CHAPTER-2

ELECTRO CHEMICAL TREATMENT OF PROCIION BLACK-5B USING CYLINDRICAL FLOW REACTOR- A PILOT PLANT STUDY

2.1.0 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-bio-degradable. 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
method using Ti/RuO$_2$ 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 working at temperature from 60$^\circ$C to 80$^\circ$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 is used as the electrolyte. In this paper the synthetic effluent was prepared from Procion Black-5B (a commercial Reactive Black 5B dye) and NaCl was used as supporting electrolyte. During the electrolysis on a continuous single pass process, COD reduction, colour removal, energy consumption and mass transfer coefficient were investigated on selected electrolyte medium under different flow rates and current densities.

2.2.0 THEORETICAL APPROACH

Most of the dye effluents contain NaCl as the major constituent. The method of treating of such solutions electrochemically is clean and easy, as they involve no addition of chemicals for supporting the electrolysis in the most of the cases. In the present study, the effluent contains 4600mg/l sodium chloride, which can be used as a supporting electrolyte. The electro chemical reactions that take place during the electrolysis are complicated 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 \[ 2\text{Cl}^- \xrightarrow{k_1} \text{Cl}_2 + 2\text{e}^- \] (2.1)

Side Reaction \[ 4\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \] (2.2)

At Cathode

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \] (2.3)

In bulk of solution

\[ \text{Cl}_2 + \text{H}_2\text{O} \xrightarrow{k_2} \text{H}^+ + \text{Cl}^- + \text{HOCl} \] (2.4)

\[ \text{HOCl} \xleftrightarrow[k_3']{k_3} \text{H}^+ + \text{OCl}^- \] (2.5)

\[ \text{Dye} + \text{OCl}^- \xrightarrow{k_4} \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- + \text{P} \] (2.6)

Since dye molecules of the effluent are electrochemically inactive, the primary reaction occurs at the anodes is chloride ion oxidation (equation 2.1) with the liberation of Cl$_2$, which is a robust oxidizing agent. As the dye effluent is generally basic or neutral condition in which case the side reaction (equation 2.2) takes place generating oxygen which is relatively weak oxidant and hence not useful in the present context of effluent treatment and this leads to reduction of current efficiency. The counter reaction (equation 2.3) 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 Cl$_2$ dissolves in the aqueous solutions due to ionization as indicated in equation 2.4. The rate of reaction is less in acidic solution due to OH$^-$ instability and considerably more in basic solution due to ready formation of OCl$^-$ (pK$_a$ 7.44) ion in equation 2.5 implying that the basic or neutral pH conditions are more favourable for conducting reactions involving Cl$_2$ [14].

28
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

\[
-r_{\text{Cl}_2} = k_2[\text{Cl}_2] 
\]

\[
r_{\text{HOCl}} = k_2[\text{Cl}_2]-k_3[\text{HOCl}]+k_3'[^H][\text{OCl}^-] = 0 
\]

\[
r_{\text{OCl}^-} = k_3[\text{HOCl}]- k_3'[^H][\text{OCl}^-]- k_4[\text{Dye}][\text{OCl}^-] = 0
\]

\[
-r_{\text{Dye}}= k_4 [\text{Dye}][\text{OCl}^-] 
\]

By using equations 2.8 and 2.9 one can easily deduces the following expression:

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

Finally as regard to bulk solution it is also to be noted that \(-r_{\text{Cl}_2} = r_{\text{Cl}^-}\) from material balance of equation 2.4, that is

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

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 equation 2.1 can be written as.

\[
-r_{\text{Cl}^-} = r_{\text{Cl}_2} = k_1 [\text{Cl}^-].
\]

where \( k_1 \) is heterogeneous electro chemical rate constant. Hence, in the following section an attempt has been made to establish a relation between the reacting species in bulk and
at the electrode surfaces. The basic relationship applicable to all electro chemical 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 electro chemical reaction rate (for the disappearance of reactant A) can be expressed as

$$-(V_R/A_e)\frac{d[A]}{dt} = i_A/nF$$  \hspace{1cm} (2.14)

where $I_A$ is the current passed in time t, $M_A$ is the molecular weight, n is the number of electrons transferred per mole of reaction, $A_e$ electrode area, $V_R$ reactor volume and $F$ is the Faraday (96,500 Coulomb or As/mol). It has to be noted $-r_A = -\frac{d[A]}{dt} = i_A a /nF$

where a is specific electrode area ($A_e/V_R$). Assuming the main electrode reaction is governed by a simple Tafel type expression, then

$$-(V_R/A_e)\frac{d[A]}{dt} = i_A/zF = k'[A]\exp(bE)$$  \hspace{1cm} (2.15)

or $-r'_{CI} = r'_{CI2} = k_1[CI'] = k_1 a[CI']\exp(bE)$  \hspace{1cm} (2.16)

