Comparative study of electrochemical oxidation for dye degradation: Parametric optimization and mechanism identification

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ABSTRACT

Present study investigates the direct and indirect electrochemical (EC) oxidation of malachite green (MG) dye in acidic and basic medium using RuO_2–TiO_2 and Pt coated Ti mesh electrodes (Ti/RuO_2–TiO_2 and Ti/Pt electrodes). The effects of process parameters such as current density (j), initial pH (pH$_o$) and NaCl (electrolyte) concentration (m) during the EC oxidation were also examined. This study investigates the effect of dissolved chlorine, chlorate, chlorite, and chlorine dioxide formed during EC oxidation at different pH. Active sites of electrodes surface promote the production of OH radicals ($^\bullet$OH). Synergistic effect of active chlorine species and $^\bullet$OH radicals significantly enhanced the indirect EC oxidation of MG dye solution with Ti/RuO_2–TiO_2 anode. Gas chromatography-mass spectrometry (GC–MS), high performance liquid chromatography (HPLC), color and chemical oxygen demand (COD) were used to identify the EC oxidative degradation mechanism with both electrodes. Acidic pH was found to promote the dye degradation. Under optimum condition, MG dye was completely decolorized and 98% COD removal was obtained after 140 min of EC treatment. Based on the intermediate and by-products identification, it seems that MG dye degradation occurred via N-methylation and conjugated structure destruction.

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1. Introduction

Dye containing wastewater from the large scale production and countless applications of colorants in manufacturing industries such as textile, leather industries and paper mills produce serious environmental water problem and health risks [1,2]. The non–aesthetic properties and the mutagenicity, the carcinogenicity and the toxicity of dyes have been largely accepted [3,4]. A large number of techniques such as catalytic oxidation, membrane filtration, coagulation, flocculation, adsorption and biological technology have been proposed for the treatment of dye containing wastewater [5–10]. Most of the commercial treatment technologies have some limitations and drawbacks such as long treatment time, sludge disposal issues, requirement of chemicals and generation of secondary pollution [11,12].

In the last decade, electrochemical (EC) treatment technologies such as electro-deposition, electro–flotation, electro–coagulation, and electro–oxidation have been attracted a lot of research attention due to its cost–effective nature and high versatility. It is an alternative for the treatment of various kinds of industrial wastewaters [13–15]. The EC technology has been recently proved to be an effective option for the treatment of dye-containing wastewater due to higher decolorization rate and chemical oxygen demand (COD) removal efficiency [16,17]. Various scientific group have frequently used EC oxidation technique particularly direct and indirect oxidation for the removal of dye containing wastewater by controlling the operational parameters and by improving the catalytic activity of the electrode materials [18–26]. The electro–catalytic behaviour and activity of electrodes depends upon the nature of electrodes materials. Titanium oxide (TiO_2), ruthenium oxide (RuO_2), iridium oxide (IrO_2), graphite, platinum (Pt), lead dioxides (PbO_2), tin oxides (SbO_2) and boron doped diamond (BDD) are frequently used dimensionally stable anodes (DSAs) for the EC treatment of dye containing effluents [16,17]. In comparison of other anodes, DSAs have high chemical and mechanical resistance even under higher current density and strong acid conditions [27–30]. For example, Ti/Pt has been employed for the EC oxidation of methylene blue [31] and methyl red [29] dye containing wastewater. Ti/$Ru_{0.3}Ti_{0.7}O_2$ has been used for degradation of acid violet 1 [32], direct black [33], direct red

[33], reactive blue 19 [34] and reactive red [35] dyes. In these studies, effects of dye concentration, pH, supporting electrolyte, cathode material, current density, anode potential and temperature have been studied and optimized. However, limited works are available in which intermediates, by-products and active chlorine species have been identified and probable dye degradation mechanism has been proposed.

In this study, malachite green (MG) dye, a triphenyl methane dye, was chosen as a model compound for EC treatment with RuO_2–TiO_2 and Pt coated Ti mesh electrodes (Ti/RuO_2–TiO_2 and Ti/Pt electrodes) due to its remarkable stability, rigid structure, and large usage in numerous coloring industries. The main objective of the proposed work was to compare direct and indirect EC oxidative degradation of MG dye solution with and without active chloro species found in electrolyte solution during the EC oxidation with both Ti/RuO_2–TiO_2 and Ti/Pt electrodes. The treatment efficiency was maximized by optimizing the operating parameters such as current density (j), solution pH, electrolyte concentration (m). A plausible scheme for dye degradation was proposed to elucidate the mechanism of dye removal.

2. Material and methods

2.1. Materials

All chemicals used in the present study were analytical grade and used without further purification. Triphenylmetane malachite green (MG) dye purchase from Yogesh Dyestuff Products Pvt., Ltd, India. Analytical grade para-nitrophenol (PNP), amino benzene (AB), benzoic acid (BA) benzophenone (BP), maleic acid (MA), oxalic acid (OA), and oxamic acid (OmA) were purchased from Sigma-Aldrich, India. Di-chloromethane, ethyl acetate, methanol, sodium chloride, sodium hydroxide, sulphuric acid, hydrochloric acid, and total nitrogen reagents were purchased from Merck. De–ionized or milli–Q water was used during the experiments. Ti/Pt and Ti/RuO_2–TiO_2 electrodes were purchased from Titanium Tantalum Co. Chennai, India.

