

# Application of Electro- Chemical Oxidation for the Treatment of Reactive Red 195 using Graphite Electrode

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## ABSTRACT

In this study, graphite electrodes have been used for electrochemical oxidation of aqueous solution of Reactive Red 195 (RR 195). As part of electrolysis, three different electrolytes were used, including NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>; and NaCl proved to be the most effective in removing the Colour of RR 195 dye from its aqueous solution. Based on the effects of the process variables dye concentration, current density, electrolyte concentration, pH and stirring speed, the highest colour removal was achieved after 90 min. At optimum operating conditions, such as 0.075% sodium chloride (NaCl) concentration, a current density of 3.75mA/cm<sup>2</sup>, pH 7, and stirring speed of 250 rpm, 94% of the color was removed. UV-Vis spectrophotometer was used to measure color removal during dye degradation. In comparison with conventional treatment techniques, this method is highly effective.

**Key words:** Electro – Chemical Oxidation, Reactive Red 195, Colour removal, Graphite electrodes, Dye removal, Decolourization.

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## INTRODUCTION

As dyeing and finishing in the textile industries has become increasingly prevalent in the surroundings over the past few decades, the environmental impact has increased significantly. It is relatively difficult to treat effluent discharges from the textile industry because of their firm color, even with insignificant concentrations of dyes. Discharging highly colored wastewater into water bodies usually results in severe environmental protests because wastewater has a highly visible color. To remove dye color and COD from wastewater, various

processes have been used, either physically (adsorption, flocculation, etc.), chemically (ozonation, chlorination, etc.) or biologically.<sup>[1,2]</sup> Moreover, physical and physicochemical methods like flocculation, filtration, precipitation, coagulation and evaporation in open ponds provide only partial solutions to the problem.<sup>[3]</sup> In general, reactive dyes are difficult to degrade, but if they undergo an electrochemical process, they can be broken down into colourless smaller molecules that can be removed in a further biological process.<sup>[4]</sup> These dyes have unbroken aromatic rings attached to their azo groups, which are responsible for the intensity of colour and the resistance to degradation under normal conditions like sunlight, water, soap, soil, etc. They are used for dyeing cotton, rayon, silk, wool and nylon.<sup>[5]</sup> Though electrochemical treatments have been reported to be effective for reduction of textile effluent colour, oxidation treatment is commonly used.<sup>[6]</sup>

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Various types of oxidation can be generally divided into two groups: those taking place on the electrode surface, known as direct oxidation and those taking place as a result of molecules forming on the anode surface, known as indirect oxidation. Both of these processes can take place simultaneously or separately in a reactor.<sup>[7,8]</sup> A few of the most important species involved in indirect oxidation are hydroxyl radicals (OH•), chlorine and hypochlorite in water purification, Ozone in sterilization as well as redox pairs species such as Cr (VI) / Cr (III). In indirect oxidation, OH• is the most effective degradant. There have been alternative approaches as well, such as the use of HCl for the degradation of organic compounds in textile effluents.<sup>[9,10]</sup> Electrochemical oxidation (EO) is one of the most versatile processes for handling water-based effluents from various industries including distilleries, agrochemicals, tanneries, pulp and paper, textiles and hospitals. An alternate aspect is that EO is compatible with most other methods, including chemical and electrochemical techniques and is usually used in conjunction with one or more of them. It includes disciplines such as material science, (micro) biology, (electro) chemistry, environmental protection and water supply systems.<sup>[11]</sup> New and novel processes need to be developed for effective treatment of various types of polluted water with relatively low operating costs as conservation guidelines and environmental regulations become more stringent. In addition to electrochemistry, wet oxidation, ozonation, and photocatalysis were used by researchers to degrade organic compounds. Among these progressive oxidation methods, electrocatalytic oxidation has gained increasing attention in recent years because of its ability to oxidize small amounts of organic substances that can be difficult to oxidize by conventional means, such as undesirable organic compounds in aqueous phase.<sup>[12]</sup>

In this study, the main objective is to investigate the electrooxidation of RR 195 dye in a batch electrochemical reactor employing graphite electrodes. The effectiveness of dye removal from its aqueous solution was studied by examining parameters such as treatment time, current density, electrode material, dye concentration and initial pH.

