LIST OF PUBLICATION

a) In Ph.D Related Work


b) Other papers


Papers communicated

Revised manuscript-Under review.-(2007)

Electrochemical treatment of Procion Black 5B using cylindrical flow reactor—A pilot plant study

S. Raghu, C. Ahmed Basha*

Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India

Received 24 January 2006; received in revised form 15 June 2006; accepted 15 June 2006

Available online 27 June 2006

Abstract

The paper presents the results of an efficient electrochemical treatment of Procion Black 5B—a pilot plant study. Experiments were conducted at different current densities and selected electrolyte medium using Ti/RuO₂ as anode, stainless-steel as cathode in a cylindrical flow reactor. By cyclic voltammetric analysis, the best condition for maximum redox reaction rate was found to be in NaCl medium. During the various stages of electrolysis, parameters such as COD, colour, FTIR, UV-vis spectra studies, energy consumption and mass transfer coefficient were computed and presented. The experimental results showed that the electrochemical oxidation process could effectively remove colour and the chemical oxygen demand (COD) from the synthetic dye effluent. The maximum COD reduction and colour removal efficiencies were 74.05% and 100%, respectively. Probable theory, reaction mechanism and modeling were proposed for the oxidation of dye effluent. The results obtained reveal the feasibilities of application of electrochemical treatment for the degradation of Procion Black 5B.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Advanced oxidation; Textile; Colour removal; Electro-oxidation; Ti/RuO₂ electrode

1. Introduction

Water is the best resources in nature and is essential for animal and plant life. Pollution of water bodies is gradually increasing due to industrial proliferation and urbanization. Nowadays, the worldwide production and use of chemical compounds have increased tremendously and many of them find their way into the environment. Many of these compounds are non-biodegradable. Therefore, the major concern is to treat the wastewater before it is discharged into environment [1]. The textile and dyeing industry has drawn the attention of environmentalist of worldwide because of its high resource consumption profile in terms of water, chemicals, energy and release of highly contaminated coloured effluent at the end of process leading to intense water pollution. The existing wastewater treatment technology is often inadequate to control the colour of effluent to minimize the toxicity of wastewater having impact on aquatic organisms [2,3]. Aerobic treatment of industrial effluents typically removes most of the biological oxygen demand (BOD) and 60–80% of COD in wastewater [4–6]. However, these treatments are ineffective for colour removals from the textile industry wastewater because most of the synthetic dyes that are non-biodegradable. In aerobic process, the azo bonds can be used as electron acceptor in the electron pathways. The products of the azo bond cleavage are lower molecular weight aromatic amines. Although they are colourless, they cannot be further degraded under anaerobic conditions. Therefore, various combined processes, such as anaerobic/aerobic [5], chemical/biological [7], and electrochemical/biological [8], processes have been under intensive study to completely mineralize organic dyes.

Though all the above methods have been found to be fairly satisfactory, considering the very stringent environmental regulations, there is a need for more effective alternatives. Anodic oxidation of some benzene derivatives (model organic pollutants) at platinum and DSA (dimensionally stable anode) anode elucidate the possibilities of the electrochemical method [9]. Dimensionally stable anode (DSA) with Ru/TiO₂ as a catalytically active layer coated on a titanium substrate by the thermal decomposition method has been successfully used and caused a technological revolution in the chloro-alkali industry since its invention in 1960s [10]. The first fundamental research on the
The electrochemical clean and easy, as they involve no addition of chemicals for different flow rates and current densities. Earlier work has proposed electrochemical treatment of xylene orange dye and dye effluents on bench scale [12]. Electrochemical oxidation of textile dye wastewater using Pt/Ti electrode was studied in a pilot plant under batch recirculation process [13]. This leads to develop a pilot plant study of electrochemical technique using Ti/RuO₂ electrode for the treatment purposes under continuous single pass process. Hence, this paper presents the treatment of Procion Black 5B by an electrochemical method using Ti/RuO₂ expanded mesh as anode, stainless-steel as cathode in a cylindrical flow reactor which is hitherto not reported on a pilot plant under continuous single pass process. It is to be pointed out that the Procion Black 5B (Remazol Reactive Black 5) dyes are considered because they work at temperature from 60 to 80 °C. They are having excellent wash fastness and light fastness properties compared to other dyes. Use for dyeing high quality quilting fabrics, tie-dye, immersion dyeing, batik, airbrush, garment dyeing, screen-printing, and spatter painting. In reactive dyeing process, sodium chloride as exhausting agent and sodium carbonate as fixing agent. The effluent generated during this process could be used as the exhausting agent and not entirely known. For time being assumptions can only be made, based on the products that can be measured. Hence the following reactions assume to take place:

At anode:

Main reaction \( 2\text{Cl}^- \rightarrow k_1 \rightarrow \text{Cl}_2 + 2e^- \) (1)

Side reaction \( 4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4e^- \) (2)

At cathode:

\( 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \) (3)

In bulk of solution:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow k_1 \rightarrow \text{H}^+ + \text{Cl}^- + \text{HOCl} \] (4)

\[ \text{HOCl} \rightarrow k_2 \rightarrow \text{H}^+ + \text{ClO}^- \] (5)

\[ \text{Dye} + \text{ClO}^- \rightarrow k_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- + \text{P} \] (6)

Since dye molecules of the effluent are electrochemically inactive, the primary reaction occurs at the anodes is chloride ion oxidation (Eq. (1)) with the liberation of Cl₂, which is a robust oxidizing agent. As the dye effluent is generally basic or neutral condition in which case the side reaction (Eq. (2)) takes place generating oxygen which is relatively weak oxidant and hence not useful in present context of effluent treatment and this leads to reduction of current efficiency. The counter reaction (Eq. (3)) at the cathode would be the reduction of the only water when no other reducible species are present. As regards to the reactions in the bulk, gaseous Cl₂ dissolves in the aqueous solutions due to ionization as indicated in Eq. (4). The rate reaction is less in acidic solution due to OH⁻ instability and considerably more in basic solution due to ready formation of OCl⁻ (pKₐ 7.44) ion in Eq. (5) implying that the basic or neutral pH conditions are more favorable for conducting reactions involving Cl₂ [14]. The direct electro oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. The indirect electro oxidation rate of organic pollutants depends on the diffusion rate of the oxidants into the solution, flow rate of the effluent, temperature and the pH. In moderate alkaline solution a cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces OCl⁻. The pseudo-steady-state theory can be applied to each of the intermediates products (HOCl and OCl⁻) taking part in the bulk solution. Taking all other reactions are irreversible processes, the rates of reactions \( r_i \) for the sequence are:

\[ -r_{\text{Cl}_2} = r_2 = k_2[\text{Cl}_2] \] (7)

\[ r_{\text{HOCl}} = k_2[\text{Cl}_2] - k_3[\text{HOCl}] + k_4[\text{H}^+][\text{OCl}^-] = 0 \] (8)

\[ r_{\text{OCl}^-} = k_3[\text{HOCl}] - k_4[\text{H}^+][\text{Cl}^-] + k_4[\text{Dye}][\text{OCl}^-] = 0 \] (9)

\[ r_{\text{Dye}} = k_4[\text{Dye}][\text{Cl}^-] \] (10)

Then using Eqs. (8) and (9) we can easily deduce the following expression:

\[ -r_{\text{Cl}_2} = -r_{\text{Dye}} = k_4[\text{Dye}][\text{OCl}^-] \] (11)

Finally as regard to bulk solution it is also to be noted that \( -r_{\text{Cl}_2} = r_{\text{Cl}^-} \) from material balance of Eq. (4), that is:

\[ -r_{\text{Cl}_2} = r_{\text{Cl}^-} = k_2[\text{Cl}_2] = -r_{\text{Dye}} = k_4[\text{Dye}][\text{OCl}^-] \] (12)

where the rate of reaction \( r_i \) and the rate constants \( k_i (i = 2, 3 \) and 4) are defined with respect to bulk and the rate expression
for main electrode reaction as per Eq. (1) can be written as:

\[-r'_{\text{Cl}} = r'_{\text{Cl}_2} = k_1[\text{Cl}^-] \tag{13}\]

where \(k_1\) is heterogeneous electrochemical rate constant. Hence, in the following section an attempt has been made to establish a relationship between the reacting species in bulk and at the electrode surfaces. The basic relationship applicable to all electrochemical reactions is Faraday’s law that relates to the amount of substance reacted at the surface to the charge \((i_A t)\) passed is \(M_A i_A t/nF\) (assuming 100% current efficiency) and the characteristic measurable parameter is current density, \(i_A\), which is \(i_A/A_e\). Thus, the electrochemical reaction rate (for the disappearance of reactant \(A\)) can be expressed as:

\[- \frac{V_R}{A_e} \frac{d[A]}{dt} = \frac{i_A}{nF} \tag{14}\]

where \(i_A\) is the current passed in time \(t\), \(M_A\) the molecular weight, \(n\) the number of electrons transferred per mole of reaction, \(A_e\) electrode area, \(V_R\) reactor volume and \(F\) is the Faraday (96,500 C or A s/mol). It has to be noted \(-r_A = -d[A]/dt = i_A a/nF\), where \(a\) is specific electrode area \((A_e/V_R)\). Assuming the main electrode reaction is governed by a simple Tafel type expression, then:

\[- \frac{V_R}{A_e} \frac{d[A]}{dt} = \frac{i_A}{nF} = k'[A] \exp(bE) \tag{15}\]

Elimination of \([\text{Cl}^-]_s\) using Eqs. (16) and (17) results as:

\[\frac{i_A}{zF} = k_1[\text{Cl}^-] \tag{18}\]

where

\[\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a \exp(bE)} \tag{19}\]

From a material balance of species \(\text{Cl}^-\) by taking note of Eqs. (12) and (13) we can write:

\[\frac{i_A}{zF} = k'[\text{Cl}_2] \tag{20}\]

\[\frac{i_A}{zF} = k''[\text{Dye}][\text{OCl}^-] \tag{21}\]

During electrolysis, since the constant current is applied, the rate of generation of \([\text{OCl}^-]\) will remain constant under a given set of experimental condition, but it varies as the applied current is altered. Then:

\[\frac{i_A}{zF} = k_{\text{obs}}[\text{Dye}] \tag{22}\]

In electrochemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion the organics are completely oxidized to CO2 and H2O. A brief explanation of reaction mechanism taking place at metal oxide electrode is enumerated below [15].

