

ELECTROCHEMICAL ADVANCED OXIDATION PROCESS FOR SYNTHETIC DYE WASTEWATER TREATMENT

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(Received 10 February, 2020; accepted 1 July, 2020)

ABSTRACT

The aim of this study is to employ mixed metal oxide plate as anode and stainless steel as cathode for decolorization of aqueous solution containing 100 mg/L of Rhodamine-B dye. This study deals with analysis of the effects of different operation parameters like initial pH, current density and different electrolytes on electro oxidation process. Results show the effective use of MMO plate as anode. Better color removal efficiency obtained at acidic and neutral pH range. Chloride ion concentration highly affects reaction rate of decolourization. Almost complete color removal can be obtained at all the employed current densities. An optimum efficiency was obtained at pH 3 and 5, at temperature of 30 °C. Also, at the current density of 15 mA /cm² in electrolyte concentration (NaCl) of 0.03 M, almost complete color removal was achieved after 10 min of electrolysis.

KEY WORDS : Mixed metal oxide, Electrochemical advanced oxidation process, Decolourization

INTRODUCTION

Due to various harmful effects of wastewater containing dyes, it has drawn major attention. Dye wastewaters is considerable source of organic and inorganic compounds, that are highly toxic, carcinogenic and non-biodegradable. Dye wastewater discharged into natural water bodies affects flora and fauna adversely as it reduces light penetration that affects photosynthesis, reduces gas solubility that decreases dissolved oxygen. It also promotes eutrophication and reduces transparency of water bodies which is an aesthetical demerit (Martínez *et al.*, 2009; Forgacs *et al.*, 2004; Robinson *et al.*, 2001).

Most commonly applied methods for treatment of dye wastewaters are coagulation, membrane filtration, adsorption, ion exchange, chemical oxidation, ozonation, bio-sorption aerobic and anaerobic biological processes (Gutierrez *et al.*, 1999; Naim and El, 2002; Hao *et al.*, 2000). All these methods have some limitations of sludge generation and induction of secondary pollutant that might be more harmful than primary pollutant. Advance

oxidation processes (AOP) are most promising techniques to overcome these limitations, as these technologies involve OH radical generation that is powerful oxidant. AOPs are destructive technologies that oxidize pollutants into simple harmless compounds and avoid generation of secondary pollutants as well as no sludge generated after treatment (Simond *et al.*, 1997; Kotz *et al.*, 1991).

Electrochemical advanced oxidation processes (EAOPs) are applied effectively for the degradation of persistent organics and dyes. Hydroxyl radicals are electrically generated during electrolysis process that helps mineralization of pollutants. EAOPs can be divided into two phases: direct oxidation and indirect oxidation. In the case of direct oxidation, hydroxyl radicals are produced on the surface of anode. In indirect oxidation, intermediate oxidizing agent is produced in the liquid and oxidation occurs at anodic surface. Use of mixed metal oxides coated Titanium plate as anode is effectively studied by many researchers for degradation of pollutants in electrolysis. Various metal oxides like PbO₂, SnO₂, IrO₂, RuO₂, TiO₂ are used as coating material (Rajeshwar and Ibanez, 1997; Mohan *et al.*, 2001). In

this study Titanium plate coated with IrO_2 , RuO_2 , TiO_2 used as anode material for degradation of Rhodamine-B dye in electrochemical oxidation process. Rhodamine-B is recalcitrant dye that is used most used in food and cosmetic industry. The effect of various process parameters such as electrolysis time, current density, electrolyte concentration and initial pH is studied.

MATERIALS AND METHODOLOGY

Material

All chemicals of analytical grade were used in this procedure of experiments. All the aqueous solutions were prepared using distilled water. Rhodamine-B dye ($\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_3$, C.I.No 45170, 479.02 g/mol) was obtained from a laboratory in India. Figure 1 shows the chemical structure of dye. Mixed Metal Oxide used in studies was purchased from Chennai (India).



Fig. 1. Chemical structure of Rhodamine-B dye

Experimental procedure

The experiments were carried out in acrylic reactor of dimensions 7 cm length, 7 cm width and 6/5 cm height. The anode used was of mixed metal oxides of TiO_2 , IrO_2 , RuO_2 coated on Ti plate. Stainless steel was used as cathode. The spacing between anode and cathode was 6 cm. The assembly was placed on a magnetic stirrer. Sodium chloride (NaCl) and sodium sulphate (Na_2SO_4) are used as supporting electrolytes and DC current was applied for the electrolysis. Batch electrolysis experiments were conducted for the decolorization of Rhodamine-B dye as a function of Initial pH varied as 3, 5, 7 and 9. Current density varied as 5, 10, 15, 20 and 25 mA/cm², supporting Electrolyte concentration (NaCl) varying from 0.01 to 0.05 M and Na_2SO_4 at 0.1 M.

Analytical Techniques

The samples were withdrawn at fixed time interval

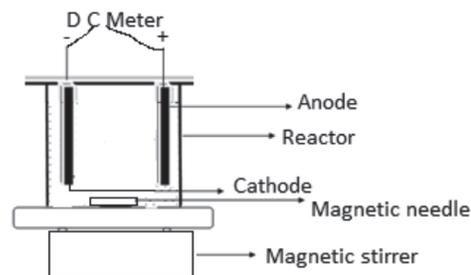


Fig. 2. Experimental setup

of 1 min, and filtered and analysed in spectrophotometer initial for colour removal. The concentration of Rhodamine-B was determined by measuring the absorbance at 554 nm wavelength. Percentage of colour removal was determined by the following equation:

$$\text{Color removal(\%)} = \left[\frac{\text{ABS}_0 - \text{ABS}_t}{\text{ABS}_0} \right] \times 100$$

Where, ABS_0 and ABS_t are the initial absorbance and final absorbance.