## MATERIALS AND METHODS

### Materials

The dye stock solution was prepared by dissolving Reactive Red 195 (CAS No: 93050-79-4) in double distilled water at a concentration of 1000 mg/L. Before the dye stock solution was used in the study, it was

diluted in order to achieve concentrations of 100 to 1000 mg/L. The dye solution was electrolyzed with 0.1N of H<sub>2</sub>SO<sub>4</sub>/NaOH as a supporting electrolyte and the pH was adjusted by adding caustic soda to the reactor.

### Methods

An electrochemical cell set-up is made from an undivided reactor with Graphite electrodes parallel and spaced by 5 cm. A 1000 ml electrochemical cell was used for this experiment, where the cathode and anode were fixed vertically and parallel to each other. A dual DC power supply supplied power needed for electrolysis. To maintain the electrolyte properly mixed, the electrolytic setup uses a magnetic paddle. The stirrer used in the cell kept the composite surface area unchanged and the current applied to the decolorization process were quantified. During chemical reaction between electrodes and electrode surfaces, oxidation and reduction occurs.

### Electrochemical oxidation procedure

In this experiment, two graphite electrodes were used as anode and cathode, respectively. We performed all experiments in an undivided electrolytic cell with a volume of 500ml. By using a magnetic stirrer, the solution was constantly stirred. Each experiment involved supplying two hundred milliliters of dye solution containing known quantities of Reactive Red 195. Using a stabilized power source equipped with a digital ammeter and voltage meter, the anode and cathode leads were connected to the terminals of the DC rectifier. A centrifuge was used for 15 min to spin the treated solution at 5000 rpm and for analysis the supernatant liquid was taken. Color removal was confirmed using spectrophotometer.

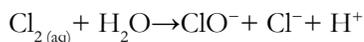
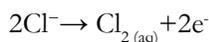
By the electrochemical oxidation of pollutants, pollutants are removed by either direct anodic oxidation with poor decontamination or with electro-generated, hydroxyl radical M [OH<sup>o</sup>] or metal oxide [MO] as shown in the following reaction.<sup>[13]</sup> Reactive dyes may degrade partially or completely according to the following mechanism.



A chromophore group (-N=N-) destroyed by anodes effectively, resulting in its discoloration, and in the presence of chloride, the degradation of dyes was accelerated by active chlorine species. The indirect method of electro oxidation occurs when strong oxidants are generated *in situ* as part of electrolysis,

which react with organic pollutants such as dyestuffs and result in their partial or total degradation.

The main oxidizing agent during electro-oxidation is active chlorine. These chlorine gaseous molecules and/or chlorine-oxygen species such as hypochlorous acid (HClO) or hypochlorite ions ( $\text{ClO}^-$ ), depending on the pH, cause the organic matter to oxidize rapidly, according to the reactions given below.<sup>[14,15]</sup>



### Analytical Procedure

A UV-Vis spectrophotometer (UV - 1700 pharma Spec, Shimadzu, Japan) was used to determine the UV-Vis spectrum of Reactive Red and its removal during electrochemical oxidation. It was found that RR 195 has a characteristic maximum absorbance (max) of 542 nm.

### Calculation

$$\text{Removal Efficiency (\%)} = \frac{c_0 - c_e}{c_0} \times 100$$

Where,

$c_0$  = Initial dye concentration before electro oxidation (mg/L)

$c_e$  = Final dye concentration after electro oxidation (mg/L)

## RESULTS

In this study, we investigated the effect of electrolyte assisted electrochemical oxidation process on decolorization and degradation of RR195 at different parameters such as dye concentration, pH, electrolyte concentration, stirring speed and current density for efficient removal. This type of electro oxidation was found to be high-performing, easy-to-use and compact facility. By using electron as a reagent, the electrochemical method is better than physiochemical and membrane technologies (the current methods for color removal) since no solid residue is produced.<sup>[16]</sup>

### Effect of electrolyte concentration

Conductivity is an important factor in conducting current in a solution. Because of higher ionic strength, electron transport will play a major role and also contribute to a better degradation rate.<sup>[17]</sup> As a result, various concentrations of NaCl solutions have been

used for the preparation of various electrolyte solutions. To minimize the chloride's negative effects, a concentration of 0.075M was optimized in other experiments. Figure 1 shows the effects of different NaCl concentrations under fixed current density, pH, and dye concentration.