The reaction may be assumed to be under diffusion control as the reacting species, Cl' in the electrolyte is dilute. The reactant CI is transported for the bulk to electrode surface where it under goes electro chemical oxidation to CI2 and it may be transported back to bulk by diffusion reaction in the bulk. Then,

$$i_A/zF = k_L ([CI] - [CI']_s)$$  \hspace{1cm} (2.17)

Elimination of $[CI']_s$ using equation 16 and 17 results as

$$i_A/zF = k_1 [CI']$$  \hspace{1cm} (2.18)

Where $1/k_1 = 1/k_L + 1/k'a \exp(bE)$  \hspace{1cm} (2.19)

From a material balance of species CI' by taking note of equation 2.12 and 2.13 we can write
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

\[
i_{\text{A}} / zF = k_{\text{obs}} [\text{Dye}] \tag{2.22}
\]

In electro chemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electro chemical combustion the organics are completely oxidized to \(\text{CO}_2\) and \(\text{H}_2\text{O}\). 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 Figure-1, Figure-2 shows a generalized scheme of the electro chemical conversion/combustion of organics on noble oxide coated catalytic anode (MO_x). In the first step, \(\text{H}_2\text{O}\) is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction.

\[
\text{MO}_x + \text{H}_2\text{O} \rightarrow \text{MO}_x(\cdot\text{OH}) + \text{H}^+ + e^- \tag{2.23}
\]

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 \(\text{MO}_{x+1}\).

\[
\text{MO}_x(\cdot\text{OH}) \rightarrow \text{MO}_{x+1} + \text{H}^+ + e^- \tag{2.24}
\]

At the anode surface the "active oxygen" can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals, \((\cdot\text{OH})\) or /and as chemisorbed (oxygen in the lattice, \(\text{MO}_{x+1}\)). In the absence of any oxidizable organics, the "active oxygen" produces dioxygen according to the following reactions:
When NaCl is used as supporting electrolyte Cl ion may react with MOₓ(*OH) to form adsorbed OCl radicals according to the following:

\[ \text{MO}_x(*\text{OH}) + \text{Cl}^- \rightarrow \text{MO}_x(*\text{OCl}) + \text{H}^+ + 2e^- \]  \hspace{1cm} (2.27)

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 MOₓ₊₁ according to the following reaction and also MOₓ(*OCl) simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

\[ \text{MO}_x(*\text{OCl}) + \text{Cl}^- \rightarrow \text{MO}_{x+1} + \text{Cl}_2 + e^- \]  \hspace{1cm} (2.28)

\[ \text{MO}_x(*\text{OCl}) + \text{Cl}^- \rightarrow \text{MO}_x + \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{Cl}_2 + e^- \]  \hspace{1cm} (2.29)

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:

\[ \frac{1}{2} \text{R} + \text{MO}_x (\cdot\text{OH}) \longrightarrow \frac{1}{2} \text{ROO} + \text{H}^+ + e^- + \text{MO}_x \]  \hspace{1cm} (2.30)

\[ \text{R} + \text{MO}_{x+1} \longrightarrow \text{RO} + \text{MO}_x \]  \hspace{1cm} (2.31)

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: RH + ‘OH → R· + H₂O; (2) Reaction of organic radical with dioxygen formed
at the anode: $R' + O_2 \rightarrow ROO'$ and (3) Further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; $ROO' + R'H \rightarrow ROOH + R'$. 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 electro chemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment [20-21]. It has been already described in detail the role of chlorine in electro chemical treatment of dye effluent via hypochlorite generation in the beginning of this section.
Fig -2.1

Scheme of the reactions and processes involved in the dye oxidation
Scheme of electro chemical oxidation of organic pollutants in presence of chloride ion.

