by Bayesian regression analysis, using R software. Graphical work was carried out using computer program Sigma Plot™ v.12.

Conclusion

Electrochemical oxidation is one of the advanced treatment method used for the decomposition of RR195 in present study. It was observed by experimental design and from statistical analysis that by increasing the dye concentration and pH, the percentage decomposition of RR195 dye decreases whereas by increasing the concentration of NaCl, percentage decomposition of RR195 increases. Bayesian regression model is applied for the justification of finding in the experimental results. The resulting fitted regression model was developed which is;

$$\text{RR195} = 129.98 + 8.5\text{NaCl} - 0.74\text{Dye Concentration} - 6.90\text{pH}$$

The decolourization of the azo reactive dye RR195 was performed at different pH values (3, 5, 7,

9 and 11), RR195 dye concentrations (20, 50, 60, 80 and 100 mg/L) and NaCl concentration (1.5, 3.5, 7 g/L). At 50 mg/L dye concentration, pH 3 and 1.5 g/L NaCl concentration, the dye shows maximum decomposition within 25 min. The decomposition of RR195 dye apparently follows the second order reaction kinetics. The high dye decomposition was achieved at 100 Am⁻² current density and only 6.11Whm⁻³ electrical energy was consumed.

The electrolyte assisted electrochemical process has two main advantages over other process i.e., use of environmental benign electrolyte (NaCl) and reduction of landfill facility cost as no sludge is produced during the process.

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