CHAPTER II
EXPERIMENTAL SETUP
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2. 1. Electroanalytical investigations

2. 1. 1. Instrumentation

A Potentiostat / Galvanostat (Princeton, NJ, USA) controlled by M270 software from EG&G Princeton Applied Research model 273A was employed for the electrochemical studies. This instrument uses the latest analog and microcomputer design to provide high performance, better precision and greater versatility in electrochemical measurements. Other than voltammetric studies, techniques like chronocoulometry, controlled potential coulometry and bulk electrolysis were also employed using this instrument. The photograph of the instrument is shown in figure 2.1.

2. 1. 2. Cell setup

The cell, made of glass, having a capacity of 15ml and the cell top made from teflon, comprises three separate holes for the insertion of electrodes viz. working electrode, counter electrode and reference electrode. The cell setup is kept in a Faraday cage of EG&G PARC model 325. Separate holes are provided in the cell top for purging and blanketing the nitrogen gas. These functions controlled through 270 software are to remove oxygen gas and to maintain an inert atmosphere above the sample solution.
2.1.3. Electrodes

Two kinds of working electrodes, wax impregnated graphite electrode (WIGRE) of 0.1257 cm\(^2\) area and glassy carbon electrode (milli electrode of EG&G PARC model) of 0.0314 cm\(^2\) area were used throughout the voltammetric studies of the dyes.

2.1.3.1. Fabrication of wax impregnated graphite electrode (WIGRE)

The commercially available graphite rod was first rubbed with emery sheet to remove the impurities present on the surface and then suspended in 1:1 HCl for about 12 hours. Then it was washed with double distilled water and dried. The dried graphite rod was immersed in boiling paraffin wax for 5 hours and cooled. Then the graphite rod was taken out and the surface of the rod was made smooth using fine emery sheet. One-centimeter long graphite rod was cut and it was fused in a glass tube. Small amount of distilled mercury was poured into the tube for electrical contact.

2.1.3.2. Pretreatment of Glassy carbon electrode

Well-known and accepted procedures for the pretreatment of glassy carbon electrode were adopted. First the electrode was washed with water-ethanol-ammonia mixture followed by ethanol-ammonia, ethanol-acetic acid and ethyl acetate-ethanol mixture. It was then washed with distilled water and trichloroethylene. With this method, oxides and surface active substances and organic compounds were removed from the electrode surface. When electrode surface was seriously contaminated, the most effective and at the same time the simplest way employed for the removal of
the contamination from the surface was to rub the electrode with the fine powder of 
\( \gamma \)-Al\(_2\)O\(_3\) \cite{128}. After rubbing, the electrode is wiped with a filter paper, and then 
rinsed with water. The fine particles of alumina adsorbed on glassy carbon electrode 
were removed by Ultrasonication in the presence of water. Finally the electrode is 
polarised at a sufficiently negative and positive potential cathodically and anodically 
repeatedly.

For controlled potential electrolysis, glassy carbon sheet of 15cm\(^2\) area served 
as a working electrode. Determination of electrochemical surface area was done by 
recording current-potential curve for the standard substrate potassium ferrocyanide 
as per the standard procedure. The electrochemical area is calculated from the 
following current expression for the reversible process by substituting all the values 
and finding out \( A \).

\[
i_p = 2.69 \times 10^5 \, n^{3/2} \, A \, D^{1/2} \, v^{1/2} \, C_o
\]

Where \( i_p \) = peak current in \( \mu \)A

\( n \) = number of electrons transferred

\( A \) = area of the working electrode in cm\(^2\)

\( D \) = diffusion coefficient in cm\(^2\)/s

\( v \) = Scan rate in V/s

\( C_o \) = concentration of ferrocyanide solution in mM
2. 1. 3. 3. **Modified electrodes**

2. 1. 3. 3. 1. **PEDOT modified GC (PEDOT/GC)**

It was prepared by potentiostatic method [129]. 0.01M ethylene dioxythiophene in acetonitrile containing 0.1M tetra butyl ammonium perchlorate (TBAP) was used. The polymerisation of this monomer was carried out voltammetrically by giving multi cycle in the potential range between –0.2 and 12V using Ag/AgCl reference electrode.

2. 1. 3. 3. 2. **Methylene blue modified GC (MB/GC)**

It is a well-known feat that the polymerised methylene blue the on glassy carbon as an electrode modifier acts as very good electrode modifier for the electrochemical studies of biologically important compounds like Myoglobin, Haemoglobin etc., [130] It was prepared as per the procedure already proposed [130]. 0.01M methylene blue solution in 50% aqueous ethanol was prepared and used for polymerisation and it was done in the potential range of 0.5V and –1.1V. The reference electrode used was Ag/AgCl.

