



Electrochemical Degradation of Reactive Red 195 from its Aqueous Solution using RuO₂/IrO₂/TaO₂ Coated Titanium Electrodes

M. UMADEVI¹, R. RATHINAM^{2*}, S. POORNIMA³, T. SANTHI⁴ and S. PATTABHI¹

¹Department of Environmental Sciences, P.S.G. College of Arts and Science, Coimbatore-641014, India

²Department of Chemistry, Sri Eshwar College of Engineering, Coimbatore-641202, India

³Department of Chemistry, Bharathiar University, Coimbatore-641046, India

⁴Department of Chemistry, L.R.G. Government Arts College for Women, Tirupur-641604, India

*Corresponding author: E-mail: rathinam.r@sece.ac.in

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The electrochemical oxidation of reactive red 195 from aqueous solution was carried out using titanium electrode in an electrochemical cell reactor. The effect of different operating parameters such as dye concentration, current density, electrolyte concentration, pH and stirring speed were investigated. The UV-visible spectroscopy confirmed the removal and degradation of reactive red 195. Three different supporting electrolytes such as NaCl, NaNO₃ and Na₂SO₄ were used for electrolysis and NaCl were found to be effective for the removal of reactive red 195 dye from its aqueous solution. The maximum percentage of colour removal was 94%, under the optimum operating conditions with electrolyte (NaCl) concentration 0.075 M, current density 25 mA/cm², pH 5 and stirring speed of 250 rpm. This method was found to be relatively more effective to the conventional treatment techniques.

Keywords: Electrochemical oxidation, Reactive Red 195, Titanium electrodes.

INTRODUCTION

More than 10,000 types of dyes are commercially available and more than 7×10^5 tons of dyes are produced every year, which can be classified as anionic and cationic based on their structure [1]. Textile effluents containing dyes, when released into water bodies, considerably affect the photosynthetic activity in water because of reduced light penetration. Even <1 ppm dye concentration in effluents can affect light penetration in water bodies. Furthermore, these dyes, along with other contaminants, subsequently deplete dissolved oxygen concentration and thus alter the aquatic ecosystem [2]. Generally, dyes are derived from petroleum products that consist of an unsaturated chromophore molecule group, which absorb light present in the visible region of the electromagnetic spectrum (400-750 nm). Most of the dyes are recalcitrant molecules that chemically lock the colour onto fibres or other materials and resist decolourization on exposure to soap, water, light or other mild chemical agents [3]. The textile industry majorly affects the environment through the release of untreated sewages into

water bodies [4]. The effluents with high dye concentration can change biological cycles when released into the aquatic environments through alteration of photosynthesis and water oxygenation and their high potential to harm living organisms and cause mutations in them [5].

Several physical, chemical and biological treatment methods are commonly used for removal of dyes from textile effluents. Presently, an efficient and cost-effective technique is urgently required for wastewater treatment. Currently, advanced oxidation process and electrochemical process are used to treat drinking water and industrial effluents. Electrocatalytic oxidation can efficiently remove organic and inorganic pollutants from industrial wastewaters [6]. Various physico-chemical processes are used to treat wastewater effluents, such as adsorption, coagulation/flocculation, precipitation, activated carbon, ozonation, membrane filtration and ion exchange. However, most of these treatments are expensive and generate pollution because of the many chemicals used in the processes [7].

Recently, electrocatalytic oxidation has received increasing attention in environment-related studies because it can

destroy undesirable organic compounds in the aqueous phase and eliminate organic substances present in minute amounts that are stable and difficult to oxidize by using conventional methods. In the electrocatalytic process, the conversion rate depends not only on the applied potential but also several factors such as (i) the specific feature of semiconductors, (ii) light diffusion, (iii) adsorption and desorption of reactants and products and (iv) electric field intensity in the space charge region [8]. The combined treatment process of electrocatalytic oxidation was observed to be effective in organic pollutant removal from wastewater [9].

