

Transactions of the SAEST 39 (2004) 113-116



Electrochemical Treatment of Disperse Yellow-7 Dye Effluent

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Received: 17 October 2003 Accepted: 30 April 2004

Abstract

It is attempted in the present work to reduce the dye from the dye-house effluent by electro oxidative destruction. Experiments are carried out in batch electrochemical cell under galvanostatic condition process using metal oxide coated on Ti as anode and stainless steel as cathode. Different oxide coated electrodes have been used as anode material in the present investigation. It is observed from the present investigation that the dye effluent can be effectively treated using electrooxidation.

Key words: Electrooxidation, textile wastewater treatment, kinetics

Introduction

Textile dye processes are among the major industrial water users; in many areas, this industry has the wastes most difficult to treat satisfactory. Textile dye wastewater is well known to contain strong color, high pH, temperature and COD and low biodegradability especially the effluent from the dyeing stages of the dyeing and finishing process. The removal of dyes color is therefore a challenge to both the textile industry and the wastewater-treatment facilities that must treat it. Dyeing wastewater is usually treated by conventional methods such as biological oxidation and adsorption. Because of the large variability of the composition of textile wastewaters, most of these traditional methods are becoming inadequate. Ozonation has been proposed as a potential alternative. It has been shown to be quite effective in decolorizing textile wastewater; however, the cost of ozonation for such purposes needs to be further ascertained interest in the use of electrochemical methods for the treatment of wastewaters. The organic and toxic pollutants present in treated wastewaters such as dyes and phenols are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc.

Electrochemical techniques have been successfully used for treatment of different kind of wastewater. Della Monica et al. [1] studied the electrochemical oxidation of sewage wastewater. The authors reported that the nitrogen compounds present in the sewage wastewater could be removed with more than 70% efficiency. The effect of current density, benzene initial concentration and electrode material on anodic oxidation was critically examined. Harrison and Mayne [2] reported on electro oxidation of organic compounds using lead oxide coated electrode. Comninellis [3] studied the phenol degradation in the presence of sodium chloride for wastewater treatment. Tomcsanyi et al. [4] studied the adsorbed intermediate of chloride oxidation using RuO₂/Tio₂ electrode. Fernandez et al. [5] presented Volmer-Kristhaltic mechanism for the chlorine evolution electrode reaction. The electrode mechanism during electrochemical oxidation is very important for its efficiency and suitability for the electrochemical process. It is attempted in the present work to study the electrooxidation of dye house effluent at various operating conditions.

Mechanism of Hypochlorite generation

Hypochlorite ions are generated during electrolysis of chloride ion present in the wastewater [6]. The reactions involved during the electrolysis of chloride ions are given as

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The chloride ions are converted into chloride at the anodic surface

$$2\text{Cl}^- \to \text{Cl}_2 + 2\text{e}^- \tag{1}$$

While water is ionized at the cathode to give hydroxyl ion and hydrogen

$$2H_{2}O+2e^{-} \rightarrow H_{2}+2OH^{-}$$
⁽²⁾

In the bulk, the liberated chlorine reacts with water to produce hypochlorous acid

$$Cl_2+H_2O \rightarrow HOCl+Cl^2+H^+$$
 (3)

The generated hypochlorous acid further dissociated to give hypochlorite ion and hydroxyl ion

$$HOCl \rightarrow OCl^{-} + H^{+}$$
 (4)

The hydroxyl ion reacts with hydrogen to from water molecule

$$\mathrm{H}^{+} + \mathrm{O}\mathrm{H}^{-} \rightarrow \mathrm{H}_{2}\mathrm{O} \tag{5}$$

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.

$$2HClO+ClO^{-} \rightarrow ClO_{2}+2H^{+}+2Cl^{-}$$
(6)

and

$$6ClO^{+}+3H_{2}O^{2}2ClO_{2}+2H^{+}+4Cl^{-}+1/2O_{2}+6e^{-}$$
 (7)

The equations 4-7 give the mechanism for generation of hypochlorite ion. The generated hypochlorite ions, and free chlorite act as main oxidizing agents in electrochemical oxidation process. The side reactions (6&7) should be controlled in order to get better oxidation efficiency.