A Schematic diagram of indirect oxidation of pollutant [16] is shown in Figs. 1 and 2 shows a generalized scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode (MOX). In the first step, H2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction:

\[\text{MO}_2 + \text{H}_2\text{O} \rightarrow \text{MO}_x(\text{OH}) + \text{H}^+ + e^- \tag{23}\]

In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide \(\text{MO}_{x+1}\):

\[\text{MO}_x(\text{OH}) \rightarrow \text{MO}_{x+1} + \text{H}^+ + e^- \tag{24}\]

At the anode surface the “active oxygen” can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals \((\text{OH})\) or /and as chemisorbed (oxygen in the lattice, \(\text{MO}_{x+1}\)). In the
In the absence of any oxidizable organics, the "active oxygen" produces dioxygen according to the following reactions:

\[
\text{MO}_4(\text{OH}) \rightarrow \text{MO}_4 + (1/2)\text{O}_2 + \text{H}^+ + e^- \quad (25)
\]

\[
\text{MO}_4 + \text{Cl}^- \rightarrow \text{MO}_4(\text{OCl}) + \text{H}^+ + 2e^- \quad (26)
\]

When NaCl is used as supporting electrolyte Cl ion may react with \( \text{MO}_4(\text{OH}) \) to form adsorbed OCl radicals according to the following:

\[
\text{MO}_4(\text{OH}) + \text{Cl}^- \rightarrow \text{MO}_4(\text{OCl}) + \text{H}^+ + 2e^- \quad (27)
\]

Further, in presence of Cl ion, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochlorite radical to the oxide forming the higher oxide \( \text{MO}_4 \) according to the following reaction and also \( \text{MO}_4(\text{OCl}) \) simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

\[
\text{MO}_4(\text{OCl}) + \text{Cl}^- \rightarrow \text{MO}_4 + \text{H}^+ + e^- \quad (28)
\]

\[
\text{MO}_4(\text{OCl}) + \text{Cl}^- \rightarrow \text{MO} + (1/2)\text{O}_2 + (1/2)\text{Cl}_2 + e^- \quad (29)
\]

In the presence of oxidizable organics the physisorbed "active oxygen" (OH) should cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products [17] according to the following reactions:

\[(1/2)\text{R} + \text{MO}_4(\text{OH}) \rightarrow (1/2)\text{ROO} + \text{H}^+ + e^- + \text{MO}_4 \quad (30)\]

\[\text{R} + \text{MO}_4 + \rightarrow \text{RO} + \text{MO}_4 \quad (31)\]

The physisorbed route of oxidation is the preferable way for waste treatment. It is probable that dioxygen participates also in the combustion of organics according to the following reaction schemes: (1) Formation of organic radicals by a hydrogen abstraction mechanism: \( \text{RH} + \text{OH} \rightarrow \text{R}^* + \text{H}_2\text{O} \); (2) reaction of organic radical with dioxygen formed at the anode: \( \text{R}^* + \text{O}_2 \rightarrow \text{ROO}^* \) and (3) further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; \( \text{ROO}^* + \text{R}^* \rightarrow \text{ROOH} + \text{R}^* \). Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water. In this case the diffusion rate of organics on the anode area controls the combustion rate [18,19]. In the same way indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment [20,21]. We have already described in detail the role of chlorine in electrochemical treatment of dye effluent via hypochlorite generation in the beginning of this section. Now let us consider the reactor.

Since the electrochemical reactors are heterogeneous system by nature as they mostly involve a solid electrodes a liquid electrolyte and evolving gases at the electrodes. Electrodes come in many forms from large sized plate fixed in the cell to fluidizable shape and sizes. Further, the total reaction system consists of a reaction (or a set of reaction) at one electrode and another reaction (or set of reactions) at the other electrode in addition to the bulk as discussed above. The two electrode reactions are necessary to complete the electrical circuit. Thus, although these reactors can, in principle, be treated in the same manner as conventional catalytic reactors; detailed analysis of their behavior is considerably more complex. Adopting the same classification for the reactors as for conventional reactors, the cylindrical electrochemical flow reactor can be considered as plug flow reactor (PFR) and the material balance equation for PFR is given by:

\[
U \frac{d[Dye]}{dx} + (-r_{Dye}) = 0 \quad (32)
\]

where \( U \) is the average velocity of trough the reactor at a distance \( x \) from the leading edge and \(-r_{Dye} = k_{obs}[Dye] \) and in the integrated form:

\[
[Dye]_x = [Dye]_0 \exp \left( \frac{U}{k_{obs}} \right) \quad (33)
\]

The rate of colour removal and COD reduction in the dye effluent depends upon the dye concentration. In addition only chromophoric compounds (azo, nitrazo, etc.) mainly influence the colour removal.

\[
\text{Dye} + (O) \rightarrow \text{colourless intermediates} + (O) \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (34)
\]

For this reaction kinetics by assuming steady-state condition in cylindrical flow cell the expression can be derived assuming plug flow:

\[
[COD]_L = [COD]_0 \exp \left( \frac{-k_{obs}aL}{U} \right) \quad (35)
\]

\[
[\text{COLOR}]_L = [\text{COLOR}]_0 \exp \left( \frac{-k'_{obs}aL}{U} \right) \quad (36)
\]
where \( k_{\text{obs}} \) is the mass transfer coefficient, with respect to COD removal where as \( k_{\text{obs}}' \) corresponds to colour removal, \( a = A_e/V_R \), 
\( a \) the specific electrode area, \( L \) length of the electrode area, \( U \) the superficial velocity [COD] the concentration of dyestuff in terms of COD at the reactor inlet [COD] \(_L\) at the reactor exit, \( A_e \) the area of electrode and \( V_R \) the volume of the reactor. If \( q \) the volumetric flow rate then \( U \) the superficial velocity, defined as \( q/A \), where \( A \) is cross sectional flow area.

3. Materials and methods

All the reagents used were of AR grade. HCl, H\(_2\)SO\(_4\), Na\(_2\)SO\(_4\), NaCl, and KOH were used as supporting electrolyte and the synthetic effluent was prepared from Procion Black 5B (a commercial Reactive Black 5B dye). The colour index of the dye was 20505 CI Reactive Black 5. It contains two chromogenic systems. The structure of dye is shown in Fig. 3 and the characteristics of effluent before and after treatment (current density—2 A/dm\(^2\) and 101/h) is presented in Table 1.

### 3.1. Cyclic voltammetry analysis

Cyclic voltammetry analyses were carried out by Potentiostan (Wenking model POS 88) and X-Y/t recorder (Rikadenki Table I Characteristics of the effluent

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Procion Black 5B dye effluent before treatment</th>
<th>Procion Black 5B dye effluent after treatment (current density: 2.5 A/dm(^2) at 101/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.6</td>
<td>13.6</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>1264</td>
<td>328</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>460</td>
<td>240</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>9600</td>
<td>9280</td>
</tr>
<tr>
<td>Chloride (mg/l)</td>
<td>3860</td>
<td>3610</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>992</td>
<td>—</td>
</tr>
<tr>
<td>Density of the effluent (kg/m(^3))</td>
<td>989.04</td>
<td>—</td>
</tr>
<tr>
<td>Colour index</td>
<td>20305 CI</td>
<td>—</td>
</tr>
<tr>
<td>Reactive Black 5B</td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>

Initial COD: 1264 ppm; \( \lambda_{\text{Max}} \): 575 nm

The COD of all samples were determined by the dichromate reflux method [22]. UV–vis Spectra of untreated dye effuent and treated effluent were measured by using a UV–visible spectrophotometer (Systronics 118). From the absorbance values the reduction in dye concentration or the colour removal was calculated by following formulae:

\[
\% \text{Colour removal} = 100 \times \frac{[\text{ABS}_0^\text{M} - \text{ABS}_1^\text{M}]}{[\text{ABS}_0^\text{M}]} \tag{37}
\]

where \( \text{ABS}_0^\text{M} \) is the average of absorbance values as it is maximum absorbency visible wavelength. \( \text{ABS}_1^\text{M} \) the value before electrolysis, \( \text{ABS}_0^\text{M} \) the value after electrolysis and the FTIR of the samples were obtained by Perkin-Elmer-Paragon 500 before and after electrolysis.

### 3.2. Electrolytic cylindrical flow reactor

A schematic view of the experimental set-up is shown in Fig. 4. The electrolytic flow reactor consist of the cathode, which was a stainless-steel pipe of 110 cm height and 7 cm diameter, and the catalytic anode, made of Ti/RuO\(_2\) coated expanded mesh.
Fig. 4. Experimental set-up of flow cell: (1) reservoir, (2) pump, (3) rotameter meter, (4) electrolytic cell, (5) voltmeter, (6) ammeter, (7) DC power supply (100A, 0-50 V), (8) treated effluent, (9) Ti/RuO₂ coated expanded mesh cylinder anode, (10) stainless-steel cathode, and (11) and (12) valves.

The effluents were taken in the reservoir, which was passed to the cell. The flow rate was measured and adjusted by rotameter. The required current was passed using regulated power supply and cell voltage was noted for each flow rate. The effluent was allowed to flow at single pass from bottom of the cell using NaCl as electrolyte medium. After attaining steady-state, the outlet samples were collected and subjected to COD, FTIR, and colour (UV-vis spectra) analysis. The various experimental conditions and parameters were studied at different current densities such as 1, 1.5, 2 and 2.5 A/dm². For each current density the experiment was repeated for different flow rate of effluent to the reactor 10, 20, 30, 40 l/h (liter per hour).

4. Results and discussion

The effect of the parameters such as flow rate and current density on rate of COD removal as well colour removal were investigated in a pilot scale cylindrical flow electrolyzer in a single pass for Procion Black 5B in a NaCl electrolyte medium. The option for the above medium was based on CV scans as given in Fig. 5. The following data such as specific power consumption, mass flux and mass transfer coefficient were computed for various flow rate and current densities is given in Table 2. The COD reduction and colour removal efficiencies shown in Figs. 6 and 7. The FTIR and UV-vis spectra obtained for the outlet samples are given in Figs. 8 and 9. All the above studies were carried out under ambient conditions.

4.1. Cyclic voltammetry studies

To understand the electrochemical behaviour of the electrolyte medium, cyclic voltammetry (CV) studies were carried

Fig. 5. Cyclic voltamgram (50mV/s) studies for Procion Black 5B dye under different electrolytic conditions: (1) KOH (0.1 M) medium, (2) Na₂SO₄ (0.1 M) medium, (3) NaCl (0.1 M) medium, (4) Cl⁻ (0.01 M) medium, (5) H₂SO₄ (0.01 M) medium with increased concentrations of: (a) background of the electrolyte, (b) 10 ppm, (c) 20 ppm, and (d) 30 ppm, (e) 40 ppm, respectively.
Table 2
Effect of current density and flow rate on power consumption, mass flux and mass transfer coefficient

<table>
<thead>
<tr>
<th>Current density (A/dm²)</th>
<th>Flow rate (lph)</th>
<th>Voltage (V)</th>
<th>Residence time (H)</th>
<th>COD (mg/l)</th>
<th>Power consumption (kWh/g COD)</th>
<th>Mass flux (g COD/h dm²)</th>
<th>Mass transfer coefficient (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Flow rate VS COD reduction

Fig. 6. Effect of COD reduction on flow rate at different current densities (•) 1 A/dm², (■) 1.5 A/dm², (▲) 2 A/dm², (●) 2.5 A/dm².