The present study was designed to investigate the efficiency in removing the reactive red 195 dye from its aqueous solution by using titanium electrode at various operating conditions in an undivided electrochemical reactor. The operating variables that affect colour removal, such as applied current density, solution pH, stirrer speed and electrolyte concentration were investigated.

EXPERIMENTAL

A reactive red 195 [CAS No: 93050-79-4] dye stock solution (1000 mg/L) was diluted to appropriate concentrations of (100 to 1000 mg/L) before using in the experiments. In addition to this, appropriate amount of supporting electrolyte was added and pH of the dye solution was adjusted by 0.1N of H₂SO₄/NaOH in the EC apparatus.

Method: The electrochemical cell set up consists of an undivided reactor with parallel titanium electrodes having an gap of 5 cm. The electrochemical cell has a volume of 1000 mL, anode and cathode electrodes were installed vertically parallel to each other. During electrolysis, required power supply was supplied through a dual DC power supply. The electrolytic set-up consists of magnetic paddle to keep the electrolyte well mixed. The chemical process occurs in such cells are oxidation and reduction, the electrode in which reduction occurs is considered as cathode and the electrode at which oxidation process is anode.

Analytical procedure: The reactive red 195 dye and its removal during electro oxidation were analyzed through UV-Vis spectrophotometer (UV-1700 pharma Spec, Shimadzu, Japan). The characteristic maximum absorbance (λ_{max}) of reactive red 195 dye was found to be 542 nm. The removal efficiency (%) was calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where C_o and C_e are the dye concentration (mg/L) before and after the electrooxidation, respectively.

RESULTS AND DISCUSSION

Effect of electrolyte concentration: The supporting electrolyte concentration is an essential parameter for effective degradation of reactive red 195 dye. Electrolyte concentrations of 0.025, 0.05, 0.075, and 0.1 M were used with a current density of 25 mA/cm², initial pH of 5, stirring speed of 250 rpm and reactive red 195 dye concentration of 200 mg/L. When the increase in the concentration of the supporting electrolyte,

colour removal efficiency increases and cell voltage reduction decreases electrical energy consumption (Fig. 1). After electrolysis for 90 min, when the supporting electrolyte concentration increases from 0.025 to 0.1M NaCl, removal efficiency significantly increases to 86.98%, 92.46%, 94.52% and 93.89%, respectively. This mainly occurs because chloride ions destroy the passivation layer and catalyze the electrode material through pitting corrosion, which is a localized corrosion type caused by high chloride concentration in the solution [10]. With an increase in electrolyte concentration, the removal efficiency of pollutant increases. Therefore, colour removal was the highest at 0.075M with 94.52% removal. This concentration was considered as optimum for further studies.

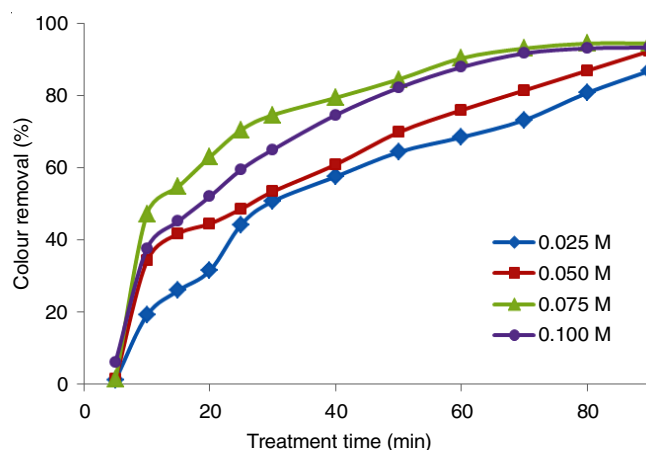


Fig. 1. Effect of supporting electrolyte concentration

Effect of applied current density: Current density majorly influences the electrochemical process. To explore the influence of current density on the treatment efficiency of the electrochemical system, current densities from 5 to 25 mA/cm² were applied in this study. The percentage of colour removal increased with increase in electrolysis time and applied current density (Fig. 2). High colour removal efficiencies were obtained with 90 min electrolysis time for current densities >15 mA/cm². With current densities of 20 and 25 mA/cm² and electrolysis time of at least 80 min, the colour removal efficiency was > 90%. With the current density of 10 mA/cm² at 90 min of

