Photoelectrocatalytic Oxidation of Textile Industry Wastewater by RuO$_2$/IrO$_2$/TaO$_2$ Coated Titanium Electrodes

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ABSTRACT

Photoelectrocatalytic Oxidation (PECO) system prominently increases the migration of photoexcited charges, hinders the fast recombination of electron-hole, and increases the period of photogenerated holes. In this article, we constructed a novel PECO system to degrade textile industry wastewater by RuO$_2$/IrO$_2$/TaO$_2$ coated titanium electrodes. The result shows that PECO treatment can effectively reduce the color and true color of the secondary pollutants present in the wastewater. It is confirmed that a synergistic effect exists between photocatalysis (PC) and electrocatalysis (EC). Moreover, we discussed the influence of pH, current density, electrolyte concentration, and stirring speed. The maximum decolorization efficiency of textile industry wastewater with a pH of 8.2 was found to be 96% under the optimum condition stirrer speed of 200 rpm, an electrolyte concentration of 0.05M, and at a treatment time of 30 mins. The UV-Visible spectra confirm the degradation of textile industry wastewater, however with limited success (Arslan-Alaton et al. 2008).

Recently, Advanced Oxidation Processes (AOPs) and electrochemical methods have been established to treat the impurities of drinking water and industrial effluents (Rathinam et al. 2015). As the guidelines worldwide have become stringent, the effluents of textile and related industries have to be treated carefully before discharge. This has resulted in a demand for environmentally friendly technologies to remove dyes from effluents (Rajabi et al. 2016).

The textile industry is one of the most water-consuming industries with a huge volume of high-quality water demand. Textile industrial wastewater is contaminated with a wide range of potential organic and inorganic pollutants that adversely affect the aquatic environment. Most annually produced dyes that are estimated at hundreds of thousands of tons are used in the textile industry. The textile industry is considered as one of the most-dye consuming industries. There are various types of dyes involved in the dying process; reactive dyes are one among them. (Nasr et al. 2019). High quantities of wastewaters containing unconsumed dyes are released into the environment by textile dyeing and printing industries which have high biological oxygen demands (BOD), high chemical oxygen demands (COD), high concentrations of suspended solids, high salt content, and high levels of color caused by residual dyes. The presence of color and its causative compounds have always been undesirable.

INTRODUCTION

The widespread disposal of industrial wastewater containing organic dyes onto the land and water bodies led to serious contamination in many countries worldwide because of their toxicity and threat to human life and the environment (Thangamani et al. 2007, Han et al. 2009). Every day, industries, agriculture, and the general population are using water and discharging many mixtures in wastewaters. Indeed, agriculture practices, industrial discharges, and human beings play an important role in polluting water. All these practices have generated various pollutants and altered the water cycle causing a global concern linked to their eventual impact on wildlife and human health (Deblonde et al. 2011). For 20 years, many articles have reported the presence of new compounds, called “emerging pollutants”, in wastewater and aquatic environments (Vogelsang et al. 2006, Rosal et al. 2010, Thattil & Rose 2019). Traditional treatment technologies in practice for the removal of dye wastewater, fail to meet strict discharge standards. Therefore, an efficient method to treat wastewater containing dye is an urgent need to comply with the discharge standards (Dai et al. 2013). Wastewater generated by textile dyeing and finishing activities is known to contain a considerable amount of pollutants, which are biologically difficult to degrade. So far, several biochemical, chemical and physical treatment methods were applied to treat textile industry wastewater,
The photoelectrocatalytic oxidation experiments were performed in a 750 mL color removal treating the textile industry wastewater using the photoelectrocatalytic oxidation technique for photoelectrochemical reactor (Fig. 1) equipped with a UV lamp with quartz jacketed 15W wavelength of 254 nm and the electrodes are assembled within a single compartment cylindrical glass cell. The reactor is connected to a cooling water circulation bath for controlling the electrodes, gas outlet, and thermometer. An internal light source is surrounded by a quartz jacket and the light source is a UV lamp. The gaps between the plates were maintained at 7 mm to minimize the ohmic losses. Electric power was supplied by a regulated DC power supply, which was obtained from M/s. Mighty Electronics Equipments Corporation Pvt. Ltd., Coimbatore, India. The four electrodes, two anodes, and two cathodes are alternatively looped internally. The UV lamp and electrodes are connected to the respective terminals of the power source. The textile industry wastewater samples containing dyes were found to contain a pH of 8.2 and electrolyte is added to the solution taken in the photoelectrocatalytic reactor. Using the magnetic stirrer we stir the sample wastewater solution in the reactor. The treated wastewater sample was centrifuged at 5000 rpm for 15 mins and the supernatant liquid was taken for analysis. The color removal is measured using a spectrophotometer.

