

A study on the degradation of synthetic dyes using tubular electrochemical reactor

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ABSTRACT

The aim of the research is to investigate the degradation of synthetic dyes, which are widely utilized in numerous textile sectors. In this study, we used electrochemical oxidation as the primary method for dye degradation, with a mixed metal oxide anode and a stainless-steel cathode. Three different dyes were used to evaluate the degradation: methylene blue, brilliant green, and fast sulphon black F. The supporting electrolyte for the experiment was sodium chloride, and the tests were conducted for 10 min while adjusting the synthetic effluent flow rate (30, 90, 120 LPM), supporting electrolyte concentration (1, 3, 5 g/L), and current density (0.32, 0.81, 1.59 A/dm²). The maximum color removal (95%) elimination using UV-Vis Spectrophotometer at 10 min of operation time, was seen for all dyes at 1.59 A/dm², 5 g/L, and 90 LPM. In the dye degradation kinetics, the hydroxyl radical plays an important role. The synthetic dye degradation rate constant (k_d) was determined to be 0.49×10^{-2} cm/s, and the half-life period $t_{1/2}$ was found to be 1.41603 min^{-1} . As a result, the suggested study was highly effective in degrading synthetic dyes in a shorter period of time with lower current density value.

Keywords: Synthetic dye; Electrochemical oxidation; Current density; Rate constant; Color removal

1. Introduction

Owing to increased population density and technological progress, the quantity of waste generated has been increasing and the demand for wastewater management is also increasing. Numerous industries consume large amounts of water for processing, and the textile industry is a major consumer of fresh water and it is also discharging a large amount of wastewater as a pollutant [1–3]. For past many decades the enormous amount of wastewater generated

from tenting and finishing processes from textile industry creates a potential threat to environment and aquatic life. The textile industry has been classified as “red” by the Tamil Nadu Pollution Control Board (TNPCB) because its wastewater contains toxic chemicals, it is dark in color, and has a high load of biological oxygen demand (BOD) and chemical oxygen demand (COD). Proper treatment methods should be adopted for this kind of waste, which contains a high concentration of toxic substances before being discharged into the environment [4]. However, there are many conventional

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treatment methods that have been practised worldwide for treating toxic wastewater, but they are not quite enough to treat the wastewater because of the complexity of pollutants prevailing in the wastewater. Apart from conventional treatment methods, there are several methods such as (electrochemical treatment, adsorption [5], Fenton [6], photocatalysis [7], ozonation [8], UV/H₂O₂ [9]) that are employed in treating small quantities of wastewater on a laboratory scale. Among the above-mentioned techniques, the electrochemical process plays a significant role in handling wastewater that contains a huge load of BOD, COD, and complex toxic substances. Depending on the type, effect of toxic effluent discharged, operational economy and their simpler applications of electrochemical reactors comprising of various sizes are employed as loop process or continuous industrial operation [10]. There are several electrochemical processes such as electro-coagulation [11], electro-Fenton [12], electro-flotation [13] to treat organic wastewater but each process has its own constraints in wastewater treatment, but still electrochemical oxidation process has been widely employed in many industrial effluents treatment process. Due to simpler design, high efficiency, no excess addition of chemical and no sludge production it makes the electrochemical oxidation process a wider application in wastewater treatment process [14]. The main advantage of electrochemical oxidation process is production of various reactive oxidation species which has capability to oxidize toxic organic pollutant [15]. Electrochemical oxidation is mainly branched into two process namely indirect oxidation (the generated oxidation species will react with dye molecule to form intermediates and remove the toxic pollutants) and direct oxidation (the pollutant molecule was degraded from complex to simpler form by electron exchange without any help of oxidant species) [16,17]. The nature of oxidant species generated over the electrode surface mainly depends on the anode material used in electrochemical process. In most of the electrochemical processes, Boron doped diamond is used as an anode material, since the cost of Boron doped diamond (BDD) electrode is very high for commercialization process. Most of the researches focussed on dimensionally stable anode electrodes such as titanium substrates, which were coated with mixed metal oxide nanoparticles like TiO₂, IrO₂, RuO₂, SnO₂ [18]. This work mainly focussed on the degradation of dye molecule using tubular electrochemical reactor for various concentrations of dye molecule, various flow rates and different current densities.

Kötz et al. [19] investigated the electrochemical treatment of organic effluent using SnO₂ as an anode and concluded that SnO₂ can be a good electrooxidation anode. Cominellis [20] studied the electrochemical oxidation of organics with simultaneous oxygen evolution using different electrode materials (Pt, Ti/IrO₂, Ti/SnO₂). The authors developed a simple mechanism for the electrochemical oxidation according to which selective oxidation occurs with oxide anodes (MO_x), forming the so-called higher oxide MO_{*n*+1}, with electrodes at the surface of which radical OH radicals are accumulated. Mohan et al. [21] reported that electro oxidation of synthetic dye house effluent using Acid blue 113 dye effluent has been carried out using a RuO₂/Ti electrode. The influence of the initial concentration of dye, supporting electrolyte, current densities, and pH on COD

reduction has been critically studied. The authors reported a more than 80% COD reduction under optimum conditions. The COD reduction is significantly affected by the initial pollutant concentration, supporting electrolyte concentration, and pH. Raghu and Ahmed Basha [22] experimented with electrochemical treatment of Procion Black 5B using a cylindrical flow reactor and reported more than 70% degradation. The present study is mainly focused on the degradation of three dye molecules using electrochemical oxidation in a tubular electrochemical reactor.