2.2. Electrochemical experiment

A circular cross-section lab-scale glass batch reactor having 1 L volume was used for the EC oxidation of MG dye containing wastewater. D.C. power supply under potentiostate/galvanostate modes was used for controlling and monitoring the electrolysis conditions during the experiments. Ti/Pt and Ti/RuO_2–TiO_2 electrodes having equal dimension 9×10 cm and 1.5 mm thickness with 90 cm^2 effective surface area were used in the present study. Electrode gap between the anode and cathode was fixed at 1.0 cm in all experimental runs. For easy stirring of the solution by a magnetic stirrer (at 560 rpm), electrode bottom was kept 5 cm above the bottom of EC reactor. During the experiments, voltage variation was controlled between the ranges of 1–15 V at $30 \pm 2\,^{\circ}C$.

Actual experimental setup is shown in Fig. S1 (see Supporting information). 0.9 L MG dye solution was taken in EC reactor in each experimental run and 0.1 N sodium hydroxide or hydrochloric acid solution was added for adjusting the initial pH of the solution to the desired level. The main characteristics of MG dye are given in Table S1.

Dye solution was prepared by dissolving the 150 mg MG dye in 1.0 L distilled water containing 0.20 M H_2SO_4. EC oxidation treatment conditions were optimized by performing the experiments over a range of experimental conditions such as $j = 56.3$–$225.2\,A/m^2$, $m = 0.2$–$0.8\,mg/L$, and pH = 2.5–8.5. During the each treatment condition samples were collected at different time intervals. After collection, each sample was centrifuged and analyzed for the remaining color and COD in solution.

2.3. Analytical techniques

Decolorization efficiency of MG dye at different treatment time during each experiment run was measured by using the UV–visible spectrophotometer (HACH, DR 5000) at a wavelength of 619 nm with ±3% accuracy. COD analyser (HACH/DR 5000) was used to analyse the COD of MG dye. For analyzing the COD, the samples were digested in COD reactor (AL 38 SC, Aqualytic) for a digestion period of 2 h at 150 °C. The percentage color (NTU) and COD (mg/L) were determined by the following expression:

$$RE\% = \frac{C_o - C_f}{C_f} \times 100 \tag{1}$$

where, C_o and C_f are the initial and final concentration of the dye solution collected at different times during the EC treatment.

The content of the degradation products was measured by high performance liquid chromatography (HPLC) by comparing the retention time of standard compounds. Agilent Zorbax Eclipse XDB–phenyl column (150×4.6 mm, 5 μm) coupled with UV detector at $\lambda = 619$ and 250 nm was used for detecting and quantifying aromatic by-products while Agilent Zorbax Eclipse XDB-C18 column (150 mm $\times$ 4.6 mm, 5 μm) at $\lambda = 210$ nm was used for detecting and quantifying the small aliphatic carboxylic acids compounds. For the analysis, 10 μL samples were first collected during the different treatment time of experiment run and filtered with 0.45 μm PTFE filter paper than injected to the column of HPLC. A mixture of mobile phase (acetonitrile: methanol: water = 60: 20: 20 (v/v) for phenyl column and methanol: phosphate buffer = 50: 50 (v/v) for C18 column) at a 1.0 mL/min flow rate was used for HPLC analysis. Nitrate (NO_3^-) ions concentration in the mineralized dye solution was measured by using the ion chromatograph (10 Avp HPLC chromatograph, Shimadzu) fitted with Shim-Pack IC–A1 S anion column and coupled with 10 Avp conductivity detector.

Gas chromatograph mass spectrometer (GC–MS) (Perkin–Elmer Auto system coupled turbo mass selective mass detector) containing DB–5 (30 m $\times$ 0.25 μm internal diameter) fused silica capillary column (95% dimethyl-siloxane and 5% diphenyl) was used for identifying intermediates generated at various treatment time during MG dye degradation. The column temperature was programmed from 70 °C (3 min) to 290 °C (1 min) at a ramp rate of 7 °C/min, split flow of 10 mL/min at 1 μL split–split less injector mode and 1 mL/min flow rate of helium as a carrier gas. The tentative species identification as a supplement to mass spectral and retention time characteristics was done by using the NIST library. The mechanism of dye degradation was schematically proposed on the basis of the results obtained.

The chlorine species (Cl_2, ClO_2^-, ClO_2 and ClO_3^-) concentration produced during EC oxidation with anodes at different treatment time with different pH (2.5, 4.5, 6.5, and 8.5) and fixed amount of NaCl (0.6 mg/L) was determined by using a sequence of iodometric titration. Titration method was used for determining the concentration of active chloro species [36,37], while ion chromatography (IC) equipped with an Ion Pack AS16 column (4 mm $\times$ 250 mm) was used for estimating the perchlorate content. A protocol based on a sequence of iodometric titrations was employed for the assessment of Cl_2, ClO_2^-, ClO_2 and ClO_3^- concentrations [36–38]. The existence of various active species was differentiated on the basis of their reactivity, which changed significantly with pH and added reagents. Some of these reactions are as shown below:

$$Cl_2 + 2\,I^- \rightarrow I_2 + 2\,Cl^- \tag{2}$$

$$ClO_2 + 2\,I^- \rightarrow I_2 + 2\,ClO_2 \tag{3}$$