Fig -2.2
Now let us consider the reactor, since the electro chemical 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 electro chemical flow reactor can be considered as Plug Flow Reactor (PFR) and the material balance equation for PFR is given by

$$U \frac{d[Dye]}{dx} + (-r_{Dye}) = 0 \quad (2.32)$$

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

$$[Dye]_x = [Dye]_0 \exp (-k_{obs}a \frac{x}{U}) \quad (2.33)$$

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.

Dye + (O) → Colourless Intermediates + (O) → CO₂ + H₂O \quad (2.34)

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

$$[COD]_L = [COD]_0 \exp (-k_{obs}aL/U) \quad (2.35)$$
\[ \text{[L]} = \text{[L]}_0 \exp(-k'_\text{obs}aL/U) \]  

(2.36)

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

2.3.0 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-2.3 and the characteristics of effluent before and after treatment (current density-2A/dm\(^2\) and 10liter per hour) is presented in Table-1.
Fig -2.3

Molecular Structure of Procion Black-5B
Table-2.1
Characteristics of the mixed effluent (Initial COD - 1264ppm, $\lambda_{Max}$ - 575Nm)

<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 10 lph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.6</td>
<td>13.6</td>
</tr>
<tr>
<td>COD (mg/litre)</td>
<td>1264</td>
<td>328</td>
</tr>
<tr>
<td>T.S.S (mg/litre)</td>
<td>460</td>
<td>240</td>
</tr>
<tr>
<td>T.D.S (mg/litre)</td>
<td>9600</td>
<td>9280</td>
</tr>
<tr>
<td>Chloride (mg/litre)</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>20505 CI Reactive Black 5B</td>
<td>---</td>
</tr>
</tbody>
</table>
2.3.1 Analytical measurements

The analytical methods of the COD of all samples were determined by the dichromate reflux method [22]. In electro chemical 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 concentration of sodium hydroxide was determined by titration with HCl using phenolphthalein as indicator. The oxidized products and the reduction in dye concentration were measured by using a UV-vis- Spectrophotometer (Systronics 118), the colour removal was calculated by following formulae:

\[
\% \text{ colour removal} = 100 \frac{\text{ABS}_o^M - \text{ABS}_0^M}{\text{ABS}_0^M} \quad 2.37
\]

where \(\text{ABS}_0^M\) is the average of absorbance values as it is maximum absorbency visible wavelength. \(\text{ABS}_0^M\) the value before electrolysis, \(\text{ABS}^M\) the value after electrolysis.

2.3.2 Cyclic voltammetry analysis

Cyclic Voltammetry analyses were carried out by Potentioscan (Wenking model POS 88) and X-Y/t recorder (Rikadenki model RW-201t). The simulated dye wastewater containing Procion Black-5B (of different concentration in the range 10-40 mg/l in different electrolyte medium HCl, H₂SO₄, Na₂SO₄, NaCl, and KOH.) was prepared and 10ml of wastewater was taken in a three-electrode electro chemical cell. The working electrode for the controlled potential was a platinum foil having the surface area of 1 cm² and the reference electrode was saturated calomel electrode and the counter electrode was a platinum wire. The electrodes were immersed in a Procion Black-5B dye solution. Cyclic Voltammetry (CV) scans were taken in the direction of decreasing potential.
starting from 0.7V to -0.8V and at a scan rate of 50mV/s. The cyclic voltammetry studies were used to find out the medium (and its optimum conditions) in which the effective indirect oxidation of dye takes place. Hence readily available Pt electrode was used for the experiments and CV was studied in different electrolyte medium such as HCl, H2SO4, Na2SO4, NaCl and KOH.

2.3.3 High performance liquid chromatography (HPLC)

Procion Black-5B and its degradation products were also carried out on a high-performance liquid chromatograph(HPLC), consisting of a Waters model 501 pump (flow rate 0.5-1.0 mL/min), Rheodyne injector containing a 20 μL sample loop, and Waters model 440UVabsorbance detector operated at 254 nm. The detector output was processed with peak simple software. Separation was achieved on a reverse phase C18 (25 cm x 4.6 mm) stainless steel column, using 40:60 to 70:30 (v/v) methanol: sodium phosphate buffer (pH 2) as the mobile phase. All solvents used were fisher scientific HPLC grade.