2. Materials and methods

2.1. Materials

All the reagents used in this process were used as such without any further purification. The dyes used in this experiment were methylene blue (122965-43-9), fast sulphon black F (3682-47-1) and brilliant green (633-03-4). The dyes used in this experiment were all microscopic stains and synthetic A.I. of 99.9% extrapure. The dyes were purchased from Loba Chemie, Chennai, Tamil Nadu 600003. Sodium chloride (99.9% extrapure) was purchased from SRL chemicals, Pallikaranai, Chennai, and Tamil Nadu 600100. DI water was obtained from an internal double distillation column.

2.2. Discussion on dyes

2.2.1. Methylene blue

Methylene blue, also known as methylthioninium chloride, is a compound that is used as a colour and a medicine [23]. It is primarily used to diagnose methemoglobinemia as a prescription. It is used to treat methemoglobin rates of more than 30%, as well as negative effects that don't respond to oxygen therapy. It has lately been used to treat cyanide poisoning and urinary tract infections, although this is not recommended at this time. It is infused into a vein on a regular basis. The structure of the methylene blue dye has been shown in Fig. 1a.

Methylene blue from fabrics has a variety of negative interactions. Stirring, hallucination, tachycardia, shortness of breath, hyperactive reflexes, nausea, diarrhea, constipation, loss of balance, and collapse are all common symptoms. It has also been reported that methylene blue also causes foetal damage during pregnancy. Reports from African countries have given skin cancer disease because of exposure to the dye.

2.2.2. Fast sulphon black (F)

Fast sulphon black F is a conductimetric indicator used in copper complexation measurement using EDTA [24]. Fig. 1b shows the structure of fast sulphon black F dye and it has been reported to cause allergic reaction including contact dermatitis, breathing conditions, eye allergies, itchy skin, oral mucosa, and upper respiratory irritation.

2.2.3. Brilliant green

Brilliant green is a triarylmethane dye, an azo dye whose molecular structure is represented in Fig. 1c. Silk and

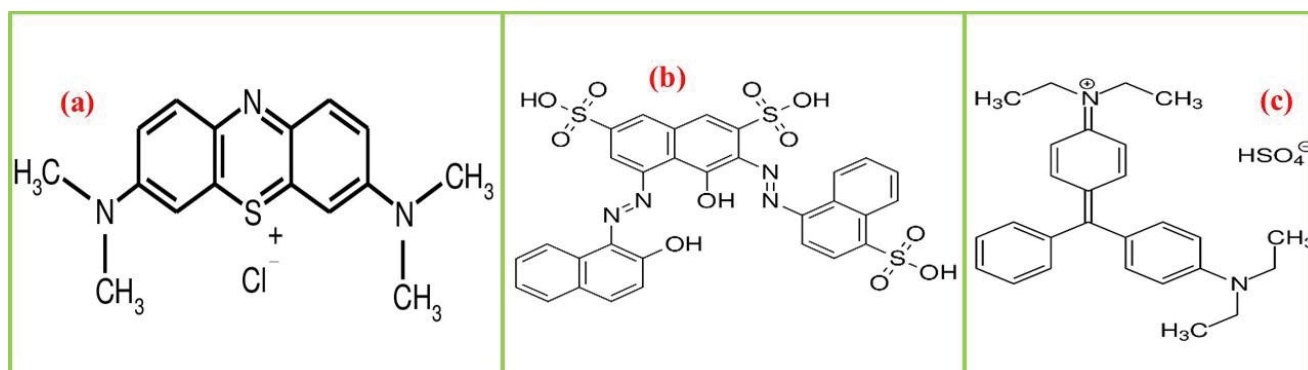


Fig. 1. (a) Structure of methylene blue dye, (b) fast sulphon black F dye, and (c) brilliant green dye.

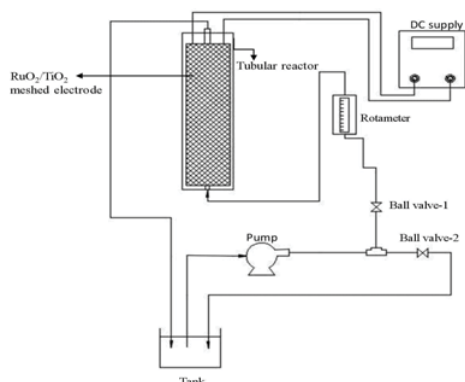


Fig. 2. Schematic representation of the tubular electrochemical reactor.

wool were stained with brilliant green. In the treatment of purulent inflammation of epidermal processes, newborn umbilical cords, bruises, cuttings, and other inadequate vital signs are advised for disinfection of fresh, postoperatively, post-traumatic scars [25].