Flow rate vs Color removal

Fig. 7. Efficiency of colour removal on flow rate at different current densities (•) 1 A/dm², (■) 1.5 A/dm², (▲) 2 A/dm², (●) 2.5 A/dm².

out. To know the actual behaviour of the real effluent it is always better to resort to study of the effect of cationic radicals such as Na⁺, K⁺, H⁺ and anionic radicals SO₄²⁻, Cl⁻, OH⁻, CO₃⁻, HCO₃⁻, and HSO₄⁻ (that are generally present in the effluent) separately and their various combination with different ionic strengths. Since the main scope of this paper is limited to demonstrate the pilot scale reactor study, in NaCl medium, in which the behaviour of Cl⁻ ions plays a vital role in indirect oxidation. CV studies were carried out to compare the electro chemical behavior of Procion Black 5B at different electrolytes such as KOH, Na₂SO₄, NaCl, HCl and H₂SO₄. CV scans are shown in Fig. 5. In case of KOH, Fig. 5(1) the reduction of Procion Black 5B occurs at —0.57 V and in Fig. 5(2) in respect of Na₂SO₄ electrolytes, the reduction peak appears at —0.21 and —0.72 V. The absence of oxidation peaks indicate that the presence of either KOH or Na₂SO₄ will not help in reduction of COD but may help in the removal of colour. The oxidation peak observed

out. To know the actual behaviour of the real effluent it is always better to resort to study of the effect of cationic radicals such as Na⁺, K⁺, H⁺ and anionic radicals SO₄²⁻, Cl⁻, OH⁻, CO₃⁻, HCO₃⁻, and HSO₄⁻ (that are generally present in the effluent) separately and their various combination with different ionic strengths. Since the main scope of this paper is limited to demonstrate the pilot scale reactor study, in NaCl medium, in which the behaviour of Cl⁻ ions plays a vital role in indirect oxidation. CV studies were carried out to compare the electro chemical behavior of Procion Black 5B at different electrolytes such as KOH, Na₂SO₄, NaCl, HCl and H₂SO₄. CV scans are shown in Fig. 5. In case of KOH, Fig. 5(1) the reduction of Procion Black 5B occurs at —0.57 V and in Fig. 5(2) in respect of Na₂SO₄ electrolytes, the reduction peak appears at —0.21 and —0.72 V. The absence of oxidation peaks indicate that the presence of either KOH or Na₂SO₄ will not help in reduction of COD but may help in the removal of colour. The oxidation peak observed
4.2. Effect of COD and colour removal

The extents of COD removal at different reaction times under various conditions are shown in Fig. 6. During the present investigation the operating parameters such as flow rate and current densities were varied to explore the effect of such parameters on COD removal. Results showed (Table 2) higher COD reduction occurred at higher charge input and electrolysis (residence time). The residence time is defined as the ratio of volume of the reactor by volumetric flow rate; at low flow rate the residence time becomes high hence the COD reduction is more as well as higher current also COD reduction is more because the generation of large amount of OCl⁻, when sufficient amount of chloride is available in the system. In this study, the increase in flow rate from 10 to 40 l/h leads to gradual decrease in the COD removal; at 40 l/h it was 20% less than that at 10 l/h because the residence time of the effluent at 10 l/h was 4 times higher than that at 40 l/h. The maximum possible COD reduction was 74.05% at 10 l/h and 2.5 A/dm².

Also, the samples were taken from outlet of the cell for analysis. The residual dye concentration was measured spectrophotometrically and associated with the decrease in the absorbance at the peak of maximum visible wavelength (575 nm) and expressed in terms of percentage. These results are shown in Fig. 7. The maximum colour removal (99.83%) was obtained at 10 l/h and 2.5 A/dm². At high flow rates (40 l/h) and lower current density (1 A/dm²), the colour reduction was found to be low (86%).

4.3. IR-spectral studies

Fig. 8 shows the IR-spectra of the dried solution residue before and after the electrochemical treatment. It can be seen that some structural changes might have occurred during the electrochemical process. The appearance of peak at 1634 cm⁻¹ indicates the presence of C=C conjugated diene group. The other peak at 3335 cm⁻¹ indicates the presence of CH₂ for CH₃. After electrolysis, there are two peaks appeared at 1003.6 and 624.64 cm⁻¹, while peaks at 1634.41 and 1385.31 cm⁻¹ are completely disappeared and 560.09 cm⁻¹ peaks shifted to 624.64 cm⁻¹. The appearance of peak at around 1003.6 cm⁻¹ suggests the formation of ClO⁻, which may generally be seen in the hypochlorite solution. Presence of peak at about 624.64 cm⁻¹ is thought to belong to C-Cl stretching. This variation in the IR-spectra can be explained by completely degradation of organic compounds and formation of chlorinated organics.

4.4. UV-vis spectrophotometer studies

The changes in absorbance characteristics of dye effluent were investigated over a large wavelength interval during the electrochemical decolourization process and the results are shown in Fig. 9. The spectra shows that there is a maximum absorbance at 575 nm in the visible region. This peak disappears gradually during the electrolysis. There are also two peaks observed at 391 and 310 nm, respectively in the UV region which become at 391 nm peak was disappeared and 310 nm...
peak shifted to 291 nm as the electrolysis progresses. This result
shows the cleavage of azoic group and total discoulouration of
the solution. The presence of the peak at 291 nm at the end of
the electrolysis, shows that the mineralization of the Procion
Black 5B it is not completely achieved. This peak can be attributed
to carboxylic acids accumulated at the final stage of the oxidation.
This is represents the residual COD present in the effluent. It is
clear from Fig. 9 that the electrochemical oxidation process has
effectively reduced the colour of the dye effluent.

4.5 Effect of flow rate and current density

To enumerate the effect of current density on power consump-
tion, the current was varied from 1 to 2.5 A/dm². The values
are given in Table 2. Shows, increase in the flow rate reduces
the power consumption of the process. This is attributable to
the preferential oxidation of easily oxidizable materials. At
1 A/dm², the power consumption at of 0.2480 kWh/kg of COD
is found to be lower at 40 l/h and the power consumption of
2.8190 kWh/kg of COD is found to be highest at 10 l/h. Increase
in the current density increases the power consumption. This
is evident from the values given in Table 2. At 1 A/dm², flow rate
of 10 l/h, the power consumption was found to be 2.8190 kWh/kg
of COD. At 2 A/dm², at same flow rate the power consumption
was increased to 11.5340 kWh/kg of COD.

Mass flux of the system decreases linearly with the decrease
in flow rate. This is shown in Table 2 at 2.5 A/dm², the mass flux
was found to be 0.1656 g COD/h dm² at flow rate of 10 l/h and
mass flux of 0.5379 g COD/h dm² at flow rate of 40 l/h. As mass
flux depends on the time of operation, the effect of residence time
plays an important role in the process. The easily oxidizable parts
present in the effluent contribute to the decrease in the COD at
low flow rate. The current density is directly proportional to the
mass flux. These results are shown in Table 2. At current density
of 1 A/dm² and flow rate of 10 l/h, the mass flux was 0.1256 g
COD/h dm², but high current density (2.5 A/dm²) and same flow
rate mass flux was increased to 0.1656 g COD/h dm².

From Table 2 shows the mass transfer coefficient increases
with increase in flow rate as well as increase in current den-
sity. Mass transfer coefficient verses flow rate under various
current densities. The mass transfer coefficient 0.0081339 cm/s
was found to be high in the case of 40 l/h and 2.5 A/dm². The
mass transfer coefficient of the process was indirectly related
to the time of operation, as time of operation reduces, mass
transfer coefficient increases steadily. It has a direct relation
to the current density at 2.5 A/dm² was 0.0081339 cm/s and
1 A/dm² was 0.0045940 cm/s at 40 l/h. Hence to degrade Pro-
cion Black 5B having the initial absorbency and COD values are
30.6 and 1264 mg/l. It has to electrolyze in order to bring down
below 250 mg/l to meet out the discharge standards. At 1 A/dm²
and 10 l/h, the final absorbency and COD values are 0.981 and
544 mg/l (96.99% and 56.92% reduction) and 2.5 Am/dm² in
10 l/h charge to bring down the absorbency and COD value are
0.052 and 328 mg/l (99.83% and 74% reduction). This is due to
rapid reaction that is followed by a slow reaction at high current
density. Murphy et al. [23] reported that pollutant removal effi-
ciency at same charge loading was independent upon the value
of current density in a direct electrochemical oxidation treat-
ment process. Here the result shows that current density strongly
influences the rate of reaction.

5. Conclusion

In the present work, dye effluents were treated using Ti/RuO₂
as anode and stainless-steel as cathode. The experiments were
carried out in cylindrical flow cell (single pass) reactors under
different conditions. Treatment using physico-chemical method
produces more sludge, involves high cost and lower efficiency.
In biological treatments the process takes longer time and gives
lower efficiency. Hence this electro chemical treatment is best
suited for treating the dye house effluent. From the results COD
reduction was found to be 74.05% and colour removal was nearly
100% at 2.5 A/dm² for flow rate of 10 l/h, respectively. The flow
rate of effluent in to the reactor is significantly affected by the
reactor performance. The decrease in flow rate and increase
in current density significantly increase the reduction of COD.
Both mass flux and mass transfer coefficient are higher in the
case of flow cell reactor method. This method is also economical.
For the industrial application, flow cell method can be recom-
ended with two or more reactors in series at a current density
of 1–2.5 A/dm².

Acknowledgements

One of the authors (S. Raghu) greatly acknowledges The
Director, Central Electrochemical Research Institute, Karaikudi,
India for his Constant encouragement. Also acknowledges Dr.
Sheela berchmans, Scientist, EEC division, CECRI, for his help-
ful discussions.

References

[1] D. Rajkumar, K. Pulainivelu, Electrochemical treatment of organic wastew-
textile dye effluent by biosorption on apple removal and wheat straw. Water
2925.
[4] S. Meric, I. Kabadashi, O. Tunay, D. Orhon, Treatability of strong wasters-
ters from polyester manufacturing industry, Water Sci. Technol. 39 (10-11)
88.
[6] I.K. Kapdan, F. Kargi, Biological decolorisation of textile dyestuff contain-
ing wastewater by Coriolus versicolor in a rotating biological contactor.
water treatment, Environmental Oriented Electrochemistry (Studies in
Environmental Science: 59), Edited by A.C. Soceira, 77–102., in press.


Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater

S. Raghu, C. Ahmed Basha*

Central Electrochemical Research Institute, Karaikudi 630 006, Tamilnadu, India

Received 13 December 2006; received in revised form 30 March 2007; accepted 30 March 2007

Available online 8 April 2007

Abstract

This paper examines the use of chemical or electrocoagulation treatment process followed by ion-exchange process of the textile dye effluent. The dye effluent was treated using polymeric coagulant (cationic dye-fixing agent) or electrocoagulation (iron and aluminum electrode) process under various conditions such as various current densities and effect of pH. Efficiencies of COD reduction, colour removal and power consumption were studied for each process. The chemical or electrochemical treatment are indented primarily to remove colour and COD of wastewater while ion exchange is used to further improve the removal efficiency of the colour, COD, Fe concentration, conductivity, alkalinity and total dissolved solids (TDS). From the results chemical coagulation, maximum COD reduction of about 81.3% was obtained at 300 mg/l of coagulant whereas in electrocoagulation process, maximum COD removal of about 92.31% (0.25 A/dm²) was achieved with energy consumption of about 19.29 kWh/kg of COD and 80% (I A/dm²) COD removal was obtained with energy consumption of about 130.095 kWh/kg of COD at iron and aluminum electrodes, respectively. All the experimental results, throughout the present study, have indicated that chemical or electrocoagulation treatment followed by ion-exchange methods were very effective and were capable of elevating quality of the treated wastewater effluent to the reuse standard of the textile industry.

Crown Copyright © 2007 Published by Elsevier B.V. All rights reserved.

