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In situ electrocatalytic oxidation of acid violet 12 dye effluent

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Abstract

Electrochemical treatment of organic pollutants is a promising treatment technique for substances which are recalcitrant to biodegradation. Experiments were carried out to treat acid violet 12 dye house effluent using electrochemical technique for removal color and COD reduction covering wide range in operating conditions. Ruthenium/lead/tin oxide coated titanium and stainless steel were used as anode and cathode, respectively. The influence of effluent initial concentration, pH, supporting electrolyte and the electrode material on rate of degradation has been critically examined. The results indicate that the electrochemical method can be used to treat dye house effluents.

Keywords: Electro-oxidation; Dye house dye effluent; Wastewater treatment

1. Introduction

The growth of industries and day-to-day changes in human activities has resulted in an increase in the volume and complexity of wastewater to the environment. The textile industry is one of the most polluting industry in terms of discharge volume and effluent composition. The procedure of dyeing consists of two steps: material dipping in hot dyeing bath and removal of un-reacted dye by reducing agent. The dyeing and finishing operations contribute a major share of wastewater generated in textile industries. The dye effluent is characterized by strong color, high COD with pH varying from 2 to 12 and the removal of color and the Chemical Oxygen Demand (COD) reduction pose greatest problems in textile industry [1,2].

Dye house effluent is usually treated by conventional methods such as adsorption, biological oxidation, coagulation, etc. Physical adsorption is effective for removal of non-biodegradable pollutant but expensive and difficult for regenerating the adsorbents. On the other hand, the biological methods are time consuming and cannot be employed where the effluents are biologically resistant [3,4]. Due to the large complexity of the composition of dye house effluent, most of these traditional methods are becoming inadequate. Ozonation has been proposed as an alternative for the conventional treatment techniques and proved to be quite effective in decolorizing dye house effluent. However, ozonation is not effective for COD and BOD reduction and further, the cost of ozonation for such purposes needs to be further ascertained to ensure the competitiveness of this method [5].

In recent years, there has been increasing interest in the use of electrochemical technique for the treatment of dye house effluent. The pollutants present in the effluent are destroyed by a direct anodic process via the production of oxidants such as hypochloride, hydroxyl radicals, ozone, etc. This technique has been successfully applied in the purification of several industrial effluents [6], landfill leachate [7] and domestic sewage [8]. Extensive literature has been reported on electrochemical treatment of industrial effluents. Della Monica et al. [8] studied electrochemical oxidation of sewage wastewater and reported more than 70% efficiency. The major contributors on electrochemical treatment of industrial wastewater are due to Comninellis [9], Tomcsanyi et al. [10], Rajeshwar et al. [11], etc. The present study focused on treatment of dye house effluent by electrochemical method with different oxide coated anodes. Further it is attempted to elucidate the mechanism of the electrochemical oxidation of organic at the electrode surface.

2. Experimental

Experiments have been conducted in an undivided electrode cell having 100 ml capacity. Different oxide coated titanium

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metals have been used as anode while stainless steel has been used as cathode in the present investigation. All the experiments were carried out under galvanostatic conditions using a DC-regulated power source (HIL model 3161) of 0–2 A and 0–30 V. The anode potential has been monitored using a reference electrode (saturated calomel electrode) connected to the working electrode and sufficient agitation has been provided inside the electrochemical cell to maintain uniform concentration. The pollutant concentrations are presented in terms of Chemical Oxygen Demand estimated by standard estimation procedure [12]. Samples were collected at different intervals of time and analyzed for COD and pH.

3. Theoretical approach

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electrocatalytic activity, oxidation occurs at the electrode surface called direct electrolysis. On metal oxide electrode, the oxidation occurs via surface mediator on the anodic surface, where they are generated continuously called indirect electrolysis. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. A more generalized scheme for direct and indirect electro-oxidation is given by Goodridge and Scott [13]. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions. The anodic oxidation of chloride ions to form chlorine molecules is given as

$$2\mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 + 2\mathrm{e}^- \tag{1}$$

The liberated chlorine form hypochlorous acid (Eq. (2)) and further dissociated to give hypochlorite ion, which is adsorbed at the surface to form physisorbed active OCl^- radical (Eq. (3)):

$$\mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{HOCl} + \mathrm{Cl}^- + \mathrm{H}^+ \tag{2}$$

$$\mathrm{MO}_X + \mathrm{HOCl} \rightarrow \mathrm{MO}_X(\mathrm{OCl}) + \mathrm{H}^+ + \mathrm{e}^- \tag{3}$$