As mentioned earlier, the generated hypochlorite ions act as main oxidizing species in the degradation of pollutant present in the wastewater. The disperse yellow-7 reacts with OCl⁻ according to the following reaction

$$C_{19}H_{16}N_4 + 46OCl \rightarrow 46Cl + 19CO_2 + 2N_2 + 8H_2O$$

$$-r_{A} = dc/dt = k[A] [C_{19}H_{16}N_{4}][ClO^{-}]$$
(11)

where A is the active area of the electrode. The rate of pollutant degradation is now function of chlorite ion concentration, dye pollutant concentration and the electrode area. The electrode area remains constant throughout processing and hence it can be ignored in the rate equation. As long as the side reactions are controlled the quantity of hypochlorite ion may also be assumed as constant during the process. The equation 11 is simplified to

$$\ln \frac{c}{c_i} = kt \tag{12}$$

Where c is the concentration of formaldehyde at unit time and c_i is the initial formaldehyde concentration. The slope of the plot of In c/ci versus electrolysis time gives the value of reaction rate constant k.

Experimental

Experiments are conducted in a batch electrochemical reactor. The experimental set-up consists of electrolysis cell has the provision for electrode insertion and sample probe. Commercially available Graphite and SS were used as anodes and cathode respectively. Synthetic effluents of known concentration [estimated before the experiments] were taken for the experiment. The pollutant concentrations are presented in terms of Chemical Oxygen Demand estimated by standard estimation procedure. The electrolysis was carried out under galvanostatic condition. Samples were collected at regular intervals of time for estimation of COD estimation. Constant cell temperature and pH were maintained for each experiment.

Results and discussions

Effect of current density

Experiments were conducted at five current densities keeping other parameters constant. The rate COD reduction increased with current density [Tables 1]. This may be explained that the rate of chloride ion oxidation, i.e. the generation of hypochlorite ion increased with current density, which eventually increases the pollutant degradation.

Effects of supporting electrolyte concentration

The supporting electrolyte plays important role in the oxidation process. The cell conductivity and quantity of hypochlorite ion concentrations are increased with increase in the supporting electrolyte. The increase in the hypochlorite ion in turn increase the rate of COD reduction [Table 2]. Notice that the observation given in Table 2 similar to Table 1 except the addition-supporting electrolyte added to the system. This observation also indicates that the formaldehyde degradation is mostly attributed by hypochlorite ions than OH radicals.

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| CD | Time | Potential (V) | | Cell | Current | % COD | Energy |
|------------|-------|---------------|---------|---------|---------|-----------|-------------|
| (A/dm^2) | (hrs) | anode | cathode | voltage | (A) | reduction | consumption |
| | | | | (V) | | | kWH/kg COD |
| 0.5 | 8 | 1.63 | 1.67 | 3.24 | 0.02 | 61.36 | 8.15 |
| 1 | 4 | 1.6 | 1.75 | 3.37 | 0.04 | 47.72 | 9.89 |
| 2.5 | 1.6 | 1.87 | 1.69 | 3.57 | 0.11 | 34 | 15.36 |
| 5 | 0.8 | 2.57 | 2.2 | 4.56 | 0.22 | 22 | 29.43 |
| 10 | 0.4 | 4.22 | 4.09 | 9.3 | 0.44 | 16 | 60.02 |

Table 1. Results obtained for electro oxidation of disperse yellow-7 without supporting electrolyte. pH: 3; NaCl: nil

Table 2. Results obtained for electro oxidation of disperse yellow-7 without supporting electrolyte. pH : 3; NaCl: $1g1^{-1}$

| CD | Time | Potential (V) | | Cell voltage | Current | % COD | Energy |
|------------|-------|---------------|---------|--------------|---------|-----------|-------------|
| (A/dm^2) | (hrs) | anode | cathode | (V) | (A) | reduction | consumption |
| | | | | | | | kWH/kg COD |
| 0.5 | 8 | 1.46 | 1.08 | 2.56 | 0.02 | 63.63 | 6.7 |
| 1 | 4 | 1.56 | 1.05 | 2.68 | 0.04 | 54.54 | 9 |
| 2.5 | 1.6 | 1.9 | 1.26 | 3.19 | 0.11 | 40.9 | 16.5 |
| 5 | 0.8 | 2.15 | 1.68 | 4.02 | 0.22 | 27.27 | 32.2 |
| 10 | 0.4 | 2.74 | 2.04 | 4.9 | 0.44 | 27.27 | 54 |