Brilliant green causes nausea and is poisonous when consumed. If contact with the eye occurs, the combination can result in grave wounds and possibly bilateral vision owing to corneal opacity.

2.3. Experimental configuration

In electrochemical studies, the cathode is titanium substrate Ti_{0.7}Ru_{0.3}O₂ which was used as a non-soluble anode (Ti/Ti_{0.7}Ru-0.3O₂) indicating that the material content is coated with 70% TiO₂/30% RuO₂. The cathode is built of stainless steel and measures 7 cm in diameter and 110 cm in height. The tube is three mm thick. A source of electricity was provided at the top edge of the pipe, whereas the mesh type anode with a 60% perforation was built with a cylindrical form of 5 cm in diameter and a height of 100 cm, leading to an efficient anode region of 628.3 cm² (1,570.8 cm² 0.4 in length). A 100 A and 0–50 V DC controlled power supply was connected with electrodes. A silicone rubber pipe was linked to the reservoir, pump, and flow meter. In the current experiment, the dye effluent has been treated by a batch recycling process.

2.4. Experimental procedure

The experiments were initially carried out by optimizing the operations of the electrochemical reactor, and the configuration of the electrochemical reactor has been shown in Figs. 3a–d. Initially, 10 mg/L of methylene blue was taken and the process variables (sodium chloride concentration, flow rate, current density). The pH of the solution was maintained at neutral (7) for the dye degradation studies. Once the optimized conditions were obtained, the other dyes, fast sulphon black (F) and brilliant green, were degraded with those conditions. Before starting the experiments, DI water should be used to clean the impurity attached to the anode. The volume of the working electrolyte was 10 L, so the concentration was prepared according to the working volume. The concentration of the synthetic dyes prepared was 100 mg. Once the required NaCl and dye solution were added, the pump was turned on and allowed to stabilize for 10 min without switching on the DC power supply. Once the system was stabilized, the DC power supply was turned on and the samples were collected for a time interval of 10 min until the dye was completely degraded.

2.5. Analytical method

2.5.1. Physicochemical characterization of synthetic dye

The dye degradation was measured in terms of color removal. Shimadzu UV-Visible Spectrophotometer (Make – Japan, Model No. UV 1800 Series) was used to measure the color removal of dye molecules.

3. Results and discussions

3.1. Effect of current density

Current density is one of the important variables in electrochemical treatment of dye effluent. The effect of current density was investigated (Fig. 4a) to study the influence of current density on electrochemical degradation of dye effluent by varying the current density in the range of 0.32, 0.81 and 1.59 A/dm² with NaCl concentration of 5 g/L and a flow rate of 60 LPM. From the experimental results, it can be observed that as the current density increases, decolorization efficiency also increases. This is may be due to the formation of more electrons which enhance the