The generated hypochlorite ion reacts with oxygen already present at the anode with possible transition of oxygen from the radical to electrode to form higher oxide MO_{X+1} (chemisorbed), i.e. Eq. (4):

$$\mathrm{MO}_X(^\bullet\mathrm{OCl}) \rightarrow \mathrm{MO}_{X+1} + \mathrm{Cl}^- + \mathrm{e}^- \tag{4}$$

$$\mathrm{MO}_X(^\bullet\mathrm{OCl}) \rightarrow \tfrac{1}{2}\mathrm{O}_2 + \mathrm{MO}_X + \mathrm{Cl}^- + \mathrm{e}^- \tag{5}$$

$$\mathrm{MO}_{X+1} \rightarrow \tfrac{1}{2}\mathrm{O}_2 + \mathrm{MO}_X \tag{6}$$

The OCl^- plays a vital role in oxidation of the organics in the electrochemical process. Oxygen is liberated if there is no degradation takes place (Eqs. (5) and (6)).

Eqs. (1)–(6) give the reaction mechanism of electro-oxidation at the oxide coated electrode. In the present investigation, ruthenium oxide coated titanium is one of the anode used for electro-oxidation. The above mechanism can be written for ruthenium oxide coated anode as

$$\mathrm{RuO}_2 + \mathrm{HOCl} \rightarrow \mathrm{RuO}_2(\mathrm{OCl}) + \mathrm{H}^+ + \mathrm{e}^- \tag{7}$$

$$\mathrm{RuO}_2(\mathrm{OCl}) \rightarrow \mathrm{RuO}_3 + \mathrm{Cl}^- \tag{8}$$

$$\mathrm{RuO}_2(\mathrm{OCl}) \rightarrow \mathrm{RuO}_2 + \tfrac{1}{2}\mathrm{O}_2 + \mathrm{Cl}^- \tag{9}$$

$$\mathrm{RuO}_3 \rightarrow \mathrm{RuO}_2 + \tfrac{1}{2}\mathrm{O}_2 \tag{10}$$

Water is ionized at the cathode to give hydroxyl ion and hydrogen

$$2\mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 + 2\mathrm{OH}^- \tag{11}$$

The hydroxyl ion reacts with hydrogen to form water molecule

$$\mathrm{H}^+ + \mathrm{OH}^- \rightarrow \mathrm{H}_2\mathrm{O} \tag{12}$$

The generated hypochlorite ions act as main oxidizing species in the degradation of dye present in the effluent. The overall desired reaction may be written as

$$[\mathrm{Dye}] + [\mathrm{OCl}^-] \rightarrow \text{intermediates} \rightarrow \mathrm{CO}_2 + \mathrm{Cl}^- + \mathrm{H}_2\mathrm{O} \tag{13}$$

During the electrochemical generation of hypochlorite ion, the following side reactions also might occur: chlorate may be formed either chemically or electrochemically when hypochlorite ions reached saturated level, i.e.

$$2\mathrm{HClO} + \mathrm{ClO}^- \rightarrow \mathrm{ClO}_3 + 2\mathrm{H}^+ + 2\mathrm{Cl}^- \tag{14}$$

and

$$6\mathrm{ClO}^- + 3\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{ClO}_3 + 6\mathrm{H}^+ + 4\mathrm{Cl}^- + \tfrac{1}{2}\mathrm{O}_2 + 6\mathrm{e} \tag{15}$$

The side reactions (14) and (15) can be controlled for better oxidation efficiency. As stated earlier, the generated hypochlorite ions act as main oxidizing species in the degradation of dye present in the wastewater. Kinetic equation for the oxidation of dye can be written as

$$-r_\mathrm{A} = \frac{\mathrm{d}c}{\mathrm{d}t} = k[A][\mathrm{Dye}][\mathrm{ClO}^-] \tag{16}$$

where A is the active area of the electrode. The rate of dye degradation becomes function of chlorite ion concentration, dye concentration and the electrode area. The electrode area remains constant throughout processing and hence it can be ignored in the rate equation and as long as the side reactions are controlled, the quantity of hypochlorite ion may also be assumed to be constant for the given reaction condition. Thus, Eq. (16) can be simplified to

$$\ln\frac{c}{c_\mathrm{i}} = k't \tag{17}$$

where c is the concentration of dye at unit time and c_i is the initial dye concentration. The slope of the plot of $\ln(c/c_\mathrm{i})$ versus electrolysis time gives the value of reaction rate constant k'.