**MATERIALS AND METHODS**

The photoelectrocatalytic oxidation experiments were performed in a 750 mL photoelectrochemical reactor (Fig. 1) equipped with a UV lamp with quartz jacketed 15W immersion low-pressure mercury arc lamp (Philips, model TUV) as irradiation with the wavelength of 254 nm and the electrodes are assembled within a single compartment cylindrical glass cell. The reactor is connected to a cooling water circulation bath for controlling the temperature at 27±2°C. The top of the reactor is provided with a holder for holding the UV lamp, electrodes, gas outlet, and thermometer. An internal light source is surrounded by a quartz jacket and the light source is a UV lamp. The gaps between the plates were maintained at 7 mm to minimize the ohmic losses. Electric power was supplied by a regulated DC power supply, which was obtained from M/s. Mighty Electronics Equipments Corporation Pvt. Ltd., Coimbatore, India. The four electrodes, two anodes, and two cathodes are alternatively looped internally. The UV lamp and electrodes are connected to the respective terminals of the power source. The textile industry wastewater samples containing dyes were found to contain a pH of 8.2 and electrolyte is added to the solution taken in the photoelectrocatalytic reactor. Using the magnetic stirrer we stir the sample wastewater solution in the reactor. The treated wastewater sample was centrifuged at 5000 rpm for 15 mins and the supernatant liquid was taken for analysis. The color removal is measured using a spectrophotometer.

The analysis of textile industry wastewater and its removal during photoelectrocatalytic oxidation were recorded using a UV-Visible spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Japan). Decolorization efficiency calculated as follows:

\[
\text{Colour removal efficiency (%) } = \left( \frac{A_0 - A}{A_0} \right) \times 100
\]

Where;

- \(A_0\): Initial concentration of dye before electrochemical oxidation (mg.L\(^{-1}\))
- \(A\): Present concentration of dye after electrochemical oxidation (mg.L\(^{-1}\))

**RESULTS AND DISCUSSION**

**Effect of Initial pH on Colour Removal**

The pH value is an important parameter in the photoelectrocatalytic process because the species of the reaction compounds and their adsorption equilibrium depend on the pH values of the solution. The pH values of solutions can influence the process through the following three routes: (i) the semiconductor flat-band potential variation (ii) adsorption isotherm of electroactive species (the adsorption of electroactive species is governed by the Langmuir adsorption equilibrium equation) (iii) photoelectrochemical oxidation of water and \(\text{OH}^-\) ions competing with other reactants to form powerful oxidants on irradiation (Shaogui et al. 2006). It affects the capacity of adsorption and dissociation of the target compounds, the charge distribution to photocatalyst surface, and the oxidation potential of the valence band. The experiment demonstrates that the dye solution concentration decreases much faster in acidic solution than that in alkaline solution.

To study the influence of pH, experiments were conducted with pH 3, 5, and 10 in addition to sample wastewater orig-
The solution pH was adjusted using sulfuric acid (0.1N H₂SO₄) or sodium hydroxide (0.1N NaOH). During the treatment process, the current density was maintained at 15 mA.cm⁻², electrolysis time of 30 mins, stirrer speed of 200 rpm, under UV illumination, and 0.05 M of NaCl as the supporting electrolyte. Fig. 2 shows that the influence of initial pH on the percentage of color removal by photoelectrocatalytic oxidation within 30 mins of the reaction.

It is clear that varying the pH strongly affected color removal efficiency and reached 98% with sample wastewater’s original pH of 8.2 within 30 mins of the treatment process, while lower color removal was observed at higher pH. This is due to the oxidation and hydrolysis of chlorine yields hypochlorous acid (HOCl) or the hypochlorite ion (OCl⁻) depending on the solution pH 10. On the other hand, a low pH solution will corrode the electrode and inhibit the activity of the electrode, even hinder the proceeding of degradation reaction (Ju et al. 2012).