### Effect of applied current density

To investigate the values of current density in aqueous solution RR195 and the removal of colour, electrolysis was performed. Higher current densities lead to higher color removal percentage which is shown in Figure 2. The degradation is attributed to the increase of  $\text{Cl}_2$ , HOCl, and OCl concentration in the solution, which eventually causes the degradation.<sup>[18]</sup> The increase in the current density followed by the electrochemical cell produces more electrons, which causes the overall reaction rate to increase.<sup>[11]</sup> Based on the results, it was determined that the optimal current density for this study was 20 mA/cm<sup>2</sup>. Colour removal at different current density are: 5 mA/cm<sup>2</sup> is 73.85%, 10 mA/cm<sup>2</sup> is

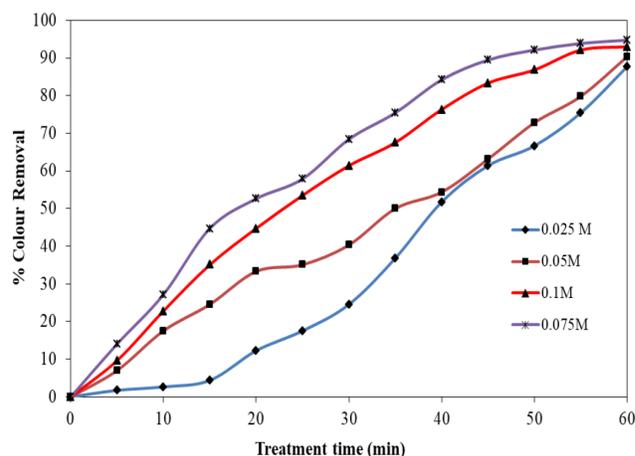


Figure 1: Effect of electrolyte concentration on colour removal.

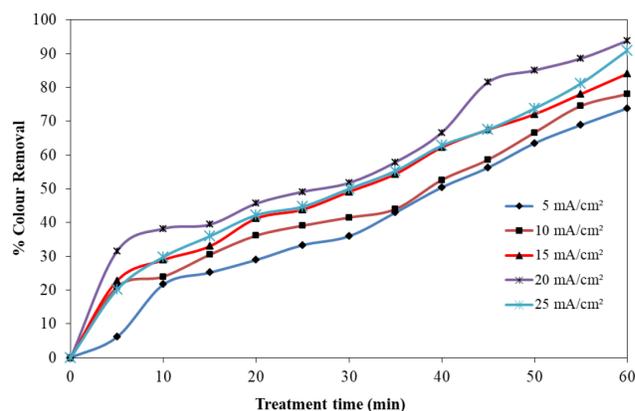


Figure 2: Effect of current density on colour removal.

78.07 %, 15 mA/cm<sup>2</sup> is 84.1%, 20 mA/cm<sup>2</sup> is 93.85%, 25 mA/cm<sup>2</sup> is 90.98%, with increasing current density up to 20 mA/cm<sup>2</sup>, the rate of removal increases.

### Effect of pH

The pH is a key operating factor affecting the electrochemical process' output. In experiments, pH ranges from 3, 5, 7 and 9 were tested using either H<sub>2</sub>SO<sub>4</sub> or HCl and NaOH when treating RR195 solution. The colour removal efficiency was found to be maximum at pH 7.0 which is illustrated in Figure 3.

### Effect stirring speed

A study was conducted to examine the effect of stirring speed on the removal of colour under optimal conditions. As Figure 4 shows increasing stirring time up to 60 min led to a rapid increase in color removal percentage. For electrochemical oxidation, 200 rpm was considered as optimal stirring speed. At 60 min, 94.64 % of the color was removed. Furthermore, the removal of colour by increasing rotation speed was increased

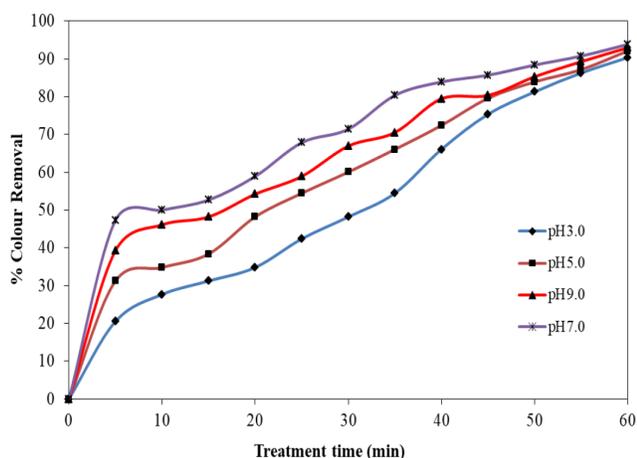


Figure 3: Effect of pH on colour removal.