2. 1. 4 **Reference and counter electrodes**

Ag/Agcl (EG&G model K0266) was used as reference electrode. A platinum wire was used as a counter electrode. Pt electrode was cleaned successively with a dilute detergent solution, isopropanol and sodium hydroxide solution. Finally it was rinsed with distilled water. All electrochemical experiments were performed at 25 ± 0.1°C.
2. 1. 5. Reagents and Chemicals used

The dyes used for the studies were of commercial grade and were recrystallised before use. The stock solutions were prepared by dissolving the compounds in 50% aqueous ethanol. Ethanol used is double distilled and water is purified with TKA water purification system. The buffer solutions prepared were given as follows.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M H2SO4 (AR grade) solution</td>
<td>1.1</td>
</tr>
<tr>
<td>Britton Robinson buffer (Merck)</td>
<td>4.0, 7.0 and 9.2</td>
</tr>
<tr>
<td>0.1M KOH (AR grade) solution</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The pH values of the buffer solutions were checked by Cyberscan 500 pH meter.

2. 1. 6. Experimental procedure for voltammetry

Under the experimental conditions, a solution of 10 ml was placed in the electrochemical cell and purified nitrogen gas was purged for 20 minutes to remove the dissolved oxygen under stirred conditions. Measurements were taken using cyclic, differential pulse and square wave voltammetry for the reaction mechanism study. Background values were recorded in the potential range \(-2.0\) to \(2.0\) V and subtracted.

Differential pulse and Square wave stripping voltammetric studies were employed for the analytical study. Dilute concentrations here takes. Accumulation of the substrate was done in the first step and they were stripped in the second step. Various experimental parameters were optimised.
2.1.7. Experimental procedure for chronocoulometry

Chronocoulometric experiments were carried out in a similar type of cell used for voltammetric studies. The chronocoulometric behaviour of the four compounds chosen were studied in 50% aqueous ethanol at all pH values.

The test solution was purged with nitrogen. The potential was stepped up from an initial potential to a final potential. A pulse width of the range 2 to 10 seconds was maintained. The initial potential was chosen, where no redox reaction occurred and the final potential was chosen where the reaction of interest was over. The cyclic voltammetric data obtained were used as the criterion to fix these potentials. Instead of measuring the current directly, it was integrated and the charge was measured. The plot of Q vs $t^{1/2}$ was found to be a straight line and the slope of this line is written as $2nFAD^{1/2}C / \pi^{1/2}$ which was derived from Cottrell equation and the unknown parameters like n was arrived at by known D value or vice versa.

2.1.8. Experimental Procedure for Controlled Potential coulometry

Controlled potential coulometry is readily performed with EG & G electrochemical analyser. The electrochemical cell as well as the electrode system was the same as utilised in cyclic voltammetry studies. Micro molar to nano molar solutions of the compound was chosen as the concentration of the substrate. In aqueous medium the study was performed at different pH condition as studied in CV experiments.
From cyclic voltammetric data the potential of electrolysis was chosen for each compound. Initially the electrolytic solution containing no substrate was taken under nitrogen atmosphere and the charge was observed. This charge was then subtracted from the total charge consumed as the former was a base charge due solely to buffer components. After the addition of the substrate, it was completely electrolysed by applying a fixed potential throughout the experiment.

When the experiment was on, the software exhibited the values of current and charges consumed and indicate the duration of the experiment also. For each second, the current and charge were updated on the screen. From the output of Q vs time curve, the total charge consumed for the electrolysis was measured and was used to calculate the number of electrons transferred per molecule by means of Faraday’s law.

\[ Q = n \cdot F \cdot N \]

Where
Q = charge in Coulomb
n = number of electrons transferred
N = number of moles / ml

2.1.9. Experimental Procedure for Bulk electrolysis

In this technique the compound was completely electrolysed under controlled potential condition by fixing a constant potential. Here the working electrode had a large surface area to minimise the electrolysis time and to isolate the product sufficiently for the characterisation. Glassy carbon of area 15 cm² served as working electrode. The counter electrode was platinum sheet of same area. Saturated calomel electrode was used as reference electrode. These three electrodes with nitrogen
purging / blanketing facility were mounted in a circular polyacrylic sheet fitted to the electrochemical cell of capacity 500ml.

From the voltammetric data obtained, the peak potential at which electroactive compound got reduced / oxidised was chosen as electrolysis potential. After completion of electrolysis the solution was neutralised and organic compounds were extracted with ether or distilled chloroform. The ether was evaporated where it was used. The chloroform was removed under vacuum distillation when it was used for extraction. The chromatography of product was then taken in silica gel. The eluents were ether benzene or benzene – ethyl acetate mixture. This was further purified by vacuum drying and recrystallisation using double distilled ethanol.

2. 2. Electrochemical Treatment

The electrochemical method for waste water treatment has recently attracted attention mainly because of the ease of operation and the increased efficiency provided by the use of compact bipolar electrochemical reactors and by the large surface area of the three dimensional electrodes [131,132]. Here, electrochemical treatment was carried out in batch static mode.