RESULTS AND DISCUSSION

Effect of different electrolyte on color removal

Fig. 3 shows the effect of different NaCl concentrations (ranges 0.01-0.05 M) on decolorization at 100 mg/L Rh-B solution, at temperature of 30 °C, current density of 10 mA cm⁻² under initial pH 7 and 500 RPM. With increase in the NaCl concentration decolorization rate increases. Electrolysis time required for complete decolorization gradually decreased with increase in NaCl dosage. It can be because of the generation of Cl^- ion which further oxidizes to Cl_2 at anode.

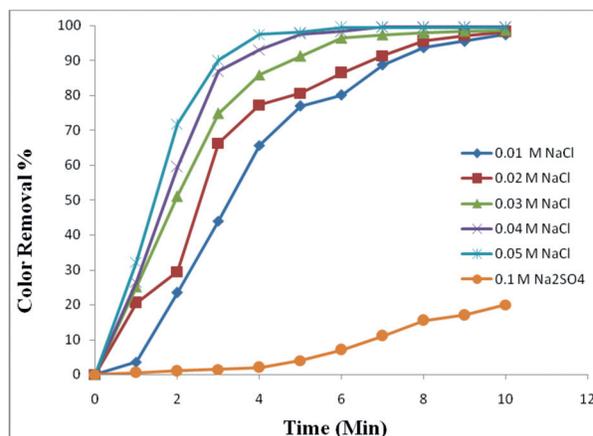


Fig. 3. Effect of electrolyte concentration on color removal

The effect of Na_2SO_4 used as an electrolyte is also shown in the Figure. Only 20 % color removal was obtained at 0.1 M Na_2SO_4 concentration. From the figure, it is observed that in the presence of NaCl, decolorization is much better compared to Na_2SO_4 (Panizza and Cerisola, 2008; Rajkumar and Muthukumar, 2012).

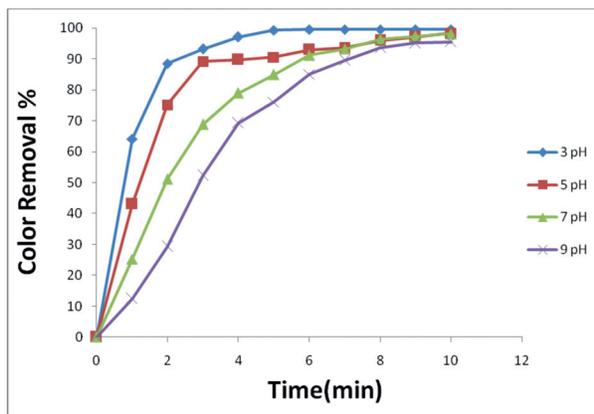


Fig. 4. Effect of Initial pH on color removal

Effect of initial pH on color removal

The influence of pH (3,5,7,9) on color removal of dye solution with concentration 100mg/L, at 0.03 mol/l NaCl concentration, Temperature of 30 °C, current density 10 mA cm⁻² and 500 RPM are shown in Fig. 4. The decolorization efficiencies were higher in acidic pH (5 and 3) followed by neutral (pH 7) and lastly alkaline (pH 9). However, faster decolorization was observed at (pH = 3 and 5) because of HOCl and Cl₂ species formed at low pH [16].

Effect of Current Density on color removal

Fig. 5 shows the effect of the applied current densities (range 5 – 25 mA/cm²) on color removal with the time during the electrolysis of dye at 100

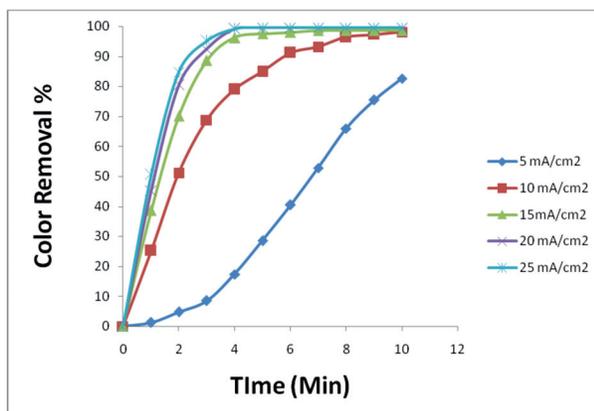


Fig. 5. Effect of current density on color removal of

mg/L RhB solution, at 0.03 mol L⁻¹ NaCl concentration, Temperature of 30 °C, initial pH of 7 and 500 RPM. With all the different current densities, decolorization of Rh-B occurred. At current density of 5 only 82% color removal can be obtained in 10 minutes of electrolysis time, but at higher current densities almost total decolorization is achieved in 10, 7, 5, 4 minutes at 10, 15, 20, 25 mA/cm² respectively. Decolorization time decreased with an increase in current density from 5 to 25 mA/cm². It was found that the Rh-B dye removal efficiencies increase with increasing the applied current densities due to higher production of oxidizing agents. In this study, higher production of active chlorine at higher current densities occurs.

CONCLUSION

Mixed metal oxide plate was successfully employed as anode for decolorization of Rhodamine-B dye waste water in this study. Effects of different operational parameters like initial pH, current density and different electrolytes on the color removal were evaluated. Followings are the findings of the study:

- MMO plate can be used as anode effectively for decolorization of dye wastewater.
- Almost complete decolorization can be obtained at various current densities and different pH in presence of NaCl as electrolyte.
- Presence of chloride ion improves color removal efficiency significantly.
- Decolorization rate at initial stage was significantly affected by initial pH, current density and electrolyte concentration.
- Color removal efficiency improved at acidic pH, even at lower current density.

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