The electro-oxidation of wastewater in the presence of a supporting electrolyte is influenced by various operating parameters. The progress of the destruction of the organic pollutant has been monitored by COD estimation. The potentials required for oxidation of organic pollutants are generally high and the production of oxygen from the electrolysis of water molecules may determine the reaction yield. The instantaneous current efficiency (ICE) may be defined as

$$\mathrm{ICE} = \left[\frac{2F\,\Delta_{\mathrm{COD}}V}{16Q}\right] \tag{18}$$

The instantaneous current efficiency is a measure of efficiency of electro-oxidation [9]. The ICE has been estimated for all the experimental runs in the present investigation and critically examined.

4. Results and discussions

4.1. Effect of current density

Experiments were conducted at five current densities keeping other parameters constant. The rate COD reduction increased with current density (Fig. 1). This may be due to the fact that the rate of generation of hypochlorite ion increased with current density, which eventually increases the pollutant degradation. The increase in hypochlorite ion approaches equilibrium with degradation of organics present in the effluent. For a given supporting electrolyte concentration, a pseudo steady state between the generation of hypochlorite ion and the degradation of pollutant may be arrived when the current density increased from the lower value. Notice that the rate of degradation increased significantly when the current density increased from 1 A dm^{-2} to 3 A dm^{-2} and becomes insignificant beyond 3 A dm^{-2}.

4.2. Effect of effluent concentration

The initial dye effluent concentration has been varied in order to check its influence on rate of degradation. As expected, the rate of degradation decreased with increased in effluent initial concentration (Fig. 2). This may be explained that the ratio of OCl^{-} to the effluent concentration decreases with increase in effluent initial concentration.

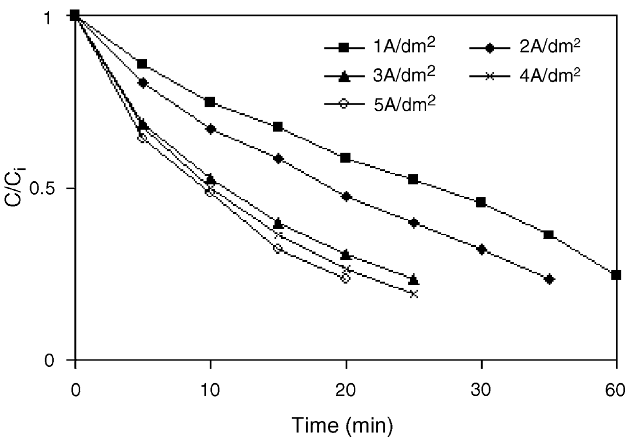

Fig. 1. Variation of COD with electrolysis time. Dye: supporting electrolyte concentration: 0.58 g l^{-1}; pH 7; dye initial concentration: 140 ppm.

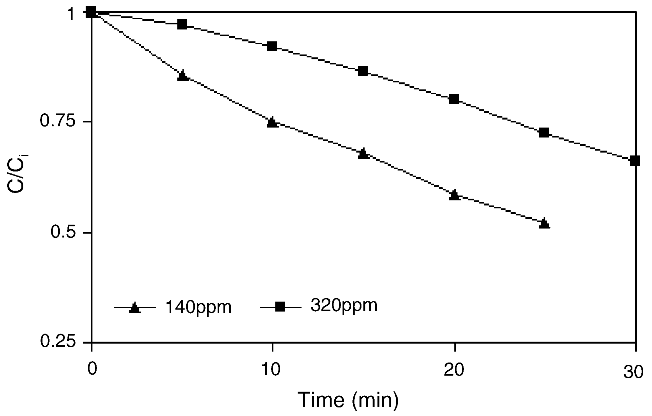

Fig. 2. The influence of initial dye concentration on electro-oxidation. Current density: 1 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}; pH 7.