Keywords: Textile dye effluent; Chemical treatment; Electrocoagulation; Ion-exchange process

1. Introduction

Many techniques have been used for treatment of waste wastewater, such as adsorption, biological treatment, oxidation, coagulation and/or flocculation, of such coagulation is one of the most commonly used techniques. Inorganic coagulants such as lime and salts of iron, magnesium and aluminum have been used over many years, but with changes in dyes and with the dye consents proposed by water authorities, these no longer given completely satisfactory treatment [1]. Not all dyes are effectively removed by inorganic coagulants; thus alum is unsatisfactory for the removal of soluble dyes such as reactive and direct dyes [2]. Organic polymers have therefore been developed for colour removal treatment and, in general, they offer the same advantages with the production of less sludge and significantly improved colour removal [1]. For the removal of colour from dye house effluent, no such effective and simple inorganic option exists for many soluble dyes [3]. Traditional methods for dealing with textile wastewater consist of various combinations of biological, physical and chemical treatment methods [4]. Common biological treatment processes are often ineffective in removing dyes, which are highly structured polymers with low biodegradability [5]. Various physical–chemical techniques are also available for the treatment of aqueous streams to eliminate dyes; chemical coagulation followed by sedimentation [6] and adsorption are the widely used ones [7], but other advanced techniques are often applied, e.g. UV [8,9], ozonation [10], ultrasonic decomposition, or combined oxidation processes [11–13].

Electrocoagulation is a process consisting of creating metallic hydroxide flocs within the wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum. This method has been practiced for most of the 20th century with limited success. Recently, however, there has been renewed interest in the use of electrocoagulation owing to the increase in environmental restrictions on effluent wastewater. In the past decade, this technology has been increasingly used in developed countries for the treatment of industrial wastewaters [14–16].

---

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.
E-mail addresses: subraghu_0612@yahoo.co.in (S. Raghu),
basha@cecri.res.in, cab.50@rediffmail.com (C. Ahmed Basha).
coagulation has been proposed for the treatment of various effluents such as wastewater containing food and protein wastes [17], textile wastewater [18], aqueous suspensions containing kaolinite, bentonite, and ultra fine particles [19,20], fluoride-containing water [21], restaurant wastewater [22,23], textile dye solution [24–25] and smelter wastewater containing has full arsenic [26]. Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium based DSA electrodes [27,28], platinum electrode [29], diamond and metal alloy electrodes [30] and boron doped diamond electrodes [31,32]. One available treatment technology widely used in recent years is Fenton oxidation. This advanced chemical oxidation technology is based on the production of hydroxyl radicals, *OH, which have an extremely high oxidation potential (+OH/H2O = +2.73 V). The Fenton oxidation process has been employed successfully to treat different industrial wastewaters [33–38]. These methods are intended to treat the textile wastewater to a level that meets the discharge standards required by the government. However, due to dwindling supply and increasing demand of water in the textile industries, a better alternative is to attempt to further improve the water quality of treated wastewater for reuse standard. Meanwhile, high treatment costs of these methods have stimulated, in recent years, the search for more cost effective treatment methods and reuse standards. In the present work, an attempt has been made to study the treatment efficiency of chemical (polymeric chemical coagulation) or electrocoagulation process for the removal of colour and COD of the effluent, followed by ion-exchange process for further lowering the colour, COD, Fe, concentration, conductivity, alkalinity and total dissolved solids (TDS).

2. Mechanism of polymeric coagulant

Textile dye-fixing agents are used as a polymeric coagulant. Direct and reactive dyes contain RSO3− group and dye-fixing agent are RN+Cl−. When these two solutions are dissolved in water, they ionize to long cations and small anions. On the other hand, when a dye is dissolved in water, it ionizes into long coloured anions and small sodium ions. When these two solutions are mixed the long ions of opposite ionic charge combine with one another to form an insoluble complex [39].

\[
\text{RSO}_3\text{Na} \leftrightarrow \text{RSO}_3^- + \text{Na}^+ \tag{1}
\]

\[
\text{R}_4\text{N}−\text{Cl} \leftrightarrow \text{R}_4\text{N}^+ + \text{Cl}^- \tag{2}
\]

\[
\text{R}_4\text{N}^+ + \text{RSO}_3^- \rightarrow \text{RSO}_3−\text{NR}_4 \quad \text{(Insoluble complex)} \tag{3}
\]

2.1. Mechanism of electrocoagulation

Four main mechanisms have been suggested to describe the process by which contaminants are removed from wastewa-ter using this system. These consist of surface complexation, electrostatic attraction, chemical modification, and precipitation.

The chemistry of surface complexation is not well understood and is specific to each effluent, but is thought to occur in the following manner [40]:

\[
\text{Dye-H} + (\text{HO})\text{Fe} \rightarrow \text{Dye-OFe} + \text{H}_2\text{O} \tag{4}
\]

\[
\text{Dye-H} + (\text{HO})\text{OAl} \rightarrow \text{Dye-OAl} + \text{H}_2\text{O} \tag{5}
\]

In addition, for forming all possible surface complexes, it may be possible to remove remaining dyestuff by simple electrostatic attraction, hydrous iron oxide. In combination with the various surface complexes, contains areas of apparent positive and negative charge. The attraction of opposite charges is sufficient to remove some dissolved species from the effluent stream. Chemical modification may occur on passage of effluent through the electrochemical cell as well as during subsequent degassing. The chemistry C=C and N=N (common in dyes) allows "catalytic hydrogenation" or reduction to occur in the presence of hydrogen gas and a catalyst. The presence of metal ions and hydrogen gas in this reaction suggests that the above could occur, but further research is required to confirm the extent of this mechanism and the conditions, which favor it. Precipitation is a mechanism by which soluble species with opposite charges react with another to form insoluble solids. This reaction often determines the success of heavy metal removal from contaminated water. In the case of dyestuffs, however, it is believed to have limited applicability [40].

3. Material and methods

All the reagents used were of Analytical Reagent grade. Polymeric coagulant (dye-fixing agent- Sandofix-WRN) and dye effluent (Procion Black 5B-Reactive dye) were collected from Textile industry. The cross-linked polystyrene bead resins, which are commercially known as Amberlite IR 120 and Amberlite IRA 400, were used.

3.1. Analytical measurements

The analytical methods of the COD of all samples were determined by the dichromate reflux method [41]. In electrochemical process the chloride ions cause interference, because they can be oxidized to Cl2 by dichromate under the analysis conditions, the samples were treated with Ag2SO4 to form a precipitate of AgCl that was separated by centrifugation. The oxidized products and the reduction in dye concentration were measured by using a UV–Visible Spectrophotometer (Systronics 118), the colour removal was calculated by following formulae:

\[
\text{Color removal (\%)} = 100 \left(1 - \frac{\text{ABS}^M}{\text{ABS}^B} \right) \tag{6}
\]

where ABS^M is the average of absorbance values as it is maximum absorbency visible wavelength. ABS^B the value before electrolysis, ABS^M the value after electrolysis.
3.2. Electrochemical cell

The electrolysis cell (Fig. 1) used in the present study consists of a glass beaker of 500 ml capacity closed with a PVC lid having provision to fit a cathode and an anode. Commercially available mild steel and aluminum were used as anodes while stainless steel was used as cathode. It is connected to 2 A and 15 V dc regulated power supply.

3.2.1. Ion-exchange experimental set up

The ion-exchange column consisted of glass column of length 60 cm and diameter 2.5 cm. It was plugged with cotton at the bottom for free flow of the treated wastewater and to hold the resin intact. The columns consisted 20 ml of cation-exchange resin (Amberlite IR 120) and other one consisted of 40 ml of anion-exchange resin (Amberlite IRA 400). The constant flow rate (5 ml/min) through the column was maintained with the help of a peristaltic pump. The flow cell is shown in Fig. 2.

3.3. Experimental procedure

The present experimental study involved two major processes such as chemical treatment or electrocoagulation (iron and aluminum electrode) process followed by ion-exchange process. These two treatments can be operated independently in batch-wise processes. Two hundred milliliters of industrial effluents (Procion Black 5B-Reactive dye) of known concentration were taken for each experiment. In this first process the effluent was chemically treated using appropriate amounts of Sandofix-WRN (cationic dye-fixing agent) under various conditions whereas in the second process, electrocoagulation was carried out under galvanostatic condition. Samples were collected at regular intervals of time for estimation of COD, colour, and power consumption. After completion of chemical treatment or electrocoagulation, the wastewater was then subjected to ion-exchange process. The ion-exchange experiments were conducted in a flow cell process.

3.3.1. Chemical treatment

In chemical treatment, textile dye-fixing agent was used as a polymeric coagulant. Four hundred millilitres of wastewater sample was taken and coagulated using Sandofix-WRN (cationic dye-fixing agent) under various pH ranges from 2 to 12 and amount of coagulant required was optimized.

3.3.2. Electrocoagulation

Electrocoagulation is the modification of electrofloation where the coagulation agent is produced in situ at the respective electrodes (The most commonly used electrodes are iron and aluminum.). In this method, the pollutant is transformed into amorphous precipitates or adsorbed on hydroxides formed at the anodes. This method is also called as electroflocculation. Four hundred millilitres of wastewater sample was taken and coagulated. In this process, mild steel/aluminum were used as anode and stainless steel was used as cathode under various current densities (0.25–1 A/dm²).

3.3.3. Ion-exchange process

After the chemical or electrocoagulation treatment, 1000 ml of treated wastewater subjected to ion-exchange columns under constant flow rate (5 ml/min). Before the ion-exchange process, the pH was adjusted to about 7 and the wastewater was filtered using glass wool to remove the suspended solids. The filtration significantly helped to avoid fouling of ion-exchange resins. The samples were taken periodically for measurements of COD,
colour, conductivity, S.S, total hardness, alkalinity, Fe and other ion concentrations.

4. Result and discussion

4.1. Polymeric coagulants

The effect of coagulant dosage on the percentage of COD reduction and colour removal for dye effluent are presented in Fig. 3. These results indicate that a significant amount of dye can be removed. It was also observed that removal efficiencies of both COD and colour increases with increase of coagulant dosage. The maximum COD reductions of 81.3\% and colour removal of about 98.2\% were obtained at 300 mg/l of coagulant.

It is evident from the results that minimum dosage amount of coagulant (300 mg/l) is required to treat the above dye wastewater. It is also observed that the COD began to appear in the electrolyte when dosage amount exceeds the optimum level. This could be due to the presence of the residual coagulant remains in the treated water. Also the pH of the electrolyte solution has been varied in order to check its influence on colour removal and COD reduction. Experiments were conducted under acid, alkaline and neutral conditions and the observed results are given in Fig. 4. It can be ascertained from Fig. 4 that the percentage of COD reduction has increased from 56\% (pH 7) to 81.3\% (pH 10) when the electrolyte pH increased to alkaline condition from neutral. On contrary, in acidic condition precipitation was not seen. Increase in the pH of electrolyte favors the precipitation reaction. Consequently precipitation of dye has been increased. The reaction was favorable at neutral (pH 7) and more acute in alkaline conditions particularly at pH 10.

4.2. Electrocoagulation

The electrocoagulation has been carried out for two different anodes, namely iron and aluminum. The optimum conditions for effective removal of COD, colour and minimum energy consumption have been studied at different current densities in batch reactor. The supply of current to the electrocoagulation system determines the amount of $Al^{3+}$ or $Fe^{2+}$ ions released from the respective electrodes. For aluminum, the electrochemical equivalent mass is 335.6 mg/Ah. For iron, the value is 1041 mg/Ah. Experiments were conducted at four current densities keeping other parameters constant. The COD reduction increased with current density (Figs. 5 and 6). This may be explained that the release of ions, i.e. the release of metal ions increased with current density, which eventually increases the reduction of COD. The efficiencies of COD removal at different reaction times in various conditions are shown in Figs. 5 and 6. These results show that 100\% COD reduction was achieved while iron electrode was used. On the other hand, it was 80\% with aluminum electrode. Figs. 7 and 8 show colour removal efficiencies at different reaction time under various current densities. The maximum colour removal efficiencies were in the order of 97.06 and 94.27\% for
The variation of power consumption with time for the different current densities applied (iron electrode) (•) 0.25 A/dm$^2$, (■) 0.5 A/dm$^2$, (△) 0.75 A/dm$^2$, (◊) 1 A/dm$^2$.