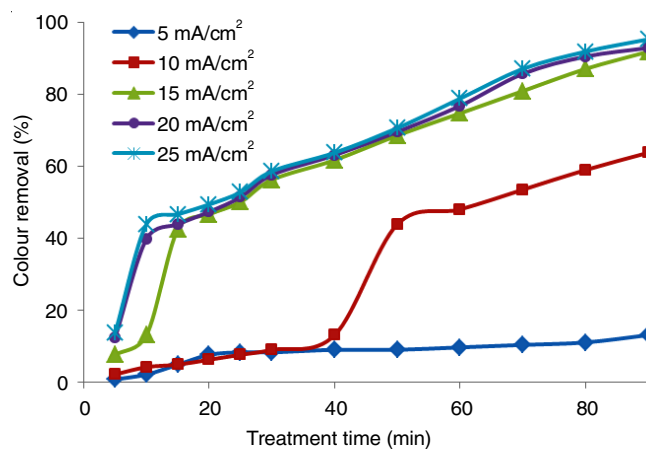


Fig. 2. Effect of applied current density

electrolysis, 63.69% efficiency was reached. Degradation efficiencies obtained were 13.01%, 63.69%, 91.78%, 92.83% and 95.20% for the current densities of 5, 10, 15, 20, and 25 mA/cm², respectively. With the current density of 25 mA/cm² at 90 min of electrolysis, the total colour removal efficiency was 95.20%.

The colour removal increases with increasing current density, which is attributed to an increase in the concentrations of Cl₂, HOCl and OCl⁻ in the cell solution, which eventually increase dye degradation. At 25 mA/cm², the highest percentage of colour removal is achieved and this may be ascribed to the fact that the discharge potential of Cl₂ increases with an increase in current density and becomes very close to the discharge potential of oxygen. Under such conditions, O₂ and Cl₂ simultaneously evolved with a consequent reduction in current efficiency and Cl₂ generation rate [11].

Effect of initial pH: To study the pH influence, experiments were conducted using four different initial pH values (3, 5, 7 and 9), and the initial pH of the solution was adjusted using H₂SO₄ (0.1 N) or NaOH (0.1 N). During the treatment process, the current density was maintained at 25 mA/cm², electrolysis time at 90 min, stirrer speed at 200 rpm and NaCl (as supporting electrolyte) concentration at 0.075 M; the maximum efficiency was achieved at pH 5 (Fig. 3).

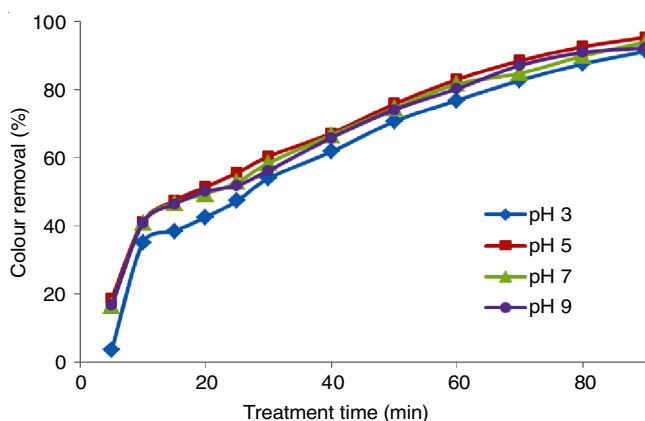
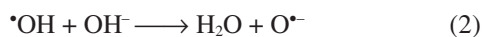