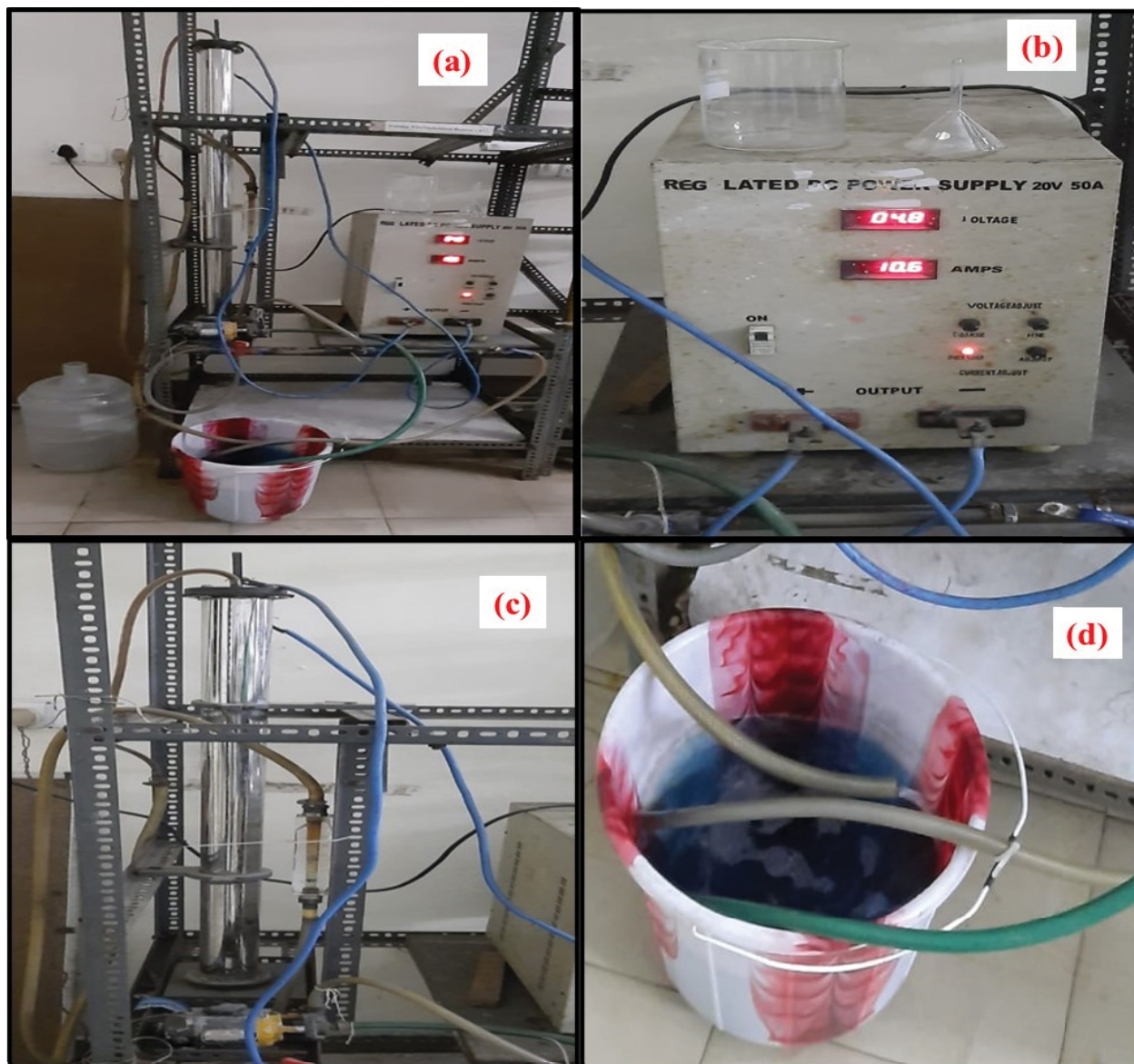
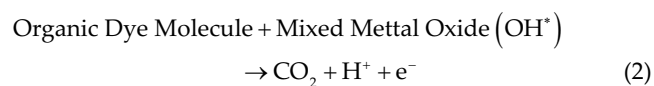
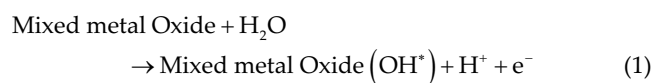


Fig. 3. (a–d) Electrochemical reactor configuration.

rate of hypochlorite ion formation which in turn enhances the decolourization of the degradation of dye molecules. However, further increase in current density generation of excess electrons may involve in splitting of water molecules instead of generating the hypochlorite ions. So, higher current density will not be helpful to degrade the pollutant [3]. Similar results have been published in the literature [26] for the removal of diuron using a high porous electrode. This phenomenon is mainly due to an increase in the generation of oxidants like hydroxyl radicals in the bulk solution [27]. The increased production of hydroxyl radicals tends to react with dye molecules rapidly, resulting in the quicker degradation of dye molecules.

Compared to other current densities such as 0.32 and 0.81 A/dm², the current density at 1.59 A/dm² shows a better dye degradation of 98% removal in terms of color within

10 min of process time. This is mainly due to the increased generation of hydroxyl radicals (OH^{*}), since the generation of hydroxyl radicals mainly depends on current density and it is directly proportional [28]. The degradation pathway of dye through electrochemical oxidation and the generation of hydroxyl radical is mainly followed by the following Eqs. (1) and (2).