The variation of power consumption with time for the different current densities applied (aluminum electrode) (•) 0.25 A/dm$^2$, (■) 0.5 A/dm$^2$, (△) 0.75 A/dm$^2$, (◊) 1 A/dm$^2$.

The 100% COD removal was achieved within 6 h with a maximum energy consumption of 78.5 kWh/kg of COD at 1 A/dm$^2$. However, at 0.25 A/dm$^2$, the maximum COD removal of 92.31% was achieved with lower energy consumption of about 19.29 kWh/kg of COD in iron electrode and 130.095 kWh/kg of COD at 1 A/dm$^2$ with 80% of COD removal in the aluminum electrode for maximum current density. Therefore, an optimum point must be carefully determined giving a faster removal rate and energy consumption quite low. Hence, the optimal current densities of 0.25 and 1 A/dm$^2$ were chosen for iron and aluminum electrodes, respectively. From the results, it is understood that, the process involving iron electrode, completely removes the dye with low electrical consumption in a short time.

4.3. Ion-exchange process

In the present study, chemically/electrochemically treated wastewater was subjected to ion-exchange process. The conductivity of the wastewater after chemical treatment and electrocoagulation treatment was observed as 4910 and 5200 µmho/cm, respectively, against the reuse standard of 100 µmho/cm. Such a high conductivity of wastewater indicates that it still contains a significant amount of inorganic salts and other ions. To remove these ions and other impurities, both cross-linked divinylbenzene-polystyrene based cationic (Amberlite IR 120) and anionic (Amberlite IRA 400) ion-exchange resins were used in the flow cell experiment. A cation-exchange resin captures positively charged ions and an anion-exchange resin negatively charged ions. In fresh resin, the cations attached to the cationic resin are H$^+$, those attached to the anionic resin OH$^-$. Treated wastewater, which was passed through the cation-exchange resin resulted in exchange of the cations (displacing of H$^+$) and subsequently passed through the anion-exchange resin absorbed anions, displacing the OH$^-$ ions. As a result, finally ion free water was obtained. The optimum ratio of resins were studied at room temperature using 100 ml of treated wastewater (5200 µmho/cm) and amount of resin (Amberlite IR 120 (H$^+$): Amberlite IRA 400 (OH$^-$) in ml) 1:1, 1:2, 1:3, 2:1 and 3:1 in...
Table 1
Water quality change after various treatment steps

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Industrial effluent</th>
<th>Polymeric chemical coagulation (300 mg/l)</th>
<th>Electrocoagulation treatment (iron) C.D. = 0.5 A/dm²</th>
<th>Electrocoagulation treatment (aluminum) C.D. = 1 A/dm²</th>
<th>Ion-exchange process</th>
<th>Reuse standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal (%)</td>
<td>-</td>
<td>81.3</td>
<td>92.31</td>
<td>80</td>
<td>Nil</td>
<td>1</td>
</tr>
<tr>
<td>Conductivity (μmho/cm)</td>
<td>5200</td>
<td>4910</td>
<td>5320</td>
<td>5260</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>Colour removal (%)</td>
<td>-</td>
<td>98.2</td>
<td>96.93</td>
<td>87.93</td>
<td>Nil</td>
<td>10</td>
</tr>
<tr>
<td>NTU</td>
<td>10.6</td>
<td>0.8</td>
<td>0.9</td>
<td>1.3</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Total hardness (mg/l)</td>
<td>36.8</td>
<td>28</td>
<td>36</td>
<td>39</td>
<td>310</td>
<td>12</td>
</tr>
<tr>
<td>Alkalinity (mg/l)</td>
<td>420</td>
<td>280</td>
<td>260</td>
<td>310</td>
<td>12</td>
<td>50</td>
</tr>
<tr>
<td>Fe concentration (mg/l)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Nil</td>
<td>0.1</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>3800</td>
<td>3680</td>
<td>3720</td>
<td>3790</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td>S.S</td>
<td>130</td>
<td>84</td>
<td>72</td>
<td>86</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Initial COD: 1040 ppm, λ_max: 640 nm.

Fig. 11. The resin ratio of Amberlite (H⁺)/Amberlite (OH⁻): (●) 1:1, (■) 1:2, ( ) 1:3, (X) 2:1 and (*) 3:1.

500 ml beaker. The solution was stirred using a magnetic stirrer for 10 min. Samples were collected every minute for measurements of conductivity. An optimal ratio of 1:2 the cationic and anionic resin was observed and is shown in Fig. 11. At the other ratios, the treated wastewater has a rather high conductivity and also has a low or high pH. It is of interest to note that the optimal ratio 1:2 of cationic to anionic exchange resins is much in line with that recommended by Jiang [42]. An experimental study was carried out to determine the break-even point of ion-exchange resin columns. It is very much important to study the operational capacity of the resin and the process. Fig. 12 demonstrates the break-even point of ion-exchange resins. The experimental data indicate that 20 ml of cation-exchange resin and 40 ml of anion-exchange resins are needed to treat 400 ml of treated wastewater containing 5200 μmho/cm effectively and the treated water can be reused in the other processes. HCl (5% solution) and NaOH (4% solution) were used for the regeneration process [43]. Water quality changes after various treatment steps were presented in Table 1. Also ion exchange treated wastewater was compared with deionized water quality. Inorganic in the treated wastewater before and after ion exchange were measured by spectrophotometer, NOVA 60 and are listed in Table 2. Three major inorganic ions such as Cl⁻, NO₃⁻ and SO₄²⁻ were measured in the wastewater before and after ion-exchange process. The inorganic ion concentrations measured in the treated wastewater after ion exchanges are nearly equal to those in the deionized water.

Table 2
Inorganic concentrations (mg/l) in the treated wastewater and deionized water

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated wastewater before ion exchange</td>
<td>2080</td>
<td>380</td>
<td>56</td>
</tr>
<tr>
<td>Treated wastewater after ion exchange</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Deionized water</td>
<td>2.6</td>
<td>0.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

5. Conclusion

The treatment systems consisted of the chemical or electrocoagulation followed by ion-exchange process. Polymeric chemical coagulant (Sandofix-WRN) and electrochemical treatment methods were employed in the present study to investigate the effectiveness of treatment of industrial dye effluents (Procion Black 5B-Reactive dye). In the case of chemical coagulation, maximum COD reduction of about 81.3% was obtained at 300 mg/l of coagulant whereas in electrocoagulation process, maximum COD removal of about 92.31% (0.25 A/dm²) was achieved with energy consumption of about 19.29 kWh/kg of COD and 80% (1 A/dm²) COD removal was obtained with energy consumption of about 130.095 kWh/kg of COD at iron and aluminum electrodes, respectively. Increase in the current density increases the power consumption. Hence, the optimization of energy consumption of the treatment methods studied, the maximum COD removal 92.31% (0.25 A/dm²) with minimum energy consumption (19.29 kWh/kg of COD) could be achieved at electrocoagulation using iron electrode. To further elevate the water quality to the reuse standard, an ion exchange
using cationic and anionic exchange resin was found necessary. Experimental results indicated that 20 ml of cation-exchange resin and 40 ml of anion-exchange resins were needed to treat 400 ml of treated wastewater containing 5200 µmho/cm effectively. The water quality of treated wastewater was observed to be consistently excellent, comparable to that of deionized water.

Acknowledgements

One of the authors (S. Raghu) greatly acknowledges The Director, Central Electrochemical Research Institute, Karaikudi, India, for his constant encouragement. Also acknowledges Dr. S. Chellammal and Dr. S. Palanichamy, Scientist, OPMEC Tuticorin, CECRI, for their helpful discussions.

References

Dye Destruction and Simultaneous Generation of Sodium Hydroxide Using a Divided Electrochemical Reactor

S. Raghu and C. Ahmed Basha*
Central Electrochemical Research Institute, Karaikudi, 630 006, India

Textile dye bath effluent contains high concentrations of organic dye, sodium chloride, and other chemicals which inhibit the activity of microorganisms during biological oxidation. Hence high concentrations of organic dye and total dissolved solids have to be removed considerably before biological treatment. In this paper, degradation of dye effluent and simultaneous generation of caustic soda in an electrochemical membrane cell was investigated. Experiments were carried out at different current densities and different flow rates using Ti/RuO₂/IrO₂ as anode and stainless steel as cathode. In the present study of dye effluent treatment the results showed that the electrochemical process could effectively remove COD and color by anodic oxidation (92.16% and 100%) and concentrate caustic soda from 40 to 210.28 g L⁻¹.

1. Introduction

Textile processing industries are widespread sectors in developing countries. Among the various processes in the textile industry, the dyeing process uses large volumes of water for dyeing, fixing, and washing. Thus, the wastewaters generated from the textile processing industries contain suspended solids, high amounts of dissolved solids, unreacted dyestuffs (color), and other auxiliary chemicals that are used in the various stages of dyeing and processing. The conventional method of textile wastewater treatment consists of chemical coagulation, and biological treatment followed by activated carbon adsorption. The conventional coagulation process generates a huge volume of hazardous sludge and poses a problem of sludge disposal. The biological treatment of textile wastewater shows low degradation efficiency because of the presence of biologically inert high molecular weight dyestuffs.¹² Hence many investigators are studying alternative oxidation methods such as ozonation, photocatalytic oxidation, and electrochemical oxidation. The photocatalytic oxidation experiments were conducted for Acid Blue 80, Acid Orange 7, Brilliant Orange K-R, and Reactive Orange 16.¹³–¹⁶ Electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye.⁷ The ozonation process was studied for the removal of color and chemical oxygen demand (COD), however, this process showed less COD removal.⁸,⁹ Researchers also investigated electrocoagulation methods for textile dye removal using aluminum or iron electrodes.¹⁰–¹⁴ Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dyestuff compounds was studied using titanium-based DSA (dimensionally stable anodes) electrodes, platinum electrodes, diamond and metal alloy electrodes, and boron-doped diamond electrodes.⁵–¹⁸ The membrane processes can meet the requirements of nanofiltration and reverse osmosis (RO), which retain not only relatively small organic molecules but also ions from dye wastewater. Removal of auxiliary chemicals, salt, and color from dye wastewater can thus be achieved in one step.¹⁹ However, high osmotic pressure differences limit the applicability of the RO process. RO membrane filtration has problems with fouling, which result in low fluxes and poor separation efficiency.²⁰,²¹ Nerini et al. studied the mediated electrochemical oxidation of organic pollutants in the presence of NaCl.²² The electrochemical treatment of Procion Black 5B using a cylindrical flow reactor, a pilot plant, was studied earlier.²³ As all the above processes need pretreatment, they increase treatment costs. Considering the very stringent environmental regulations, there is an urgent need for development of alternative but cost-effective methods. This necessitates developing a laboratory-scale study of electrochemical membrane techniques for treatment purposes. Most investigators provided information on color and COD removal during the dye degradation and not provided for the recovery of chemicals (caustic soda) by an electrochemical-membrane process. Hence, in the present study, an attempt was made to generate sodium hydroxide (98–99%) as a byproduct during degradation of dye effluent, using a commercially available electrolytic divided cell.