2. 2. 1. Instrumentation

The electrolysis was carried out under galvanostatic condition. The direct current for electrolysis was drawn from an electronic power supply APLAB model (SPECTRA LAB) where in the current was controlled with a precision of ± 1%. The electrode potentials and cell voltage were measured with respect to SCE using high precision multimeter Philips model. The current density was varied from 0.5 to
6.5A/dm². The total quantity of current was fixed, based on the extent of
decolourisation on applying charge. During electrolysis, the samples were drawn
periodically for every half an hour. The current efficiency for the electrooxidation of
the dye degradation and the power consumption also was calculated.

2. 2. 2. Cell setup

The cell set up for the static treatment method is discussed below.

In this case, the electrolysis was carried out in static mode. A particular
quantity of electrolyte was electrolysed at a time under the given experimental
conditions.

The cell set up used for the batch mode electrolysis is shown in figure 2.2. A
cylindrical glass cell was used with an outside diameter of 20cm, a wall thickness of
0.5cm and a height of 24cm. The top cover was made of teflon. Two electrodes were
fixed on the top cover in addition to salt bridge. An eltek magnetic stirrer model
MS201 with speed regulator was fixed at the bottom of the cell.

2. 2. 3. Electrodes

The main emphasis in this investigation has been on the anodic oxidation and
hence naturally the choice of the type of the anode employed for the purpose plays
an important role. The development of new electrolytic processes, whether synthetic
or environmental in objective, has been much retarded by the restricted selection of
available anode materials. Planar graphite was tried for this investigation. Graphite
sheets with high purity were used as anodes. They were quite soft and it was easy to
renew the surface simply by rubbing with fine sandpaper. However because of the presence of high percentage of micro-pores, a large residual current may result if they are not subjected to such a treated. A convenient way of blocking these pores is to soak the sheet in melted paraffin. The sheet was put in a vessel containing melted paraffin, and then the vessel was put in an evacuated dessicator to let the pores be filled with paraffin.

2.2.4. Reagents and chemicals

Synthetic effluents containing the dyes were prepared by dissolving the dye in double distilled water. Initially stock solution of 2 gpl was prepared and the electrolyte for the treatment was prepared by required dilution.

The other chemicals, used in the treatment processes, sulphuric acid, sodium hydroxide and sodium chloride were of Merck AR grade chemicals.

2.2.5. Analysis

The electrolyte samples were analysed for estimating the undegraded organics in the solution at different stages of the electrolysis by the following methods.

2.2.5.1. COD estimation

It determines the amount of oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant, potassium dichromate.
2.2.5.2. Principle

The test was based on treating the sample with a known amount of dichromate, digesting at an elevated temperature to oxidise the organic matter and titrating the unconsumed dichromate. The amount of oxygen equal to the amount of dichromate destroyed is reported as COD.

2.2.5.3. Interference:

In COD estimation studies, fatty acids and aliphatic compounds are oxidised with difficulty. Cl and NO$_2$ interfere with the estimation. Interference caused by Cl was eliminated by adding mercuric sulphate (HgSO$_4$) to the sample prior to the addition of other reagents. Silver sulphate (Ag$_2$SO$_4$) added to the concentrated sulphuric acid stimulates the oxidation of aliphatic and aromatic compounds. Interference caused by nitrite is avoided by the addition of sulphamic acid to potassium dichromate solution.

2.2.5.4. Reagents

(i) 0.25 N Potassium dichromate (Merck AR grade)
(ii) Concentrated H$_2$SO$_4$ (Merck AR grade)
(iii) 0.1 N Standard Ferrous ammonium sulphate (Merck AR grade)

2.2.5.5. Procedure

20 ml of the sample was taken in the reflux flask and 0.4 g of HgSO$_4$ was added. 10 ml of standard potassium dichromate and 30 ml of sulphuric acid containing silver sulphate were added while constant by stirring. This process of adding while stirring prevents fatty acids from escaping out because of high temperature.
colour turns green either fresh sample with lesser aliquot or more dichromate and sulphuric acid must be taken The content was refluxed in COD digester (Spectralab model) for a minimum of two hours at a temperature of 155°C. The mixture was cooled and then diluted to 150 ml. The excess dichromate present in the solution was estimated by using Spectralab Auto Burette model AB 20 and COD end point detector model AB 92 with 0.1 N ferrous ammonium sulphate as titrant. The end point was read automatically. The blank was also refluxed in the same manner using distilled water instead of the sample and analysed as before. Using these values the COD was calculated as follows:

\[
\text{COD (mg/l)} = \frac{(a-b) N \times 8 \times 1000}{\text{ml of sample}}
\]

Where

- \(a\) - Volume of FAS required for blank
- \(b\) - Volume of FAS required for sample
- \(N\) - Normality of FAS

2.2.5.6. Spectral studies

The UV-VIS spectral studies were carried out using UV-VIS spectrophotometer JASCO model.
FIG. 2.1 EG & G PARC Potentiostat / Galvanostat Model 273 A
Fig 2.2 Cell Setup used for Batch Electrolysis
A - anode  B - reference electrode  C - cathode  D - saltbridge
E - electrolyte  P - power supply