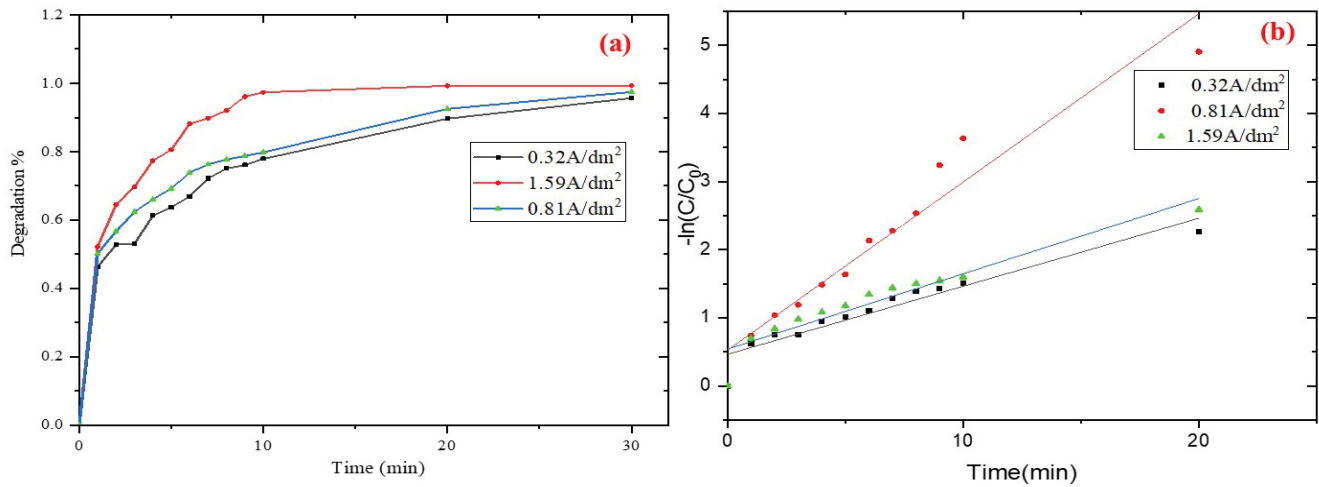


Fig. 4. (a) Degradation curve for methylene blue dye and (b) kinetic plot.

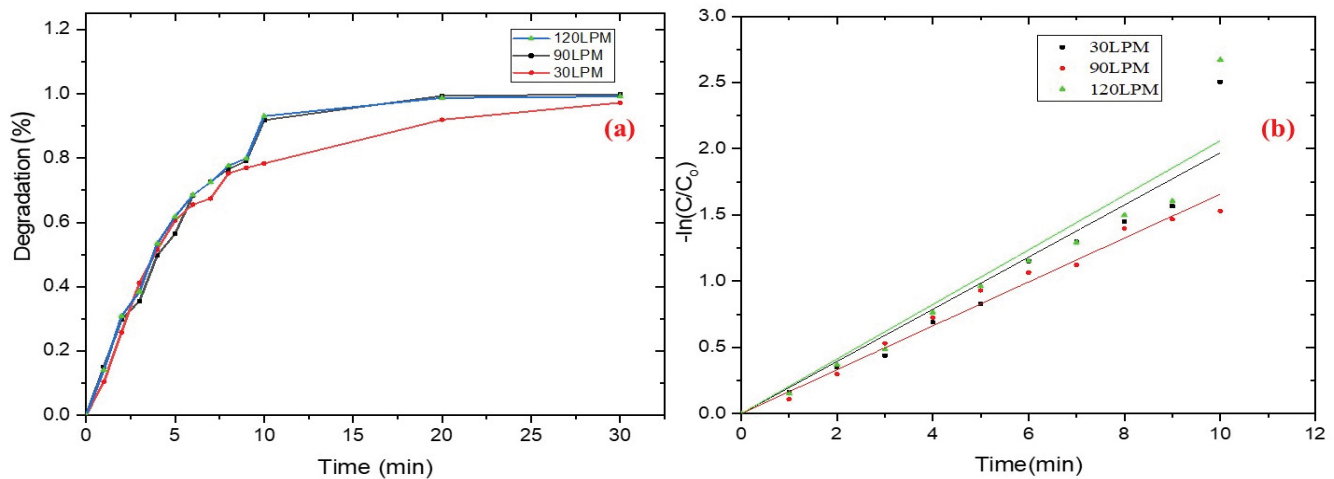


Fig. 5. (a) Degradation curve for methylene blue dye and (b) kinetic plot.

The kinetic graph (Fig. 4b) shows how deterioration is pseudo kinetic of the first-order. The rate constant $k_h = 0.72 \times 10^{-2} \text{ cm/s}$ and half-life ($t_{1/2} = 0.9562 \text{ min}$). The energy consumption calculated [29] for this study was 4.128 kWh/kg dye removed, and it was found in the previous report [30] that the energy consumption was very low, because the pollutant concentration was much lower than the current consumption for this current work.

3.2. Effect of flow rate

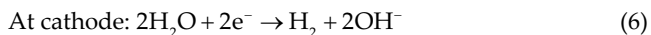
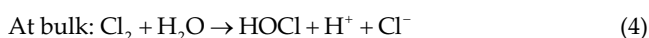
The effect of flow rate on dye degradation removal was investigated (Fig. 5a) by varying three different flow rates such as 30, 90 and 120 LPM. The experimental results revealed that the degradation of dye enhances with an increase in the dye effluent flow rate. This may be due to the fact that at higher effluent flow rates destruction of organic contents is higher because of increased formation of oxidants in the dye degradation process [3]. This kind of oxidation is indirect electrooxidation in the presence of

chloride. The flow rate effects shown at 120 and 90 LPM are more similar and have faster degradation when compared to 30 LPM. The similar degradation of dyes observed at 120 LPM was mainly due to the reaction time between the hydroxyl radicals produced and the dye molecule, which was lower when compared with 90 LPM. Based on the observed results, the optimum flow rate was determined to be 90 LPM. Since the life time of hydroxyl radicals is very much lower at a very high rate, such as 120 LPM, the hydroxyl radical does not have any potential effect on dye degradation.