2. Experimental Section

All the reagents used were of analytical grade. Procion Black 5B is a commercial azo dye whose color index is 20505 CI Reactive Black 5. It contains two chromogenic systems. The structure of the dye is shown in Figure 1, and the experimental setup is shown in Figure 2. Nafion 315 cation exchange membrane was used in the experiment. All the solutions were prepared with distilled water. Industrial dye effluent (dye bath) obtained from the Indian textile industry contains 54 g L⁻¹ sodium chloride, 12.8 g L⁻¹ sodium carbonate, 6.2 g L⁻¹ sodium hydroxide, and other organic compounds (dye, surfactant). For investigations a synthetic dye effluent containing 1 g L⁻¹ dye, 50 g L⁻¹ sodium

Figure 1. Structure of Procion Black 5B.
chloride, 12 g L⁻¹ sodium carbonate, and 5 g L⁻¹ sodium hydroxide was prepared. The characteristics of the dye effluent before and after electrochemical treatment are shown in Table 1.

### Table 1. Characteristics of the Dye Effluent Before and After Treatment

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before Treatment</th>
<th>After Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
<td>480</td>
<td>320</td>
</tr>
<tr>
<td>TSS (mg L⁻¹)</td>
<td>530</td>
<td>90</td>
</tr>
<tr>
<td>TDS (mg L⁻¹)</td>
<td>680</td>
<td>59</td>
</tr>
<tr>
<td>Chloride (mg L⁻¹)</td>
<td>310</td>
<td>16</td>
</tr>
<tr>
<td>Sodium chloride (mg L⁻¹)</td>
<td>50000</td>
<td>900</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>992</td>
<td></td>
</tr>
<tr>
<td>Color index</td>
<td>20505 CI Reactive Black 5B</td>
<td></td>
</tr>
</tbody>
</table>

*Current density 2.5 A dm⁻² for 12 h.*

### 2. Electrochemical Membrane Cell

The electrochemical reactor consisted of a titanium expanded mesh anode coated with TiO₂/RuO₂/IrO₂ and had an area of 0.4 dm²; the stainless steel cathode of size 70 mm × 70 mm × 1 mm and the cation-selective membrane (Nafion 315) were fixed in a PVC frame with gaskets so that the cell was divided into two compartments. The distance between electrodes was 1.5 cm. The reactor was connected to a 2 A and 30 V dc APLAB regulated power supply. The anolyte compartment connected to a 6 L capacity effluent reservoir and catholyte compartment was connected to a 500 mL capacity sodium hydroxide reservoir. Both compartment reservoirs were connected to the peristaltic pump using silicone rubber tubes.

### 2.3. Experimental Procedure

About 5 L of dye effluent was passed through the anolyte compartment, and 200 mL of 40 g L⁻¹ caustic soda solution was passed through the catholyte compartment using a double head peristaltic pump under batch recirculation mode at different flow rates of 25, 50, 75, 100, and 125 mL min⁻¹. The hardness of the effluent was automatically removed due to increasing pH (pH of the dye effluent was 12) and then filtered using a glass wool/micron filter to remove the suspended solids. This filtration significantly helped to avoid fouling of the membranes. Whenever the membrane becomes fouled, the cell voltages increases and the membrane needs cleaning. During the electrolysis at various current densities and various flow rates, recovery of caustic soda, COD reduction, color analysis, and HPLC data were measured. The various experimental conditions and parameters measured in the effluent are depicted in the respective figures and tables.

### 3. Results and Discussion

#### 3.1. Mechanism of Dye Degradation and Recovery Of Caustic Soda

Most of the reactive dye effluents contain sodium chloride as the major constituent because in reactive dyeing of cotton process sodium chloride is used as exhaust agent. The method of treating such solutions electrochemically is clean and easy as they involve no addition of chemicals for supporting the electrolysis in most cases. In the present study, the amount of sodium chloride present in the effluent is 50 000 mg L⁻¹, which is acts as a supporting electrolyte. The electrochemical reactions that take place during the electrolysis are complicated and are not entirely known. For the time being only assumptions can be made, based on the products that can be measured. Hence the following reactions are assumed to take place in the anodic and cathodic compartments along with bulk reactions:

- **Main anodic reaction:**
  \[
  2
t\text{Cl}_2^- \rightarrow \text{Cl}_2 + 2e^- \\
  (2)
  \]

- **Side anodic reaction:**
  \[
  4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4e^- \\
  (3)
  \]

- **Bulk reactions in the anodic compartment:**
  \[
  \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{Cl}_2^- + \text{HOCI} \\
  (4)
  \]
  \[
  \text{HOCI} \rightarrow \text{H}^+ + \text{OCI}^- \\
  (5)
  \]
- **Cathodic reaction:**
  \[
  \text{H}_2\text{O} + e^- \rightarrow 1/2\text{H}_2 + \text{OH}^- \\
  (7)
  \]
- **Bulk reaction:**
  \[
  \text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH} \\
  (8)
  \]
Table 2. Destruction of Dye Effluent and Simultaneous Recovery of Sodium Hydroxide

<table>
<thead>
<tr>
<th>sample no.</th>
<th>current density (A dm$^{-2}$)</th>
<th>cell voltage (V)</th>
<th>recovery of NaOH (g L$^{-1}$)</th>
<th>energy consumption for NaOH generation (kWh kg$^{-1}$)</th>
<th>energy consumption for COD removal (kWh kg$^{-1}$)</th>
<th>overall energy consumption (kWh kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>4.6</td>
<td>210.28</td>
<td>3.176</td>
<td>5.755</td>
<td>2.047</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>4.1</td>
<td>126.72</td>
<td>2.781</td>
<td>3.547</td>
<td>1.559</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3.8</td>
<td>108.23</td>
<td>2.619</td>
<td>3.193</td>
<td>1.439</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>3.5</td>
<td>89.16</td>
<td>2.515</td>
<td>2.81</td>
<td>1.327</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>3.1</td>
<td>72.18</td>
<td>2.265</td>
<td>2.28</td>
<td>1.136</td>
</tr>
</tbody>
</table>

For textile industry effluents, the application of indirect electrochemical oxidation mediated by chlorine/hypochlorite was studied earlier. Color removal and COD reduction occurred only in the presence of sodium chloride. Thus, decolorization occurs in the dye effluent because of the reaction between the generated chlorine/hypochlorite and the dye molecule. The indirect electrochemical treatment involves the application of an electrical current to the wastewater containing chloride to convert chloride to chlorine/hypochlorite which oxides the pollutants and is then reduced to chloride ion. In this process the dye effluent enters at the anolyte side of the cell. Sodium ions migrate across the membrane into the catholyte. Hydroxide forms at the cathode by the reduction of water. The catholyte product is thus sodium hydroxide or caustic soda. Chloride ions migrate to the anode. Hypochlorous acid (HOCl) which forms at the anolyte oxidizes the dye effluent.

3.2. Effect of Current Density and Flow Rate. The results of the experiments that were conducted at the flow rate of 50 mL min$^{-1}$ and at five different current densities of 1.0, 1.5, 2.0, 2.5, and 5.0 A dm$^{-2}$ are presented in Tables 1 and 2 as well in Figures 3 and 4. The COD reduction was increased with increase in electrolysis time and current density (Figure 3). This might be due to the fact that the rate of generation of hypochlorite (OCl$^-$) increased with increase in current density, which eventually increased the pollutant degradation. The increase in hypochlorite (OCl$^-$) reaches equilibrium with the degradation of organics present in the effluent. For a given supporting electrolyte in the anolyte concentration, a pseudo steady state between the generation of hypochlorite (OCl$^-$) and the degradation of pollutant may be arrived at when the current density increases. In 12 h of operation of the cell the maximum COD reduction was found to be 92.16% at 5 A dm$^{-2}$.

Figure 4 shows the residual dye concentration that was measured spectroscopically and associated with the decrease in the absorbance at the peak of maximum visible wavelength and expressed in terms of percentage. The decolorization efficiency was observed as 99.48% with a current density of 2.5 A/dm$^{-2}$ for 12 h, and then it remained almost constant at higher current densities. The initial and final pH values of the wastewater observed in the treatment process are presented in Table 1. The value of pH decreases gradually during the electrochemical reaction because of migration. The pH decrease is dependent on the operating conditions employed (e.g., current density, NaCl concentration, recirculation time). However, the final pH value was around ~2. This is due to the migration of Na$^+$ ions toward the cathode compartment and the formation of hypochlorous acid in the anolyte compartment. Increase in the current density and the electrolysis time was attributed to the increased formation of OCl$^-$ in the anolyte solution.

In the case of an undivided cell system, the COD reduction achieved was around 74%. However, in the divided cell system the COD reduction

![Figure 3](image-url)  
Figure 3. (a) Variation of the extent of unconverted COD with electrolysis time at various current densities. Conditions: [COD$_0$] = 4080 mg L$^{-1}$; [NaCl] = 50 g L$^{-1}$; flow rate = 50 mL min$^{-1}$. (b) Effect of current density on COD reduction. Conditions: same as (a) and duration of electrolysis = 12 h.

![Figure 4](image-url)  
Figure 4. Color removal efficiency with time at various current densities. Conditions: same as Figure 3a.
achieved was 92.16% due to more generation of ClO⁻ ions and HClO due to decrease in the pH from 12 to around 2.

The pH influences strongly the degradation process; in fact, in acid media (<2) the main active species is Cl₂, in neutral media HClO is the active species, and in alkaline media (>11) the active species is ClO⁻. Furthermore, at pH close to neutrality a large amount of chlorate is formed. It should be noted that pH has a significant effect on the electrochemical degradation of organics over titanium catalytic coated anodes in the pH range 2–12.

Figure 5 shows the reduction of COD and recovery of NaOH with time at different flow rates of 25, 50, 75, 100, and 125 mL min⁻¹. As seen from the figure, the trend of the COD reduction and the recovery of NaOH were strongly influenced by the hydrodynamic conditions and, in particular, the degradation of dye and NaOH generation were favored by a high flow rate, indicating that oxidation and generation are mass transfer controlled processes.