2.3.4 Electrolytic cylindrical flow cell

A schematic diagram of the experimental setup is shown in Fig 2.4. The electrolytic flow reactor consisted of the cathode, which was a stainless steel pipe of 110cm height and 7cm diameter, and the catalytic anode, made of Ti/RuO2 coated expanded mesh cylinder, measuring 100cm long and 5cm diameter which was held axially inside the cathode such that 1cm as inter-electrode distance. Provisions were made for electrical connections so as to constitute an electrolytic cell. The capacity of the cell is 4.5 liters. Additionally, the cell has one inlet at the bottom cover and one outlet at
the top cover. It is connected to 100A and 50V DC regulated power supply. Reservoir, pump, flow meter and electrolytic flow recter are connected using silicone rubber tubes.

2.3.5 Experimental procedure

The effluents were taken in the reservoir, which was passed to the cell. The flow rate was measured and adjusted by Rota meter. 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 viz. 1, 1.5, 2 and 2.5 A/dm². For each current density the experiment was repeated with different flow rates of effluent to the reactor 10, 20, 30, 40 lph (liter per hour).
**EXPERIMENTAL SETUP OF FLOW CELL:**

1. Reservoir  
2. Pump  
3. Rotameter meter  
4. Electrolytic Cell  
5. Voltmeter  
6. Ammeter  
7. D.C. Power Supply (100A, 0-50V)  
8. Treated effluent  
9. Ti/RuO$_2$ coated expanded mesh cylinder Anode  
10. Stainless Steel Cathode  
11 and 12 Valves.
2.4.0 RESULTS AND DISCUSSION

This chapter deals with the theoretical approach for the electro chemical oxidation of organic pollutants in presence of chloride ion, Scheme of the reactions and processes involved in the dye oxidation, 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 2.5. The following data such as specific power consumption, mass flux and mass transfer coefficient, computed for various flow rate and current densities are given in the Table-2.2. The COD reduction and colour removal efficiencies are shown in fig 2.6 & 2.7. The FTIR, HPLC and UV-VIS spectra obtained for the outlet samples are given in the figure 2.8, 2.9, 2.10&2.11. All the above studies were carried out under ambient conditions.

2.4.1 Cyclic voltammetry studies

To understand the electro chemical behaviour of the electrolytic medium, cyclic voltammetry (CV) studies were carried out. To know the actual behaviour of the real effluent it is always better to resort to studying 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 2.5. In case of KOH, Fig (2.5.1) the reduction of
Procion Black-5B occurs at -0.57V and in Fig (2.5.2) in respect of Na₂SO₄ electrolytes; the reduction peak appears at -0.21V and -0.72V. 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 at -0.04V in Fig 2.5.4 appears even in the volammogram for the background electrolyte [curve (a)]. With increase in addition of Procion Balck-5B current increase is insignificant. This suggests that the electro chemical oxidation of dyes is not favorable in these media. Similar observation is made in Fig-2.5.5. The curve (a) shows an anodic peak around -0.4V, which is due to background electrolyte. Addition of dye was examined at various dye concentration from 10 to 40 ppm, which causes peak current increase to a small extent, compared to Fig 2.5.4. In NaCl (Figure-2.5.3) electrolyte medium the redox behavior of Procion Black-5B occurs at cathodic peak -0.57V and at anodic -0.14 V. A reversible electro chemical process for Procion Black-5B is observed in NaCl. In the entire cases (Fig- 2.5.3, 2.5.4 and 2.5.5) peak currents increased, which would have aided in the removal of colour and COD. In all the electrolytes, it was observed, that Procion Black-5B did not give any separate electro chemical response or it did not get oxidized directly on the electrode surface in all the electrolytes. The background electrolyte gives a peak on the anodic side in the case of Fig-2.5.3, 2.5.4 and 2.5.5. The dye undergoes oxidation at the peak potential of background response, which indicates that the dye is indirectly oxidized by some reactive species in the background electrolyte. This suggests that the oxidation of Procion Black-5B occurs by indirect oxidation by hydroxyl or other oxidant reagent electro generated from the electrolyte (mainly ClO⁻ ions in NaCl), among all the results, the redox behavior of Procion Black-5B in NaCl was good when compared to other electrolytes.
Cyclic Voltammogram (50mVs\(^{-1}\)) studies for Procion Black-5 B dye under different electrolytic conditions: 1. KOH (0.1M) medium, 2. Na\(_2\)SO\(_4\) (0.1M) medium, 3. NaCl (0.1M) medium, 4. HCl (0.01M) medium, 5. H\(_2\)SO\(_4\) (0.01M) medium with increased concentrations of a) Background of the electrolyte b) 10 ppm, c) 20 ppm, d) 30 ppm, e) 40 ppm respectively
2.4.2 Effect of COD and Colour removal