When the pH value was less than 4, the molecule in the dye was in cationic form and its adsorption on the catalyst surface became difficult because of an electrostatic repulsive force. As a result, the efficiency of the photoelectrocatalytic degradation of textile wastewater was relatively low with pH less than 4 while the efficiency was increased with pH greater than 4. Thus, the oxidizing ability of photo-generated holes was raised, i.e. the hydroxyl radicals production was facilitated in the oxidation of water (or hydroxide ions) by photo-generated holes. At neutral pH, more readily water (or hydroxide ions) underwent oxidation to generate hydroxyl radicals on the catalyst surface (Daghrir et al. 2013). The degradation capacity of the system in this extremely dark-colored media is mainly due to the electrochemical generation of oxidant species, which can be photochemically transformed in the bulk of the solution in an even more reactive radical (Tauchert et al. 2006). Therefore, the photoelectrocatalytic degradation of textile industry dye wastewater was more efficient at the original pH of 8.2.

In the photoelectrocatalytic method, the degradation rate of certain contaminants such as pentachlorophenol, humic acid, and benzotriazole is found to be maximum and much faster in an acidic solution than in an alkaline solution. It is proven that the degradation rate of 4-chlorophenol was enhanced in both alkaline and acid solutions (Wang et al. 2009). However, the effect of pH in photocatalytic reactions cannot be generalized (Daghrir et al. 2012). Studies have reported that photoelectrocatalytic oxidation without initial pH adjustment was more effective in removing phenol, compared to pH 3.0 and pH 11. Photoelectrocatalytic oxidation degradation of BPA is favored at strongly acidic conditions with the extent of enhancement reaching as much as about 90%. Working at slightly acidic, neutral, or alkaline conditions reduces degradation rates by as much as 3 to 4 times (Yavuz & Kapoor 2006). Therefore, pH is an important operational parameter determining the efficiency of photocatalytic removal of different pollutants in wastewaters (Hadjiltaief et al. 2016).

Effect of Electrolyte Concentration on Colour Removal

An electrolyte plays a vital role in the photoelectrocatalytic process. In the photoelectrocatalytic process, the efficiency of current intensity, voltage, and consumption of electrical energy is affected by the conductivity of the solution. The conductivity must be high to ensure good ion transfer in the effluent. When the conductivity is too low, the resistance is
too high and consequently, an increase of the applied voltage is observed. High ionic strength leads to faster electron transport and better degradation rate (Ju et al. 2012) so that the effect of electrolyte on the degradation of textile wastewater was investigated. Solutions with various ionic strengths were obtained by preparing various concentrations of NaCl aqueous solution in this study. As anions of the supporting electrolyte participate in the decomposition reaction of dye molecules, careful selection of electrolytes is essential in maximizing the decolorization efficiency of a given compound.

In this study, the supporting electrolyte used is NaCl. The NaCl concentrations (0.025, 0.05, 0.1M) were tested. Each test was performed with sample wastewater with a pH of 8.2 and under a constant current density of 15 mA.cm⁻², electrolysis time of 30 mins, stirrer speed of 200 rpm under UV illumination. The result shown in Fig. 3 indicates that the textile industry wastewater degradation efficiency increases with the concentration of electrolyte. This can be attributed to the surplus free Cl⁻ since the electrolyte can enhance charge transfer to the reactor, leading to an increase in the efficiency of direct electrochemical oxidation and the capture of a photogenerated electron by the external electric field (Wenbing et al. 2005). In chloride solutions, the Cl⁻ ions adsorbed on the working electrode may be oxidized to produce Cl₂ as oxidants which may decolorize dye wastewater (Ali Baddouh et al. 2018). In addition, the photogenerated hole or OH• can oxidize free chloride ion into active chlorine as one of the products in dye wastewater degradation, and then the active chlorine (Cl•, ClO⁻) promotes oxidation of dye wastewater. These results indicate that the adsorption of chloride ions is preponderant at lower pH. As a consequence, the contribution of chloride oxidation is diminished under conditions where the pH of the solution is neutral or alkaline, and the formation of hydroxyl radicals under these conditions could be the preponderant process.