3.3. Current Efficiency and NaOH Recovery. The theoretical amount of the cathodic generation of NaOH can be computed by Faraday’s law. According to Faraday’s law, 1 g-mol of products will be produced when 1 faraday of charge is applied. Since cathodic reduction of sodium is a one-electron-transfer reaction, the current efficiency (CE) can thus be calculated by eq 10:

\[
m = \frac{I M}{z F}
\]

where \(I\) is the current in amperes, \(t\) is the time in seconds, \(F\) is the Faraday constant (96,487 C mol⁻¹), \(M\) is the molecular weight of NaOH (g mol⁻¹), \(z\) is the number of electrons transferred in the reaction, \(m'\) is the experimental yield, and \(m\) is the theoretical quantity of NaOH. The percent current efficiency for recovery of NaOH is shown in Figure 6. In the first four current densities, the current efficiencies were found to be 91.64, 93.34, 97.15, and 99.26%, respectively; the current efficiency was found to increase linearly up to 2.5 A dm⁻². When the current density increased to 5.0 A dm⁻², the current efficiency fell to 96.98%. The current efficiency (CE) of dye degradation can be calculated from COD values using the following relation:

\[
CE = \frac{CO_D - CO\Delta}{8I\Delta} \times 100 \quad (11)
\]

where \(t\) and \(\Delta\) denote the time in seconds, \(I\) is the current (amperes), \(F\) is the Faraday constant (96,487 C mol⁻¹), \(V\) is the volume of the electrolyte (dm³), and \(8\) is the equivalent weight of oxygen. In the electrochemical degradation of pulp and paper mill wastewater, Mishra et al.²⁷ had reported current efficiencies ranging from 400 to 500% and others²⁸ reported current efficiency increases above 100%. In this investigation, too, for indirect electrochemical degradation of dye effluent the current efficiencies increased above 100%. Here formation of such as chlorine (Cl₂), hypochlorite (OCl⁻), and chlorate (ClO₃⁻) may occur and these intermediate products may chemically oxidize dye effluent in a long period of electrolysis. The current efficiency depends on the current density as well as the types of anions and residence time. Significantly enhanced current efficiency, up to 455.87%, was obtained. The current efficiency decreases with an increase in the current density. During the electrolysis, the increase in the current density decreases the
current efficiency from 455.87% to 267.83%. Again it should be noted that COD is not a chemical compound to follow Faraday’s law in a thermodynamic sense. These higher value efficiencies may only indicate that there exists a large chemical reaction to contribute to COD reduction. During the electrolysis, the higher current efficiency value is obtained due to an initial period of electrolysis, when the effluent contains more sodium chloride (50 g L\(^{-1}\)) and oxidized products of sodium chloride enhance the high CE. Also indirect oxidation of the process is not dependent on the operating conditions employed (e.g., electrode, current density, NaCl concentration, recirculation time). At higher current density, the size of the bubble was large, which leads to an increase in resistance and hence an increase in the cell voltage (3.1 to 4.6 V).

Figure 6b shows the buildup of NaOH concentration with time for different current densities. At 5 A dm\(^{-2}\), the recovery of NaOH maximum obtained was from 40 to 210.28 g L\(^{-1}\) and in the other four current densities (1, 1.5, 2 and 2.5 A dm\(^{-2}\)) recoveries of NaOH were found to be 72.18, 89.16, 108.23, and 126.72 g L\(^{-1}\), respectively.

3.4. High-Performance Liquid Chromatography (HPLC).

The HPLC samples were prepared from ether-extracted dried solution. The residue was dissolved in a small volume of HPLC-grade methanol, and the same sample was used for HPLC. Figure 7 shows the HPLC plots for the following three samples: the initial dye Procion Black 5B represented by plot a and the other two samples represented by graphs b and c for the residues obtained after 12 h of electrolysis time carried out at 2.5 and 5 A dm\(^{-2}\), respectively. With respect to electrolyzed solutions of dye, no product information was available from the HPLC determination. From Figure 7, plot a indicates the two peaks at 2.6 and 3.2 min with 4.8 and 1.3 V, respectively. For the second sample (the residues obtained after 12 h of electrolysis time carried out at 2.5 A dm\(^{-2}\)), both peaks area were shifted 3.3 and 3.9 min with decreased 0 and 1.6 V, respectively, as represented by plot b. This indicates the existence of a very small amount of parent dye and correspondingly lower carbon atom number than the original dye molecule. Chemical reduction of azo linkage commonly results in the formation of lower molecular weight aromatic amine entities and products with the parallel elimination of color in the reduced solution of the dyes. Fourier transform infrared studies\(^{22}\) indicated that the treated effluent contains very low concentrations of chlorinated organic compounds at low residence time. Hence, in this study, the electrolysis time and current density were increased and experiments were conducted. No peaks were observed in curve c of Figure 7 which is due to increase of the current density (5 A dm\(^{-2}\)) and electrolysis time for 12 h. This result indicates the complete degradation of organic compounds and without formation of chlorinated organic compounds for long electrolysis time and high current density. It is clear that from increasing the time of electrolysis complete degradation of dye takes place.

3.5. Energy Consumption. The energy consumption was very important to study in the electrochemical process. The advantages claimed for Ti/RuO\(_2/\)IrO\(_2\) (DSA) anodes over a graphite electrode are (i) lower cell voltage (3.90 V compared to 4.97 V for graphite), (ii) lower power consumption (2740 kWh per ton of Cl\(_2\) compared to 3580 kWh per ton of Cl\(_2\)), and (iii) electrode erosion taking place only at graphite electrode, not in DSA.\(^{20}\)

The results, which are presented in Figure 8 and Table 2, show that the operational current density significantly influences the power consumption. Only a few percent of the total energy requirement of the electrochemical step is needed for pumping the electrolyte around the electrolyte cycle and a small fraction of the energy is necessary to maintain a sufficiently fast flow through the electrodes.

The specific energy consumption for electrolysis, \(E\), kWh kg\(^{-1}\), is computed using the following expression:

\[
E = \frac{V_{cell}I/10^3}{(C_0 - C_f)V/10^3}
\]

where the numerator represents the power input in kWh, \(V_{cell}\) is the cell voltage in volts, \(I\) is the current applied in amperes in the circuit, and \(t\) is the duration of electrolysis in hours for bringing the initial concentration, \(C_0\) (mg L\(^{-1}\)), of effluent to final concentration, \(C_f\) (mg L\(^{-1}\)), in the volume of the reservoir, \(V\), in liters.

At 5.0 A dm\(^{-2}\) with the flow rate of 50 mL min\(^{-1}\) the energy consumption was 5.775 kWh kg\(^{-1}\) of COD for 12 h with 92.16% COD removal, whereas 31.37% COD reduction was obtained at 1.0 A dm\(^{-2}\) with the energy consumption about 2.28 kWh kg\(^{-1}\) of COD. The maximum recovery of NaOH was found to be 210.28 g L\(^{-1}\) at 5.0 A dm\(^{-2}\) with an energy consumption of 3.176 kWh kg\(^{-1}\) of NaOH. When the cell was operated at the lower current density (1.0 A dm\(^{-2}\)), the energy consumption was 2.265 kWh kg\(^{-1}\) of NaOH; the recovery of NaOH decreased to 72.18 g L\(^{-1}\).

However, at 5 A dm\(^{-2}\) with the flow rate of 50 mL min\(^{-1}\), the overall specific energy consumption was observed to be
2.047 kWh kg⁻¹ of COD removal with simultaneous buildup of NaOH. That is, at 5 A dm⁻² with the flow rate of 50 mL min⁻¹ the power consumption of 5.775 kWh kg⁻¹ of COD removal was from 4080 to 320 mg L⁻¹ while at the same flow rate and current density, if the computation was done based on NaOH recovery the power consumption was 3.176 kWh kg⁻¹ for simultaneous buildup of NaOH from 50 to 210.28 g L⁻¹. The overall energy consumption of the process was found to increase with increasing current density as shown in Table 2.

3.6 Cost Estimation. The cost of treatment of the waste generation from chemical production significantly contributes to the total production cost. In this study a process is developed for removal of organic matter and the generation of some chemicals. This process involves simple operation and the ability to generate byproduct sodium hydroxide. At the same time environmental advantages are realized such as reduced emission of gaseous species and reduced disposal of liquid effluent during the process development.

At the present levels, the caustic soda price is around rupees (Rs.) 24 per kg (May 2007), while the cost of electric energy paid by the industry in Tamilnadu, India, is about Rs.4.00 per kWh. With the specific energy consumption for the caustic, recovery was 2.781 kWh/kg of NaOH. From the experimental results, 5 dm³ volume of effluent (92.16% COD reduction) energy consumption was obtained at 0.1082 kwh. Simultaneously, 200 mL of caustic soda (210 mg L⁻¹ NaOH) was also recovered. The average value of 5 m³ volume of effluent treatment gives roughly a treatment cost of Rs.433/-. The quantity of caustic soda recovered is around 34 kg, and the cost is Rs.816/-. Also, recovery of chlorine and hydrogen gas are not studied and presented. On an industrial scale, "treatment of dye bath effluent and simultaneous generation of sodium hydroxide using electrochemical membrane process" favors the economic balance of the process.

At the present levels, the caustic soda price is around rupees (Rs.) 24 per kg (May 2007), while the cost of electric energy paid by the industry in Tamilnadu, India, is about Rs.4.00 per kWh. With the specific energy consumption for the caustic, recovery was 2.781 kWh/kg of NaOH. From the experimental results, 5 dm³ volume of effluent (92.16% COD reduction) energy consumption was obtained at 0.1082 kwh. Simultaneously, 200 mL of caustic soda (210 mg L⁻¹ NaOH) was also recovered. The average value of 5 m³ volume of effluent treatment gives roughly a treatment cost of Rs.433/-. The quantity of caustic soda recovered is around 34 kg, and the cost is Rs.816/-. Also, recovery of chlorine and hydrogen gas are not studied and presented. On an industrial scale, "treatment of dye bath effluent and simultaneous generation of sodium hydroxide using electrochemical membrane process" favors the economic balance of the process. However, in this process there is a need for considerable capital investments. Then, besides the caustic recovery, significant savings in the purchase of chemicals used in the mercerization, dyeing, printing, and neutralization processes should be achieved, since most of the dyes are electrolytically destroyed, and additional savings due to the reduction of hazardous sludge handling and disposal costs is also accomplished.

4. Conclusion

In the present study an attempt was made to generation of sodium hydroxide as byproduct during degradation of dye effluent, using Ti/TiO₂–RuO₂–IrO₂ anode and stainless steel used as cathode. The experimental results showed that the electrochemical process could effectively remove color, reduce COD, and recover caustic soda from the dye effluent. The maximum COD reduction, color removal, and caustic recovery were 92.16%, 100%, and 210.28 g L⁻¹, respectively. The optimization of simultaneous recovery of caustic (~99% current efficiency) and COD removal (~66.67%) could be achieved at a current density of about 2.5 A dm⁻² during the electrolysis with minimum energy consumption.

In the present investigation completely degraded organic compounds, without formation of chlorinated intermediate compounds, were identified at high current density and increased electrolysis time. However, further investigation is necessary in order to identify lower molecular weight aliphatic compounds. Hence activated carbon polishing treatment is recommended for the removal of other aliphatic/organic compounds before the discharge of treated water.

The results of the study show that the electrochemical membrane process offers an interesting alternative economical method for the treatment of dye bath effluents.

Acknowledgment

We greatly acknowledge the Director, Central Electrochemical Research Institute, Karaikudi, India, for his constant encouragement. S.R. acknowledges Dr. Chellamani and Dr. S. Palaniyam, Scientist, OPMEC, Tuticorin, CECRI, for their helpful discussions.