The extents of COD removal at different reaction times under various conditions are shown in Fig-2.6. 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-2.1) that higher COD reduction occurred at higher charge input and electrolysis (residence time) 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 and hence the COD reduction is more. At 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 lph to 40 lph led to gradual decrease in the COD removal; at 40 lph it was 20% less than that at 10 lph because the residence time of the effluent at 10 lph was 4 times higher than that at 40 lph. The maximum possible COD reduction was 74.05% at 10 lph and 2.5A/dm².
Effect of COD reduction on flow rate at different current densities

---♦--- 1A/dm², ---□--- 1.5A/dm², ---▲--- 2A/dm², ---✗--- 2.5A/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 (575nm) and expressed in terms of percentage. These results are shown in Fig-2.7. The maximum colour removal (99.83%) was obtained at 10lph and 2.5A/dm². At high flow rates (40lph) and lower current density (1A/dm²) the colour reduction was found to be low (86%).
Fig-2.7

Efficiency of colour removal on flow rate at different current densities,

---♦--- 1A/dm², ---■--- 1.5A/dm², ---▲--- 2A/dm², ---×--- 2.5A/dm²
2.4.3 IR-Spectral studies

Figure 2.8 shows the IR spectra of the dried solution residue before and after the electro chemical treatment. It can be seen that some structural changes might have occurred during the electro chemical process. The appearance of peak at 1634 cm$^{-1}$ indicates the presence of C=C conjugated diene group. The other peak at 1385 cm$^{-1}$ indicates the presence of CH def for CH$_3$. After electrolysis, there are two peaks appeared at 1003.6 cm$^{-1}$ and 624.64 cm$^{-1}$, while peaks at 1634.41 cm$^{-1}$, 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$_3^-$, which may generally be present 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 that the organic compounds have been degraded completely and resulted in the formation of chlorinated organics.
Fig-2.8

Changes of infrared absorption bands of untreated (A) and treated (B) dye effluent, (operating condition: current density 2.5A/dm² at 10 lph).
2.4.4 High performance liquid chromatography (HPLC):

The dye effluents were extracted before and after electrolysis using ether and allowed to complete dryness at room temperature. Then the residues were dissolved in small volume of HPLC-grade methanol for HPLC analysis. Figure 2.9 shows, the initial dye and different time intervals of electro chemical treatment of Procion Black-5B. No product information (Procion Black-5B) was available from the HPLC determination of the electrolyzed solutions for different hours. From the figure 2.9(a), indicates the two peaks at 2.6min and 3.2min with 4.8V and 1.3V respectively. When an increase the electrolysis time for 4 hours, both peaks, areas were shifted 3.3 and 3.9min with decreased 0V and 1.6V respectively. Figure 2.9 (b), indicates the existence of very small amount of parent dye and correspondingly lowers carbon atom number than the original dye molecule present after 4 hours. Since chemical reduction of azo linkage commonly results in the formation of lower molecular weight of aromatic amine entities and products the parallel elimination of colour in the reduced solution of the dyes. But In the case of FTIR studies, very low concentration of chlorinated organic compound formation takes place at low residence time. Hence studied to increase the electrolysis time was increased. Figure 2.9(c, d) represents, the increase the electrolysis time for 8 and 12 hours, no peaks were observed. From the results indicates the completely degradation of organic compounds and without formation of chlorinated organics compounds for long time of electrolysis. From the Figures 2.9, it’s clear from to increase the time of electrolysis completely degradation of dye takes place.