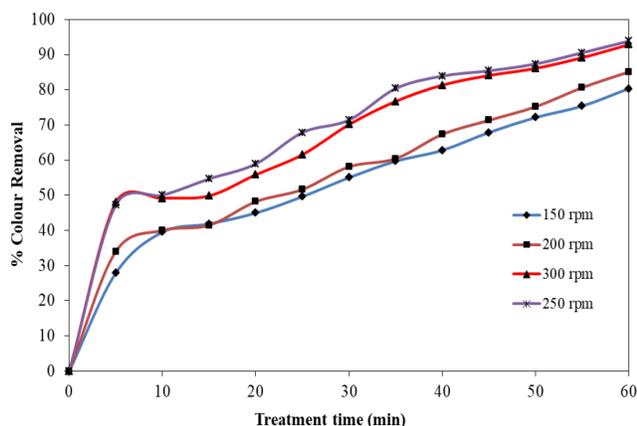


Figure 4: Effect of Stirring speed on colour removal.

up to 200 rpm, beyond that, there was no significant improvement in colour removal by increasing rotation speed. It appears that hydrodynamic conditions strongly influence the rate at which colour was removed. The higher magnetic stirrer speeds result in a faster, more efficient electrochemical reaction. This evidence demonstrates that colour removal reactions are diffusion-controlled. The increase in rotational speed produces greater turbulence, which reduces the thickness of the diffusion layer at the electrode surface and helps mix the electrolyte better. The anode surface receives more reactants and products, improving transfer efficiency.<sup>[19]</sup>

### Effect of dye concentration

The dye concentration plays a significant role in the electrochemical process, and this has been studied in the 200 ppm to 800 ppm range. In terms of the amount of color removal, it was observed that as concentration increased, the amount was reduced as shown in Figure 5. As a result, the oxidizing species generated throughout all of the operational parameters are identical, it can be explained that the percentage of colour removal decreases when the initial concentration is high as the Reactive Red 195 molecules and their degradation intermediates percentage are more.<sup>[18,20]</sup>

### UV-Visible absorbance changes in the degradation of Reactive Red - 195

The UV-visible absorbance of the initial and final electrolysis is shown in Figure 6a and 6b. As the treatment time and the applied current density increases by 20 mA/cm<sup>2</sup>, the peak is gradually disappearing with time, indicating high removal after 60 min of electrolysis. Figure 6a. shows that a maximum absorbance peak is at a 542 nm. Based on the electrochemical treatment, it can be concluded that Reactive Red 195 is completely removed from the aqueous solution when the electrochemical treatment was applied.

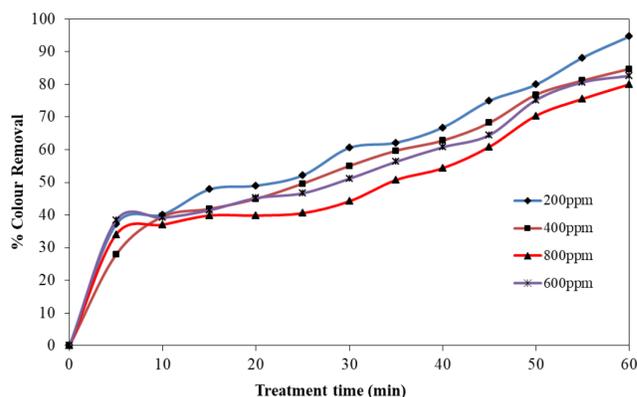


Figure 5: Effect of dye concentration on colour removal.

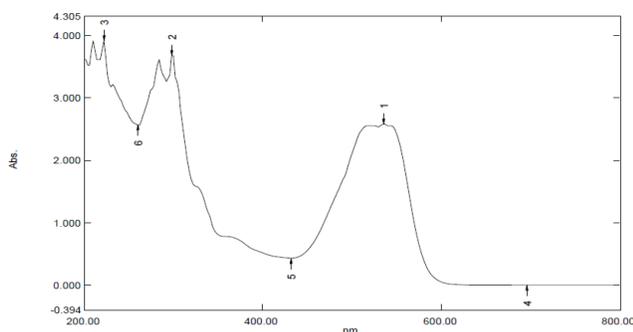


Figure 6(a): UV- Visible of Reactive Red 195 before treatment.