While considering the indirect oxidation mechanism, the transportation of Cl ions from bulk to electrode interfaces rises and reduces the resistance of electrodes as the rate of recirculation increases. This is because of increase in the transfer coefficient which was noticed at greater flow. At 30 LPM the recirculation will be lower as there is a bypass in the flow stream. From the kinetic plot (Fig. 5b), it can be confirmed that the degradation is pseudo-first-order and $R^2 = 0.96936$.

3.3. Effect of NaCl concentration

The influence of supporting electrolyte concentration on dye degradation process is studied by varying its concentration from 1 to 5 g/L for different electrolysis time. Fig. 6a depicts the effect of supporting electrolyte on dye removal efficiency, and it was observed that dye removal efficiency was directly proportional to the concentration of supporting electrolyte. It is also observed from the literature that the addition of sodium chloride is more useful in the degradation of dye effluent. However, further increase is not effective because of the formation of layer on the surface of the anode, that acts as an insulation which results in the decrease in electrode potential which in turn impacts the system performance [3]. On addition of sodium chloride to the dye effluent during electrolysis, the colour removal efficiency improved. Similar types of results have been previously reported [31]. An increase in the concentration of supporting electrolyte eventually affects the solution conductivity, which in turn supports the higher evolution of the hydroxyl radical. The interaction between the hydroxyl radical and dye molecule also gets favored by the increased supporting electrolyte concentration. The generation of HOCl and Cl^- ions also favors the dye degradation efficiency as described in the following equations:



From the experimental results, it is observed that addition of sodium chloride as supporting electrolyte can improve the removal efficiency and minimize electrolysis time [31]. This may be due to the reaction between the electrogenerated chlorine/hypochlorite and the dye effluent.

Faster transport as well as stability will increase the electron and hole generation, improving the dye degradation efficiency. From the results, it is also observed that the dye degradation percentage of 95.82 was found to be higher in 10 min of time for a supporting electrolyte concentration of 5 g/L, whereas for other concentrations it was much lower. So, for the further study, the optimum value of supporting electrolyte concentration is fixed as 5 g/L. A similar pattern of results has been reported for the electrocatalytic degradation of diuron by using a high-pored carbon electrode [27]. From the kinetic plot (Fig. 6b), it can be found that the rate constant $k_h = 0.49 \times 10^{-2} \text{ cm/s}$ and $h_{1/2} = 1.41603 \text{ min}^{-1}$.

3.4. Degradation of different dye under optimized condition

Initially, the operating conditions for the electrochemical oxidation process were optimized using methylene blue dye, and the optimized conditions were 1.59 A/dm² current density, supporting electrolyte concentration of 5 g/L and a 90 LPM flow rate. Using the above optimized conditions, fast sulphon black and brilliant green dye degradation was carried out for a dye concentration of 10 mg/L. The degradation of synthetic dye was measured using a UV-Vis spectrometer and the spectrum for the dye removal is shown in Figs. 7a–c.

Methylene blue degradation is already discussed in section [3.1–3.3]. The degradation of fast sulphon black F showed an absorbance peak at 488 nm, which is close to the reported peak at 526 nm. Under degradation of brilliant green, the peak is observed in 623.3 nm which is also close to reported peak at 625 nm [14], so it can be observed that the chosen dyes have the assumed structure.

Figs. 8a–d and 9a–c show the degradation of dyes. It can be inferred that brilliant green underwent 90% removal in 10 min and overall degradation is 99.01%. But fast sulphon black at 10 min only underwent a removal of 36.5% and linearly increased with time till 99.15% removal. Methylene blue shows a very similar pattern to that of brilliant green during degradation. The linear degradation of fast sulphon black indicates that the azo bond in the structure is stable and strong. The kinetic plots are fitted in first order plots.