53
The HPLC chromatograms of Procion Black-5B are presented in Figures 2.9. (a) Procion Black-5B dye effluent and Treated effluent for (b) 4 hours, (c) 8 hours, (d) 12 hours at 2A/dm².
2.4.5 UV-VIS Spectrophotometer studies

The changes in absorbance characteristics of dye effluent were investigated over a large wavelength interval during the electro chemical decolourization process and the results are shown in Figure 2.10. The spectra show 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. In the UV region which become at 391 nm peak was disappeared and 310 nm peaks shifted to 291 nm as the electrolysis progresses. This result shows the cleavage of azoic group and total discolouration 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 is not completely achieved. This peak can be attributed to carboxylic acids accumulated at the final stage of the oxidation. This represents the residual COD present in the effluent. It is clear from Figure 2.10 that the electro chemical oxidation process has effectively reduced the colour of the dye effluent.
Fig-2.10

UV-VIS Spectra of untreated dye effluent (A) and treated effluent (B),
(operating condition: current density 2.5A/dm² at 10 lph).
2.4.6 Effect of flow rate and current density

To elucidate the effect of current density on power consumption, the current was varied from 1A/dm² to 2.5A/dm². The values given in Table-2.2. Show that increase in the flow rate reduced the power consumption of the process. This is attributable to the preferential oxidation of easily oxidizable materials. At 1A/ dm², the power consumption at of 0.2480kWh/kg of COD was found to be lower at 40 lph and the power consumption of 2.8190kWh/kg of COD was found to be highest at 10 lph. Increase in the current density increased the power consumption. This is evident from the values given in Table-2.2. At 1A/ dm², flow rate of 10 lph, the power consumption was found to be 2.8190 kWh/kg of COD. At 2A/dm², at same flow rate the power consumption was increased to 11.5340 kWh/kg of COD.

Table-2.2 shows that mass flux of the system decreases linearly with the decrease in flow rate. At 2.5 Ams/ dm², the mass flux was found to be 0.1656 g COD/hr. dm² at flow rate of 10 lph and mass flux of 0.5379 g COD/hr. dm² at flow rate of 40 lph. 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 was directly proportional to the mass flux. At current density of 1Ams/dm² and flow rate of 10 lph, the mass flux was 0.1256 g COD/hr.dm², but high current density (2.5Ams/ dm²) and same flow rate mass flux was increased to 0.1656 g COD/hr. dm².

Table-2.2 shows that the mass transfer coefficient increases with increase in flow rate as well as increase in current density. Mass transfer coefficient versus flow rate under various current densities. The mass transfer coefficient 0.0081339cm/s was found to be high in the case of 40 lph and 2.5A/dm². The mass transfer coefficient of the
process was inversely proportional 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 2.5A/dm² was 0.0081339cm/sec and 1Ams/dm² was 0.0045940cm/sec at 40lph. Hence to degrade Procion Black-5B having the initial absorbency and COD values are 30.6 and 1264mg/l. It has to electrolyze in order to bring down below 250mg/l to meet out the discharge standards. At 1A/dm² and 10 lph, the final absorbency and COD values were 0.981 and 544mg/l (96.99% and 56.92% reduction) and 2.5Am/dm² in 10lph charge to bring down the absorbency and COD value were 0.052 and 328mg/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 efficiency at same charge loading was independent upon the value of current density in a direct electro chemical oxidation treatment process. Here the result shows that current density strongly influences the rate of reaction.

At the present levels, mixed dye effluent chemical treatment cost is around Rs.15-20 per m³ volume of the effluent. In electro chemical process, 60-70% COD reduction and 100% of colour removal was obtained at the energy consumption of 4kWh to 6kWh per m³ volume of the effluent. The cost of electric energy paid by the industry in Tamilnadu is about Rs 4.00 per kWh. It gives roughly a treatment cost of Rs .24/- (6kWh). In this method, treatment cost is slightly higher. But, most of the dyes are electrolytically destroyed, and an additional savings due to the reduction of hazardous sludge handling and disposal costs.
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<th>Voltage (V)</th>
<th>Residence time (h)</th>
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<th>Power consumption (kWh/gCOD)</th>
<th>Mass Flux (gCOD/h.dm²)</th>
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2.5.0 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. Wastewater treatment using physico-chemical method produces more sludge, involving high cost and lower efficiency. In biological treatments the process takes longer time and gives lower efficiency. Hence the electro chemical treatment is best suited for treating the dye house effluent. In the present study, results showed 74.05% COD reduction and colour removal was nearly 100% at 2.5 A/dm² for flow rate of 10 lph. The flow rate of effluent in to the reactor was 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. For the industrial application, flow cell method can be recommended with two or more reactors in series at a current density of 1A/dm²-2.5Ams/dm².
2.6.0 REFERENCES