Fig. 3. Effect of initial pH

Thus, undesirable side reactions, such as oxidation of free chlorine to chlorate and per chlorate ions and formation of chlorate through the chemical combination of HOCl and hypochlorite ions, which are at equilibrium in water, are possible. The electrolysis of water and cathodic reactions involved hypochlorite ion loss [12]. Increased acidity enhances free radical formation [13] and therefore, organic materials could be easily oxidized [14], whereas in basic media [15], hydrogen peroxide derived from electrode surface, an oxidant in the Fenton's reaction, was unstable and decomposed into O⁻ and water (eqn. 2).



Therefore, some of its oxidation ability was lost and the oxidation proceeded slowly in basic conditions. In previous studies [16], similar results were observed for the electrochemical oxidation of tannic acid present in the wastewater by using RuO₂/IrO₂/TaO₂ coated titanium and graphite anodes.

Effect of stirring speed: The stirring speed is mainly associated with the efficient transfer of coagulant matter, which is formed by the electrode solution, in the reactor. If the coagulant matter does not disperse with the reactor efficiently, the reactor content cannot be homogenous, leading to regional differences. The chosen stirrer speed of 250 rpm was found suitable to mix the electrolyte cell well and strong enough to break up flocs formed during the processes [17]. The highest removal efficiency of 94.42% was reached at 250 rpm of stirrer speed and 90 min of treatment time (Fig. 4). The removal efficiencies for 150, 200, 250 and 300 rpm were 90.41%, 91.78%, 93.83% and 92.46%, respectively with the current density of 25 mA/cm². When the stirring speed was increased from 250 to 300 rpm, the flocs degraded and adsorbed colour desorbed. This decreased colour removal efficiency.

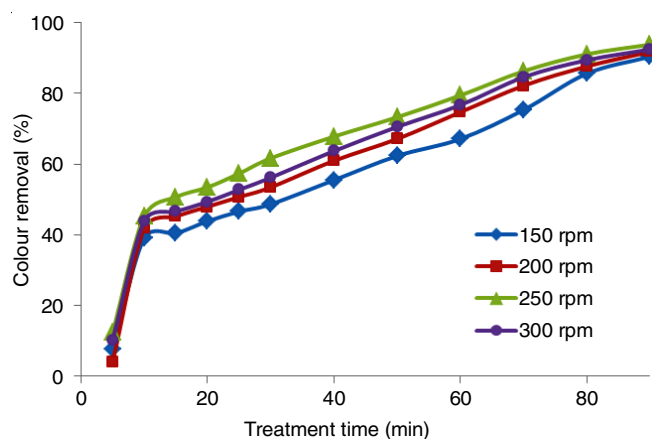


Fig. 4. Effect of stirring speed

Effect of dye concentration: The dye concentration of reactive red 195 is significant, from a practical viewpoint, in the electrocatalytic oxidation process for pollutant removal. Fig. 5 shows that the initial dye concentration influences colour removal. As expected, the colour removal rate decreases with an increase in the initial dye concentration, which is because the high dye concentration consumes Cl₂ and OCl⁻ rapidly, leading to a consequent decrease in their concentration at a given current density and achieving the maximum colour removal of 94.52% at 200 ppm dye concentration.