4.3. Effect of pH

Experiments were conducted under acid, alkaline and neutral conditions and the observed results are given in Fig. 3. It can be ascertained from Fig. 3 that the rate of COD reduction increased significantly when the electrolyte pH increased to 7 from 4. Increase in electrolyte pH increases the OH radicals favors the hydrolysis reaction and consequently the rate of oxidation. The reaction was favorable at neutral and alkaline conditions.

4.4. Influence of anode on oxidation

Three different materials (ruthenium/lead/tin oxide coated titanium) have been used as anode in the present investigation and the influence of anode material on rate of oxidation is plotted in Fig. 4. The figure is plotted concentration, i.e. c/c_{i} versus electrolysis time. It can be noticed from Fig. 4 that ruthenium oxide coated titanium anode gives better result than other electrodes for the given experimental conditions. Say for example at a given electrolysis time of 20 min, ruthenium oxide coated titanium anode shows more than 25% COD reduction than lead oxide coated anode.

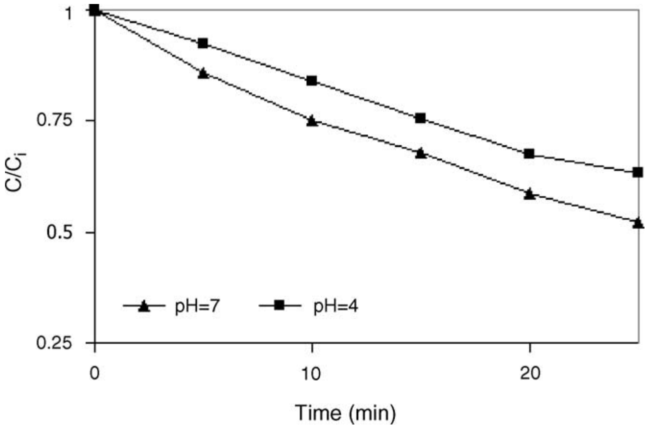

Fig. 3. The influence of pH on rate of degradation. Dye initial concentration: 140 ppm; current density: 1 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}.

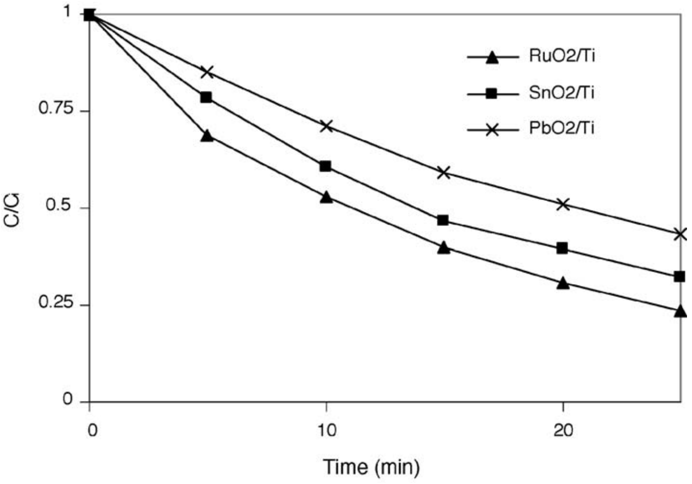

Fig. 4. Influence of anode material on COD reduction. Initial dye concentration: 140 ppm; current density: 3 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}; pH 7.

4.5. Variation of anodic potential and cell voltage

The variation of cell voltage and anodic potential with electrolysis time is presented in Fig. 5. It may be noticed from the figure that a marginal increase in both the anodic potential and the cell voltage with electrolysis time. The increase of potential and cell voltage is more pronounced after 30 min of electrolysis time.

4.6. Percentage of COD reduction and ICE

As stated earlier, the instantaneous current efficiency was calculated for all the experiments in the present investigation. The variation of ICE along with percentage of COD reduction with current density is given in Fig. 6. It can be noticed from the figure that the percentage COD reduction and instantaneous current efficiency increased with increase in current density initially and decreases beyond certain current density value. However, the ICE and percentage COD reduction show decreasing trend beyond the current density of 3 A dm^{-2}.