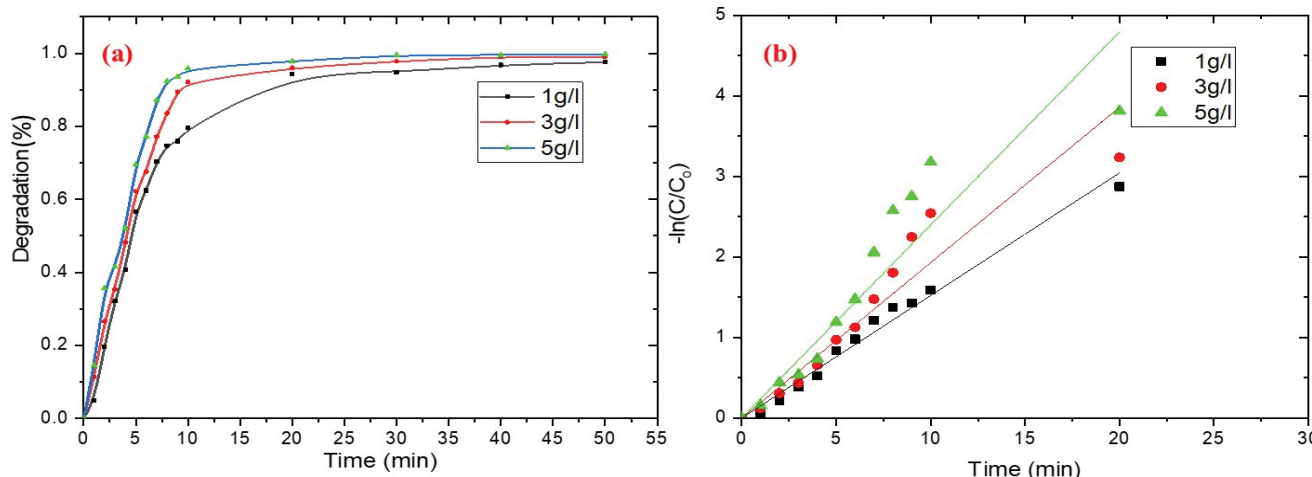


Fig. 6. (a) Degradation curve for methylene blue dye and (b) kinetic plot.

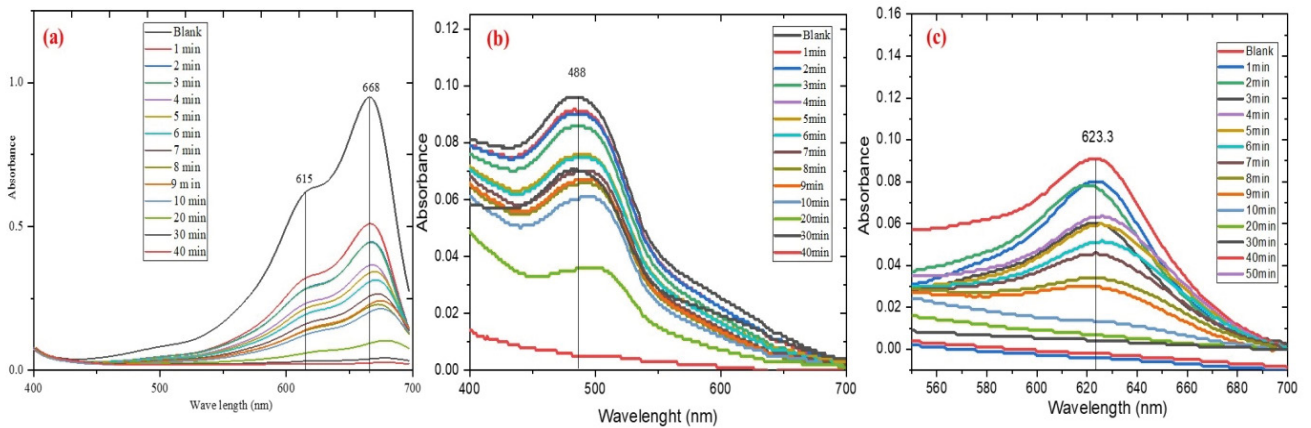


Fig. 7. Absorbance spectra for (a) methylene blue, (b) fast sulphon black F, and (c) brilliant green.