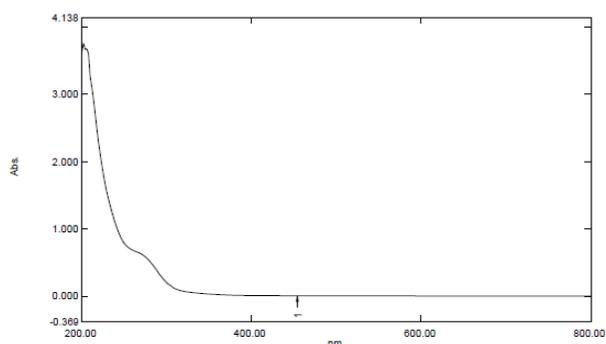


Figure 6(b): UV- Visible of Reactive Red 195 after treatment

## DISCUSSION

Synthetic dyes are of great environmental concern due to their widespread usage and their low removal rate during aerobic waste treatment. The reactive dyes are difficult to degrade in general, electrochemical processes can break them down into smaller molecules that are colorless and can be removed in another biological process.<sup>[4]</sup> The electrochemical oxidation (EO) process is widely used for the treatment of water-based effluents from various industries including distilleries, agrochemicals, tanning, pulp and paper, textiles and hospitals. The concentration of electrolyte, the applied current density, pH, stirring speed and dye concentration are among the factors considered in this study that explain how colour is removed from aqueous solutions.

When NaCl electrolyte is added to reactive red 195, an increase in chloride concentration will result in a greater percentage of colour removal. According to the Nernst equation, an increase in NaCl concentration leads to a decrease in  $\text{Cl}_2$  discharge potential.<sup>[21]</sup> As a result of active chlorine being produced, the concentration of NaCl is increased.<sup>[22]</sup> As a predecessor to this study, we reported similar results in the electrochemical oxidation of bisphenol A using graphite electrodes.<sup>[23]</sup> According

to Faraday's Law, the hypochlorite content increases with increasing current density.<sup>[24]</sup> As the current density increases above  $20\text{mA}/\text{cm}^2$ , the percentage of colour reduction does not substantially increase. This may be due to the fact that  $\text{Cl}_2$  discharge potential increases with current density and becomes close to  $\text{O}_2$  discharge potential. Under such conditions,  $\text{O}_2$  and  $\text{Cl}_2$  evolve simultaneously with the result that current efficiency and rate of  $\text{Cl}_2$  generation are reduced.<sup>[21]</sup>

Due to the chlorine/chloride present in the solution in the form of hypo chlorus acid, which exhibit a higher oxidation potential than hypochlorite, the colour removal percentage was higher in acidic medium.<sup>[25]</sup> RR 195 aqueous solution has a colour removal value of 93.85% with pH 7, so this is the optimal pH value for the treatment. For the electrochemical oxidation of aqueous RR195 solution, the pH of initial solution was chosen as 7 due to the high removal of color and was utilized throughout the experiments<sup>[26]</sup> and the removal of colour from its aqueous solution was confirmed by UV-Vis absorbance before and after treatment.

## CONCLUSION

The present study optimizes electrochemical oxidation parameters for the treatment of aqueous solution of RR195 using Graphite Electrodes and analyzes the degradation products. In this investigation, optimized conditions such as electrolyte concentration (NaCl), pH, stirring speed, current density, dye concentration were evaluated. The optimum conditions of all parameters were successfully achieved with higher percentages of 93.85%. UV - Visible spectrum showed that degradation and mineralization are almost completely achieved at the electrolysis process. Therefore, it can be concluded that under optimal conditions of laboratorial operation, RR195 can be decolorized and degraded by electrochemical oxidation.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

## ABBREVIATIONS

**COD:** Chemical Oxygen Demand; **EO:** Electrochemical Oxidation; **RR 195:** Reactive Red 195 dye; **UV-Vis:** Ultra Violet-Visible spectroscopy.

## SUMMARY

Application of Electro-Chemical oxidation for the treatment of aqueous solution of RR195 was studied in this experiment and the results shows that the effective removal of RR 195 dye from its aqueous solution. The highest colour removal was achieved after 90 min. under the optimum operating conditions, such as 0.075% sodium chloride (NaCl) concentration, a current density of 3.75mA/cm<sup>2</sup>, pH 7, and stirring speed of 250 rpm, 94% of the color was removed.

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