Table 3. Results obtained for electro oxidation of disperse yellow-7 without supporting electrolyte, pH; 7; NaCl: 1g1⁻¹

| CD | Time | Potential (V) | | Cell voltage | Current | % COD | Energy consumption |
|------------|-------|---------------|---------|--------------|---------|-----------|--------------------|
| (A/dm^2) | (hrs) | anode | cathode | (V) | (A) | reduction | kWH/kg COD |
| 0.5 | 8 | 0.91 | 1.67 | 2.64 | 0.02 | 64.06 | 6.59 |
| 1 | 4 | 1.64 | 1.91 | 3.53 | 0.04 | 54.68 | 10.33 |
| 2.5 | 1.6 | 1.4 | 2.15 | 3.89 | 0.11 | 56.25 | 12.17 |
| 5 | 0.8 | 1.69 | 3.16 | 5.16 | 0.22 | 53.12 | 17.10 |
| 10 | 0.4 | 2.8 | 4.08 | 7.32 | 0.44 | 29.68 | 43.41 |

Table 4. Results obtained for electro oxidation of disperse yellow-7 without supporting electrolyte, pH; 10; NaCl: 1g1⁻¹

| CD | Time | Potential (V) | | Cell | Current | % COD | Energy |
|------------|-------|---------------|---------|---------|---------|-----------|-------------|
| (A/dm^2) | (hrs) | anode | cathode | voltage | (A) | reduction | consumption |
| | | | | (V) | | | kWH/kg COD |
| 0.5 | 8 | 1.45 | 1.1 | 2.54 | 0.02 | 77.77 | 5.23 |
| 1 | 4 | 1.48 | 1.03 | 2.68 | 0.04 | 66.66 | 6.43 |
| 2.5 | 1.6 | 1.76 | 1.44 | 3.21 | 0.11 | 66.66 | 8.48 |
| 5 | 0.8 | 2.02 | 1.75 | 3.38 | 0.22 | 44.44 | 15.37 |
| 10 | 0.4 | 2.25 | 2.12 | 4.7 | 0.44 | 22.22 | 37.23 |

Effect of pH

The pH of the electrolyte solution has been varied in order to check its influence on dye degradation. Experiments were conducted under acid, alkaline and neutral conditions. Tables 2 to Table 3 compare the results obtained at three different pHs. Notice that the rate of COD reduction has been increased from 63% to 78% when the electrolyte pH is increased from 3 to 10. Increase in the pH of electrolyte increases the OH radicals favors the hydrolysis reaction. Consequently oxidation of dye has been increased. The reaction was very favorable at neutral and alkaline conditions.

Conclusions

Dye house effluent has been treated with in situ generated hypochlorite ions. Experiments were conducted in a batch electrochemical cell covering wide range in operating conditions. The mechanisms of the anodic oxidation of chloride ion and the oxidation of dye with hypochlorite ion are critically studied in this investigation.

References

- Della Monica, H.Agostian and Cegline A., An Electrochemical Sewage Treatment Process. J Appl. Electrochem., 10 (1980) 527
- 2. Harrison, J.A.; Mayne, J.M. The oxidation of aromatic organic compounds at a lead dioxide electrode. Electrochem.

Acta., 28 (1983) 1223

- Comninellis, Ch. And Pulgarin, C. Electrochemical Oxidation of Phenol for Wastewater treatment (1991)
- Tomesanyi, L., Molner, f.; Liszi, J.; De Battisti, A. The effect of RUO₂/TiO₂ ratio on the rate of an outer sphere electron transfer reaction on mixed oxide electrode' Electrochem. Acta., 11 (1994) 1923
- Fernandez, J.L, Maria, R.M. and Abel C.C, Analysis of the volmer-Krishtaltic mechanism for the c hlorine electrode reaction, Electrochem. Commun., 2 (2000) 630
- Goodridge, F. and Scott, K. 'Electrochemical engineering: A guide to design of electrolytic plant' Pub. Plenum press, NY (1995) 104

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