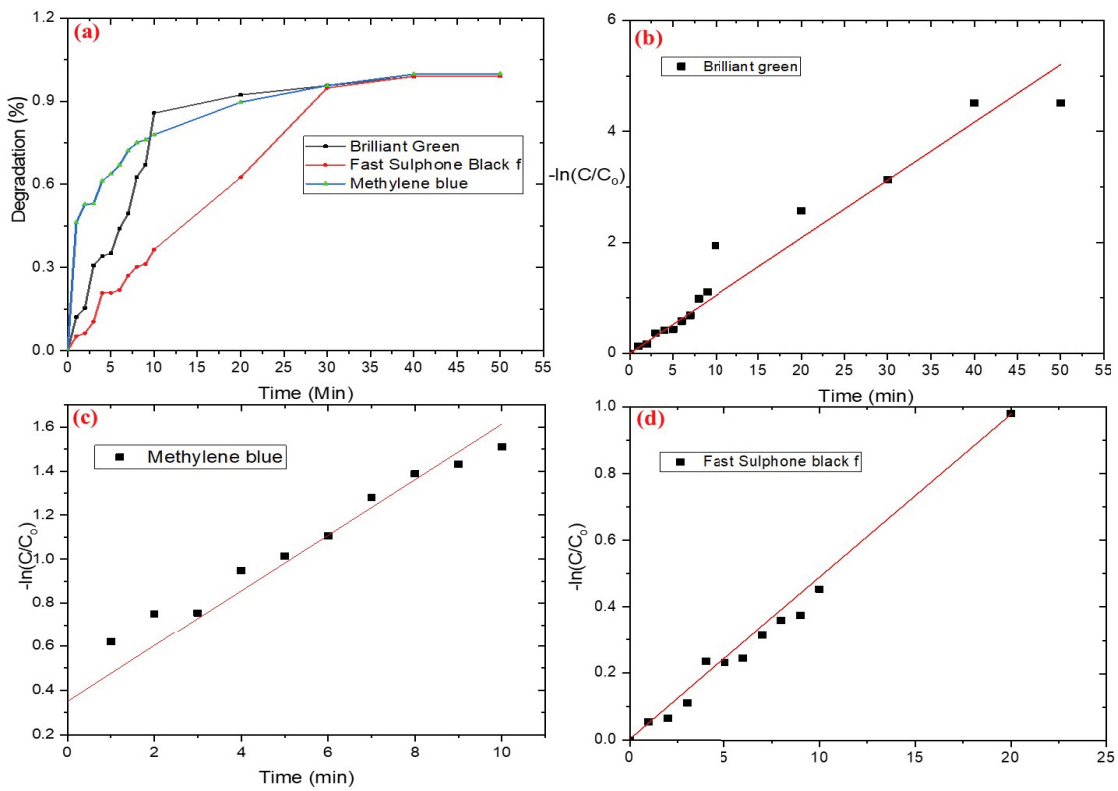


Fig. 8. (a) Degradation curve for methylene blue, brilliant green and fast sulphon black F, (b) kinetic plot for brilliant green. Kinetic plot for (c) methylene blue and (d) fast sulphon black.



Fig. 9. Degradation of dye (a) methylene blue, (b) fast sulphon black, and (c) brilliant green.

The R^2 values were found to be 0.9431, 0.9918, and 0.98651 for methylene blue, fast sulphon black (F) and brilliant green, respectively. The heterogeneous rate constant k_h value was found to be 0.13×10^{-2} , 0.07×10^{-2} , 0.1×10^{-2} cm/s for methylene blue, fast sulphon black (F), and brilliant green, respectively.

3.5. Kinetics of degradation

The kinetics of the tubular electrochemical column with circulation are illustrated below for various supported electrolyte concentrations and amperage densities. In this scenario, the reservoir is considered to be a totally mixed tank, and the column is considered to be a plug flow. Under steady-state conditions, the rate of reaction for dye removal in a batch with a recirculation column may be stated in Eq. (6):

$$\frac{C}{C_0} = e^{-\left\{\frac{t}{\tau}\left[1 - \exp\left(-\frac{k_h A_e}{Q}\right)\right]\right\}} \quad (7)$$

where τ is residence time.

From the plot $-\ln(C/C_0)$ vs. t , having the slope $\left[\left(1 - \exp\left(k_h A_e / Q\right)\right) / \tau\right]$ the rate constant k_h can be calculated. The electrochemical column's kinetic curve at various current densities.

As the current density rises from 0.32 to 1.59 A/dm², the k_h increases from 0.1×10^{-2} to 0.11×10^{-2} cm/s. The creation of the OH⁻, OCl⁻ radical is increased at greater current densities, resulting in a faster rate of deterioration. The variation of heterogeneous rate constant is as follows: 0.15×10^{-2} , 0.19×10^{-2} , and 0.24×10^{-2} cm/s when the recirculation flow is raised at NaCl concentration of 5 g/L. The improvement of the heterogeneous frequency at greater flow rates is the result of increased ion conductivity owing to bulk movement and reduces the active electrode impedance. Similarly, for the various dye concentrations, heterogeneous rate constants are computed and different current densities are shown in Tables 1 and 2.

4. Conclusion

Degradation of synthetic dyes was studied using a tubular electrochemical reactor with Ti/Ti_{0.7}Ru_{0.3}O₂ as an anode material. For methylene blue removal, the operating conditions optimized for the electrochemical oxidation process were 90 LPM flow rate with 5 g/L supporting electrolyte concentration at a current density of 1.59 A/dm² for a time period of 20 min. From the results, it was clearly noted that current density and supporting electrolyte are directly proportional to dye degradation. Using the optimized operating conditions, fast sulphon black F and brilliant green dye removal was carried out quickly. To predict the order of dye degradation, kinetic plots were plotted and it was observed that dye degradation follows pseudo-first-order kinetics. From the study, it was observed that for all the synthetic dyes, the degradation removal percentage obtained was 95 for an overall time period of 10 min. According to the findings of this study, electrochemical oxidation processes are very viable and more effective method for dye

Table 1

Heterogeneous rate constant for current density variation for methylene blue dye

Current density (A/dm ²)	k_h (cm/s)
0.32	0.1×10^{-2}
0.81	0.2×10^{-2}
1.59	0.11×10^{-2}

Table 2

Heterogeneous rate constant for NaCl variation for methylene blue dye

NaCl concentration (g/L)	k_h (cm/s)
1	0.15×10^{-2}
3	0.19×10^{-2}
5	0.24×10^{-2}

degradation processes and can be scaled up for large-scale industrial processes.

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