Literature Cited


*Received for review May 13, 2007
Revised manuscript received May 14, 2008
Accepted May 14, 2008*

IE070675B
Evaluation of electrochemical oxidation techniques for degradation of dye effluents—A comparative approach

S. Raghu a,⁎, Chang Woo Lee b,⁎, S. Chellammal a, S. Palanichamy a, C. Ahmed Basha c

a Offshore Platform and Marine Electrochemistry Centre, Unit of Central Electrochemical Research Institute, Harbour area, Tuticorin-628 004, Tamilnadu, India
b Green Energy Center, Department of Chemical Engineering, Kyung Hee University, 1 Seochun, Gihung, Yongin, Gyeonggi 446-701, South Korea
c Central Electrochemical Research Institute, Karaikudi-630 006, Tamilnadu, India

ARTICLE INFO
Article history:
Received 15 January 2009
Received in revised form 16 April 2009
Accepted 14 June 2009
Available online 21 June 2009

Keywords:
Electro-oxidation
Dye effluent
Wastewater
Colour removal
Electrochemical degradation

ABSTRACT

The high energy cost of an electrochemical method is the fatal drawback that hinders its large scale application in wastewater treatment. The traditional single-chamber electrochemical method used in the waste water treatment mainly focused on anodic oxidation, but hydrogen produced on the cathode and indirect electrochemical treatment involves application of an electrical current to the wastewater containing chloride to convert into chlorine/hypochlorite. The two-compartment electrolytic cell, separated by an anion exchange membrane, has been developed in this work. In the new reactor, indirect oxidation at anode, indirect oxidation by hydrogen peroxide and ultraviolet/hydrogen peroxide (UV/H2O2) at cathode can occur simultaneously. The electrochemically produced hydrogen peroxide at the cathode by reduction of oxygen is affected by passing atmospheric air. Therefore "dual electrochemical oxidation" in one electrochemical reactor was achieved successfully. Compared to a traditional one-cell reactor, this reactor reduces the energy cost approximately by 25-40%, and thus the present work becomes significant in wastewater treatment. Experiments were carried out at different current densities using Ti/RuO2/IrO2 as anode and carbon felt gas diffusion electrode used as a cathode fed with oxygen containing gases to produce hydrogen peroxide. During the various stages of electrolysis, the parameters such as, effect of pH, chemical oxygen demand (COD), colour, energy consumption were monitored. UV-vis spectrometry, Fourier transform infrared spectroscopy (FTIR), high-performance liquid chromatography (HPLC) studies were carried out to assess efficiencies of dye degradation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Textile wastewaters from dyeing and finishing processes in the textile industry have been a serious environmental problem for years. Carcinogenic products such as aromatic amines due to the large consumption of azo dyes in the dyeing processes contain considerably strong colour, a broad range of pH varying from 2 to 12, high chemical oxygen demand (COD) concentration and suspended particles, and low biodegradability [1-4]. These are usually treated by conventional methods such as biological oxidation, chemical coagulation and activated carbon adsorption [5,6].

Biological methods cannot be applied to most textile wastewaters due to the toxicity of most commercial dyes to the organisms used in the process [7]. Chemical coagulation is not effective for the removal of dissolved reactive dyestuffs [8]. Activated carbon adsorption has the associated cost and difficulty of the regeneration process and a high waste disposal cost. Advanced oxidation processes such as ozonation, UV and ozone/UV combined oxidation, photocatalysis (UV/TiO2), Fenton reactive and ultrasonic oxidation are not economically feasible [9,10].

Many investigators are studying alternative oxidation methods like ozonation, photo catalytic oxidation, electrochemical oxidation, etc. The photo catalytic oxidation experiments were conducted for Acid Blue 80 [11], Acid Orange 7 [12], Brilliant Orange K-R [13] and Reactive Orange 16 [14]. The electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye [15]. Ozonation process was studied for the removal of colour and COD [16], however; this process showed less COD removal [17]. Researchers also investigated electro-coagulation methods for textile dye removal using aluminum [18] or iron [19,20] electrodes.

Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium based DSA electrodes.
TEXTILE TECHNOLOGY

An Overview of Wastes Produced During Cotton Textile Processing and Effluent Treatment Methods

B. Ramesh Babu*, A.K. Parande, S. Raghu, and T. Prem Kumar

ABSTRACT

This review discusses cotton textile processing and methods of treating effluent in the textile industry. Several countries, including India, have introduced strict ecological standards for textile industries. With more stringent controls expected in the future, it is essential that control measures be implemented to minimize effluent problems. Industrial textile processing comprises pretreatment, dyeing, printing, and finishing operations. These production processes not only consume large amounts of energy and water, but they also produce substantial waste products. The manuscript combines a discussion of textile processes, such as desizing, mercerizing, bleaching, dyeing, finishing, and printing, with a discussion of advanced methods of effluent treatment, such as electro-oxidation, bio-treatment, photochemical, and membrane processes.

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment. The toxic effects of dyestuffs and other organic compounds, as well as acidic and alkaline contaminants, from industrial establishments on the general public are widely accepted. Increasing public concern about environmental issues has led to closure of several small-scale industries.

Interest in ecologically friendly, wet-processing textile techniques has increased in recent years because of increased awareness of environmental issues throughout the world. Consumers in developed countries are demanding biodegradable and ecologically friendly textiles (Chavan, 2001). Cotton provides an ecologically friendly textile, but more than 50% of its production volume is dyed with reactive dyes. Unfortunately, dyes are unfavorable from an ecological point of view, because the effluents generated are heavily colored, contain high concentrations of salts, and exhibit high biological oxygen demand/chemical oxygen demand (BOD/COD) values.

In dyeing textiles, ecological standards are strictly applied throughout processing from raw material selection to the final product. This has become more critical since the German environmental standards regarding dye effluents became effective (Robinson et al., 1997). The main challenge for the textile industry today is to modify production methods, so they more ecologically friendly at a competitive price by using safer dyes and chemicals and by reducing cost of effluent treatment/disposal. Recycling has become a necessary element, not because of the shortage of any item, but because of the need to control pollution. There are three ways to reduce pollution: (1) use of new, less polluting technologies; (2) effective treatment of effluent so that it conforms to specified discharge requirements; and (3) recycling waste several times over before discharge (Sule and Bardhan, 1999), which is considered the most practical solution.

The objective of this review is to discuss the various processing stages in the textile industry and the methodologies adopted for treating textile wastewater. A variety of water treatment techniques (Table 1) are discussed from an environmental point of view. Conventional and novel techniques discussed include electro-oxidation, biological treatment, photochemical processing, ion-exchange, and a variety of membrane techniques.

TEXTILE OPERATIONS

The textile industry comprises a diverse and fragmented group of establishments that produce and/or process textile-related products (fiber, yarn, and fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establish-
Nanoparticulate platinum films on gold using dendrimer-based wet chemical method

S RAGHU, SHEELA BERCHMANS, K L N PHANI and V YEGNARAMAN
Central Electrochemical Research Institute, Karaikudi 630 006, India
E-mail: kanalaphani@yahoo.com

Abstract. There is a growing interest in devising wet chemical alternatives for physical deposition methods for applications involving thin films, e.g., catalysis. Deposition of platinum on thin gold films is often a problem leading to incomplete coverage and improper adhesion to solid surfaces. Gold substrates often need pre-activation for achieving complete coverage. We demonstrate here that dendrimers with proper functionalities and size work as well-defined nucleating agents and adhesion promoters. This feature is demonstrated using an amine-terminated dendrimer of generation 4.0. This approach allows one to obtain adherent nanoparticulate films of platinum on gold. Unlike other nucleating agents and adhesion promoting compounds, dendrimers have a well-defined ordered structure in terms of their space filling ability.

The stability of the films obtained with adsorbed dendrimers is demonstrated using the electrocatalytic reactions of fuels like methanol. The films formed without dendrimers cannot sustain the electro-oxidation currents due to the instability of the films while the films formed with dendrimers can sustain currents for longer duration and for several cycles. The dendrimer-derived Pt films exhibit higher catalytic activity compared to other methods.

Keywords. Nanoparticulate films; platinum; electrocatalysis; adhesion promoters; PAMAM dendrimers.

PACS Nos 82.45.Fk; 82.45.Mp; 82.35.Np; 68.37.Ps

1. Introduction

Highly dispersed high surface area catalysts are used in many catalytic and electrocatalytic processes and are very important for heterogeneous catalysis and fuel cell applications. In majority of fuel cells, the catalysts used are platinum and platinum alloy colloidal particles that are either supported or unsupported [1-3]. Various support materials have been explored for the preparation of platinum-based catalysts [4-6]. Recently, there has been growing interest in devising wet chemical alternatives for physical deposition methods for applications involving thin films. Deposition of platinum on thin gold films is often a challenging problem leading to incomplete coverage and improper adhesion. Such films often pose problems in obtaining sustained current in devices such as fuel cell membrane–electrode assemblies due to peeling-off of the catalyst films. In this work, we have explored the use
The formation of electrocatalytically active thin films of Pt on a denrimer adhesion layer self-assembled on gold substrates is described in this work.
Platinum–Dendrimer Nanocomposite Films on Gold Surfaces for Electrocatalysis

S. Raghu • R. G. Nirmal • J. Mathiyarasu • Sheela Berchmans • K. L. N. Phani • V. Yegnaraman

Received: 15 May 2007 / Accepted: 3 June 2007 © Springer Science+Business Media, LLC 2007

Abstract In this communication, we report a strategy for the preparation of Pt nanoparticles encapsulated in Generation 4.5 (Polyamido amine) PAMAM dendrimer and subsequent chemical linking of the nanocomposite to the gold electrode through a self assembled cystamine monolayer. The modification resulted in the formation of a robust electrochemically active thin film with very high surface area, reflected by the enhanced hydrogen adsorption coverage. Interestingly, TEM images revealed self-assembly of Pt nanoparticles and the SAED (Selected Area Electron Diffraction) patterns showed the presence of Pt single crystals (111). The Pt-dendrimer nanocomposite film obtained using the novel modification procedure exhibited high electrocatalytic activity for the oxidation of organic fuels like methanol, ethanol and ethylene glycol. The film did not suffer from degradation even after repeated use in solution-phase voltammetry. It is however observed that the intermediate SAM layer and the bulky PAMAM dendrimer (generation 4.5) have slowed down the electron transfer kinetics which is reflected by a relatively high overpotential for methanol oxidation. Nevertheless this shortcoming is more than compensated by the existence of Pt(111) planes, which alleviate CO poisoning.

Keywords Dendrimers • Platinum–dendrimer nanocomposite • Electrocatalysts • Self-assembly • Cystamine • Template synthesis

1 Introduction

Recently, synthesis of nanostructured materials with high surface area has received significant interest since these materials possess unique properties and lend themselves to a number of impressive applications in catalysis, fuel cells and chemical sensors [1–5]. Nanostructured Pt materials have excellent catalytic properties and preparation of electrocatalysts incorporating these materials is a contemporary and challenging task. In this communication, we report the synthesis of high surface area Pt nanoparticles encapsulated by dendrimers and a novel strategy for linking the dendrimers to the electrode surface to yield robust, electrocatalysts.

Dendrimers are outstanding candidates for template synthesis of nanoparticles because of their regular structure and chemical versatility [6]. The terminal functional groups serve as handles to facilitate surface immobilization. Dendrimer-encapsulated nanoparticles can be nearly monodisperse. Though they are passive against aggregation, major part of the surface is free for them to be catalytically active [7–13]. The synthesis and characterization of dendrimer-encapsulated monometallic Pd and Pt clusters and their use as catalysts for hydrogenation, oxygen reduction and Heck coupling reaction have been reported [6]. Recently, dendrimer-encapsulated Pd–Pt catalyst was found to exhibit a cooperative effect, which is attributed to the presence of bimetallic nanoparticles [14–17]. Core-shell bimetallic nanoparticles are interesting models for the formation of alloys at angstrom scale. In all these cases, hydroxyl and amine terminated dendrimers were employed. In view of their functional advantages, dendrimer molecules, mostly utilized for solution-phase reactions, offer themselves as apt candidates for immobilization on electrode surfaces to yield enhanced electroactivity.