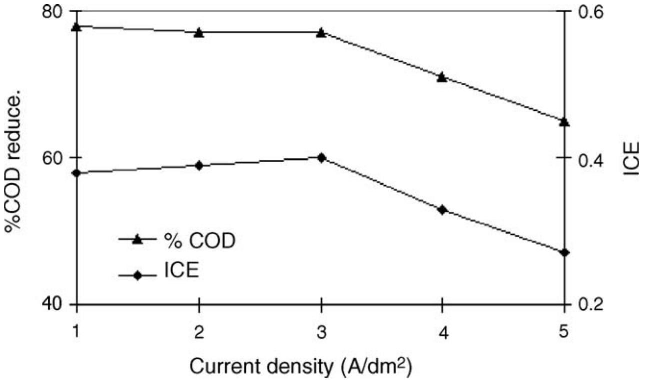

Fig. 5. Variation of percentage COD reduction and instantaneous current efficiency (ICE) with current density. Initial dye concentration: 140 ppm; supporting electrolyte concentration: 0.58 g l^{-1}; pH 7.

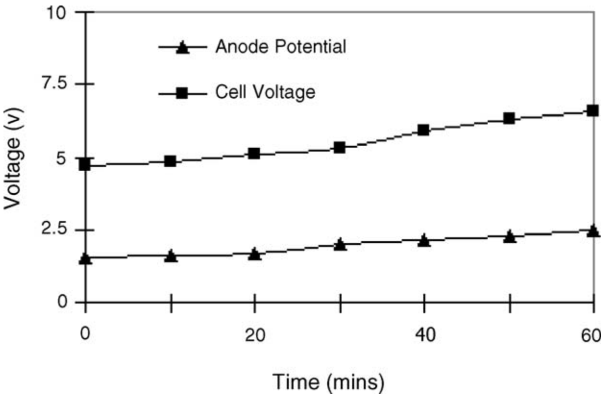

Fig. 6. Variation of cell voltage with current density. Initial dye concentration: 140 ppm; current density: 3 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}; pH 7.

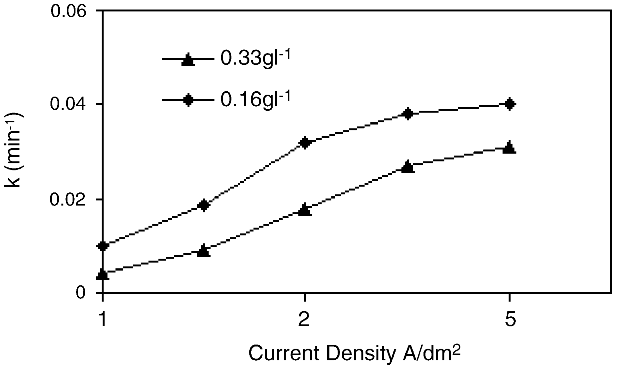

Fig. 7. Variation of reaction rate constant with initial dye concentration. Current density: 3 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}; pH 7.

The rate constant, k' was estimated from $\ln(c/c_\mathrm{i})$ versus electrolysis time. The rate constant has been estimated for all the experimental runs carried out in the present study. Fig. 7 gives the variation of reaction rate constant with current density. It can be noticed from Fig. 7 that the rate constant is influenced by the initial concentration of organic present in the effluent. It can also be observed from the figure that the reaction rate constant influenced by the current densities. However, the increase in reaction rate constant becomes insignificant beyond the current density of 3 A dm^{-2}. The variation of reaction rate constant with electrolyte pH is given in Table 1. It can be noticed from Table 1 that the electrolyte pH does not have significant effect on reaction rate constant k'.

Table 1
Variation of reaction rate constant with initial pH

k' (min^{-1})	pH
4	0.02
7	0.025
9	0.022

Initial dye concentration: 140 ppm; current density: 3 A dm^{-2}; supporting electrolyte concentration: 0.58 g l^{-1}.

5. Conclusion

Experiments were carried out to dye house effluent using electrochemical technique covering wide range in operating conditions. Different electrodes ruthenium/lead/tin oxide coated titanium and stainless steel were used as anode and cathode, respectively. The influence of effluent initial concentration, pH, supporting electrolyte and the electrode on rate of degradation has been critically examined. The following conclusions can be made:

(i) the COD reduction is significantly effected by the initial pollutant concentration, supporting electrolyte concentration and pH;
(ii) ruthenium oxide coated titanium anode gives better oxidation rate than other tin and lead oxide coated electrode materials;
(iii) it can be concluded that electrochemical technique is as an alternative for the conventional treatment techniques and proved to be quite effective in decolorizing dye house effluent.

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