An increase in the concentration of NaCl has been found to increase the generation of active chlorine (Murugananthan et al. 2011). Decolourization of paper mill effluents was found to increase with the increase in NaCl concentration (El–Ashtoukhy et al. 2009). Additionally, it must be assumed that due to the high complexity of chemical, photochemical and electrochemical reactions involving chlorine generation one could possibly form other oxidants during this photoelectrochemical process (Fraga et al. 2009). NaCl releases chloride ions in the liquid phase, which can electrochemically and/or photochemically generate highly reactive chlorohydroxyl radicals (ClOH⁺), as well as chloride radicals (Kiwi et al. 2000); Furthermore, anodic reactions may generate free chlorine, chlorine dioxide, and hypochlorite (Daskalaki et al. 2013). To minimize the chlorides’ negative influence, an optimum concentration of 0.05 M was adopted in other experiments.

**Effect of Current Density on Color Removal**

As most applications of photoelectrochemical systems involve the transfer of electrons across the solid/electrolyte interface, current density applied potential recording techniques are commonly used for their characterization. It is reported that the rate of degradation increases significantly when the applied current density increased (Mohan et al. 2007). To investigate the influence of current density on treatment efficiency of the electrochemical system, different current densities from 5 to 25 mA.cm² were experimentally analyzed under the conditions:

![Fig. 3: Effect of supporting electrolyte concentration on color removal.](image-url)
30 mins treatment time and 200 rpm stirrer speed. Fig. 4 shows that color removal percentage increased with electrolysis time and increased with applied current density.

In all cases, the color removal rate was much faster during the first 20 mins of electrolysis. With the current density of 15 mA.cm\(^{-2}\) and at 5 mins electrolysis time, color removal efficiency reached 96.2%. The complete color removal was achieved at 15 mA.cm\(^{-2}\) after 30 mins of electrolysis.

After 30 mins, the total removal efficiency of color was 92.4% for the current density of 5 mA.cm\(^{-2}\), while almost complete degradation was observed at the current densities 10, 15, 20, and 25 mA.cm\(^{-2}\). It is clear that percentage color removal increases with increasing current density; this is attributed to an increase of Cl\(_2\), HOCl, and OCl\(^-\) concentrations in the solution, which eventually increases the dye degradation (Raghu & Ahmed Basha 2008). Beyond 15 mA.cm\(^{-2}\), there is no significant increase in the percentage of color removal; this may be attributed to the fact that the discharge potential of Cl\(_2\) increases with current density and becomes close to the discharge potential of O\(_2\). It is explained by the fact that an external electric field could not only decrease the rate of recombination of electron-hole pairs but could also improve direct and/or indirect electrooxidation reactions of anodes under higher applied cell voltages.

It is well known that the amount of applied current density determines production rate, and adjusts the rate and size of the bubble production, hence affects the growth of flocs (Daneshwar et al. 2003). Current density can be formulated as CD = I/S, where CD is the current density (mA\(^{-2}\)), I is the current (A), and S is the total area of the anode (m\(^2\)) (Parsa et al. 2011).

From these results, it is clear that applied current improves the photoelectrochemical process due to minimization of charge e^-/h+ recombination up to 15 mA.cm\(^{-2}\), when maximum optimization is obtained. In addition, at higher current density the process could be limited by mass transporting conditions and/or chlorate production as a parallel reaction occurring at the photoanode following the electrochemical reaction expressed in Eq. 1 or aqueous solution by a chemical reaction in Eq. 2 as demonstrated below:

\[
6\text{OCI}^- + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 6\text{H}^+ + 4\text{Cl}^- + 1.5\text{O}_2 + 6\text{e}^- \quad (1)
\]

\[
2\text{HOCl} + \text{OCl}^- \rightarrow \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^- \quad (2)
\]

**Effect of Treatment Time and Stirring Speed on Colour Removal**

The influence of electrolysis time was explored at a constant current density of 15 mA.cm\(^{-2}\), stirrer speed 200 rpm, and supporting electrolyte concentration of 0.05 M. Fig. 5 shows the effect of treatment time on the color removal. It was noted that the color removal increased from 0 to 60 mins, indicating that dye wastewater color removal was directly proportional to treatment time. The rate of degradation is high at the beginning of the process and reduces gradually to a monotonical value at the end of the process. This phenomenon was consistent with that of the electrochemical degradation of 4-chlorophenol reported by Wang et al. (2009). In view of reducing power consumption and further optimizing the electrochemical oxidation, all other experiments were conducted within 30 mins of treatment time.