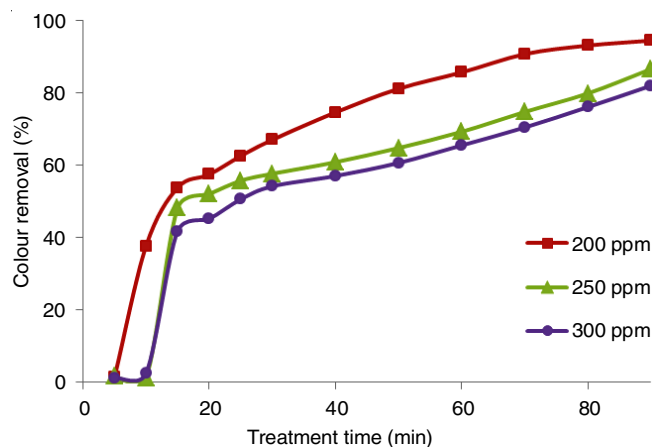


Fig. 5. Effect of dye concentration

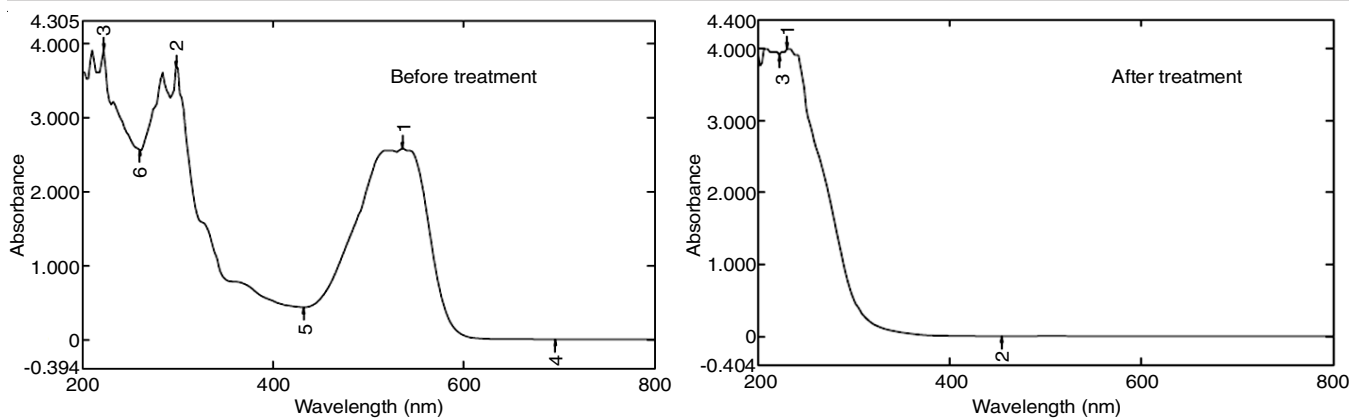


Fig.6. UV-visible of Reactive Red 195 before and after treatment

The results can be explained in terms of diffusion control, assuming that degradation occurs on the electrode surface mediated by hydroxyl radicals. At a low initial concentration, the electrocatalytic reaction is faster than diffusion. When the initial concentration increases, more organic substances are transferred to the surface of the electrode and the colour reduction process decreases. The $\cdot\text{OH}$ radicals generated are limiting in this case and the degradation efficiency decreases with an increased initial dye concentration [18].

UV-visible absorbance changes in the degradation of reactive red 195 dye: The UV-visible absorbance of the initial and final electrolysis is presented in Fig. 6. The UV region at 542 nm was due to reactive red 195. Thus, the peak disappears gradually during the electrooxidation process with increasing treatment time and high removal was achieved at 90 min of electrolysis with 25 mA/cm² of applied current density. Thus, the electrochemical treatment completely removes the reactive red 195 dye from an aqueous solution.

Conclusion

In present work, the electrochemical oxidation process for the treatment of reactive red 195 dye using titanium electrodes and analysis of degradation product was performed successfully. The optimized conditions such as electrolyte concentration, pH, stirring speed, current density, dye concentration were investigated. From all over results, under optimum condition with electrolyte (NaCl) concentration 0.075 M, current density 25 mA/cm², pH 5 and stirring speed of 250 rpm, the colour removal reached 94%. The UV-visible spectrum showed that degradation of reactive red 195 dye and the mineralization was absolutely reached during electrolysis. It can be concluded that under optimized laboratorial condition, the treatment of reactive red 195 dye by electrochemical oxidation is highly effective and efficient.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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