To verify the important role of mass transfer on the photoelectrocatalytic oxidation of textile industry wastewater, the influence of stirrer speed during anodic oxidation of waste-
water was studied by varying the stirrer speed. The stirring speed of the solution causes an increase of contact between flocs and agglomeration during the process. Experiments were performed at different stirrer speeds, in the range of 150 to 300 rpm under the following experimental conditions; 15 mA.cm\(^{-2}\) of applied current density and treatment time of 30 mins. Fig. 6 shows that the percentage color removal decreases from 90.98% to 85.72% as the stirrer speed increases from 150 to 300 rpm.

It can be seen from the results that increasing color removal was obtained under different stirrer speeds and the color removal is higher with the presence of a stirrer. The result shows that enhancing effect of stirrer speed on the rate of color removal becomes less pronounced at high stirrer speeds (e.g. >200 rpm) probably because of the diffusion-controlled cathodic reduction of hypochlorite and its anodic oxidation reaction are favored at higher stirrer speed. Also by increasing stirrer speed, color removal is increased up to 200 rpm, beyond that there is a significant decrease in colour removal. An increase in stirrer speed leads to a more rapid and more actual electrochemical process. This confirms that the color removal reaction is diffusion-controlled when there is an increase in rotational speed. There will be an increase in the intensity of turbulence and a reduction in the diffusion layer thickness at the surface of the electrode that improves the mixing conditions in the electrolyte in bulk. This enhances the rate of transfer of reactants and products to anode surface (El-Ashtoukhy et al. 2009).

![Fig. 5: Effect of treatment time on color removal.](image1)

![Fig. 6: Effect of stirrer speed on color removal.](image2)
Effect of Applied Current Density on Energy Consumption

It is critical to evaluate the electrical energy consumption in textile wastewater treatment to determine whether photoelectrocatalytic oxidation is financially viable for the removal of color from textile industry wastewater. Once the required currents and corresponding voltages were obtained from the photoelectrocatalytic oxidation tests, the amount of energy used was estimated.

In Fig. 7, the minimum energy consumption was 5.64 kWh.m\(^{-3}\) at 5 mA.cm\(^{-2}\) current density for 30 mins treatment time under the optimum conditions. The energy consumption in the high current density was increased because of polarization. The energy consumption was increased from 5.64 kWh.m\(^{-3}\) to 18.52 kWh.m\(^{-3}\) while increasing applied current density from 5 mA.cm\(^{-2}\) to 25 mA.cm\(^{-2}\) under the optimum conditions. The present experiment was conducted at an applied current density of 15mA.cm\(^{-2}\).

UV-Visible Absorbance Spectra Analysis

Fig. 8 shows the time-dependent UV–visible spectrum of textile industry wastewater during the photoelectrocatalytic oxidation process. As it is clear from this figure, the absorption peaks diminished and finally disappeared under reaction, which indicates that the wastewater had been degraded and color was removed. However, it is remarkable to note that the overall absorbance of the curve decreases when the photoelectrocatalytic treatments are applied, likely due to colloidal and suspended particles. It is found that there is no new absorption bands appeared in either the visible or ultraviolet regions.

![Fig. 7: Effect of applied current density on energy consumption.](image1)

![Fig. 8: UV-visible spectrum of textile industry wastewater.](image2)
CONCLUSION

From the results, it can be concluded that the color removal efficiency of textile industry wastewater reached 98% within 30 mins, while lower color removal was observed at higher pH. The maximum color removal was achieved at a current density of 15 mA.cm$^{-2}$, electrolysis time of 30 mins, stirrer speed of 200 rpm under UV illumination. The color removal was directly proportional to treatment time and photo-electrocatalytic oxidation was found to be effective for color removal. The color removal efficiency of textile industry wastewater after treatment was confirmed using UV-visible spectroscopy. This study suggests that the photoelectrocatalytic oxidation technique is effective and reliable for a wide variety of future applications.

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