Summary of the investigation
CHAPTER X

SUMMARY OF THE INVESTIGATION

Synthetic dyes and pigments are widely employed in textile industries and in the manufacture of food colourants, paints, printing inks and biological stains. The toxicity of these chemicals necessitates the world to categorize the dyes, according to the magnitude of their toxicity and the removal of them from the waste streams. Electroanalytical chemistry plays an important role in the detection of traces of dyes and their destruction. This investigation throws more light on the electrochemical studies of dyes.

CHAPTER I

Introduction and Scope of the investigation

This chapter deals with the introduction, which is necessary for the present investigation, the basic principles, utility of electrochemical techniques such as cyclic voltammetry, chronocoulometry, controlled potential coulometry, differential pulse stripping voltammetry and square wave stripping voltammetry in the elucidation of reaction mechanisms and spectroscopic techniques like UV-VIS, FTIR and spectroelectrochemistry in detail. It also describes the role of stripping voltammetry in the environmental analysis. This chapter discusses the reasons for the selection of the reactive dyes, reactive blue 19, reactive red 2, reactive orange 4, reactive yellow 107 and reactive black 5. It covers the perusal of literature and elaborates the scope of the investigation.

CHAPTER II

Experimental Setup

The second chapter describes the instrumental aspects, methodologies and procedures employed during the investigation. This includes the description of EG&G
Princeton Applied Research model 273A Potentiostat / Galvanostat and other equipments employed in the investigation. The procedure for UV-VIS spectroscopy, FTIR spectroscopy, in situ spectroelectrochemical, cell setup, electrodes, pretreatment of electrodes, the chemicals employed, preparation of analytes, experimental methods individually for all electroanalytical studies and electrochemical treatment are presented in detail.

CHAPTER III
Electrochemical studies of reactive dyes on glassy carbon electrode [GCE]

This chapter discusses the results obtained from the electrochemical studies of selected reactive dyes using glassy carbon electrode. Cyclic voltammetry, chronocoulometry and controlled potential coulometry studies were performed. For reactive blue 19 cyclic voltammetric studies were carried out at selected pH 4.0, 7.0, 9.2 and pH 13, since peak response was not observed in more acidic pH. With increase in pH the peak potential decreased and the peak current increased. The effects of scan rate and concentration were studied. In pH 4.0, 7.0, 9.2, one prominent anodic peak and one cathodic peak (nearly with same current) was observed. Both the anodic peak II and cathodic peak were considered for correlation. Of the two plots, peak current vs. scan rate and peak current vs. square root of scan rate, good correlation was observed in the latter plot. The plots of log peak currents and log scan rate yielded a slope value less than 0.5. These facts suggest that the overall reaction of both oxidation and reduction are diffusion controlled. The fractional an value that was calculated from the slope of the plot, peak current vs. log v and the absence of counter cathodic peak in the reverse scan indicated irreversible oxidation and reduction. The peak current increased with increase in concentration in both the case. At pH 13, apart from the above two peaks, one additional anodic peak was observed. Here also the main anodic peak was found to
be an irreversible diffusion controlled oxidation. The cathodic peak had a reversible counterpart and followed a diffusion controlled mechanism.

Chronocoulometry and controlled potential coulometric studies were carried out and a suitable mechanism was proposed. The number of electrons transferred is 1 in acid and neutral pH and 2 in basic pH conditions. The influence of the kinetic parameter was discussed by calculating the rate constant and it was seen that the electron transfer was found to be in a faster rate in the optimum pH 13.0.

Considering the reactive red 2, the cyclic voltammetric studies were carried out in the pH range 1.0 to 9.2 since peak response was not observed in other pH media. In pH 1.0 and 4.0, one well defined anodic peak and a broad cathodic peak were observed whereas in pH 7.0 and 9.2, only the anodic peak was noticed. Due to high peak current response, the anodic peak was considered for further studies. The correlation studies indicated irreversible and adsorption controlled process in all pH media. The number of electrons transferred in the overall process was determined by controlled potential coulometry. The diffusion coefficient ‘D’ was experimentally found out from chronocoulometric studies. In all the four pH, the number of electrons transferred was two. The pH 1.0 with high current and high rate of electron transfer was selected as the best pH for the electrochemical determination of the dye reactive red 2.

Regarding the reactive orange 4 the cyclic voltammetric studies of RO 4 were carried out in the pH range 1.0 to 6.0, since there was no characteristic effect from pH 7.0. Three representative pHs were chosen for study. At all pH viz. 1.0, 4.0 and 5.0, two anodic peaks and one cathodic peak in the reverse scan were observed. Of the three peaks, anodic peak I showed prominence with higher current in the pH range 1.0 to 6.0 and was chosen for the correlation studies. Good correlation was seen with the plot peak current vs. square root of scan rate and the slope value got from the logarithmic plot of peak current vs. scan rate was less than 0.5 in the chosen pH range. Hence it
may be considered that the overall reaction was controlled by diffusion. In pH 4.0 and 
5.0, the anodic peak and the cathodic peak did not satisfy the criteria for reversibility. 
In pH 1.0 the potential difference between the anodic peak I and the cathodic peak was 
found to be around 100 mV. Hence, it can be considered that the oxidation of RO 4 at 
pH 1.0 may be considered as quasi reversible. Maximum peak response was observed 
in pH 1.0 and was chosen as the best pH for the determination of reactive orange 4. The 
diffusion coefficient value was calculated from the chronocoulometric studies and 
the number of electrons transferred was found to be two by controlled potential 
coulometric studies. The standard rate constant values at all pH were calculated.

Considering the dye reactive yellow 107, there was no response from the pH 
5.0. The dye RY 107 is active only in acid pH. Therefore the studies were limited to pH 
1.0, 2.0, 3.0 and 4.0. One anodic peak and one cathodic peak in the reverse scan were 
observed in pH 1.0 and 2.0. But in pH 3.0 and 4.0, only the anodic peak was observed. 
Since the anodic peak had high current density compared to cathodic peak, it was 
considered as analytical signal. The correlation plots revealed that the oxidation of 
reactive yellow 107 was an irreversible diffusion controlled one in all chosen pH. Here 
also, the chronocoulometric and controlled potential coulometric studies were carried 
out. The standard rate constant values were also calculated from the plot of log ipa vs. 
(E-Ei). It may be noticed that high current response was observed in the acidic pH viz. 
pH 1.0. A suitable mechanism was also proposed.

Similar to the previous samples, studies were carried out for the dye reactive 
black 5. Cyclic voltammograms were recorded in the pH range 1.0 to 13.0 and it was 
observed that there was no characteristic response after pH 7.0. Therefore the detailed 
cyclic voltammetric analyses of RB 5 were carried out in the three representative pH 
media viz 1.0, 4.0 and 7.0. Two anodic peaks and a cathodic peak in the reverse scan 
were observed at all the three pHs considered. Of the three peaks the anodic peak I was
found to be sharp and had higher current in all the experimental conditions. Linearity was observed in the plot of peak current vs. scan rate with good correlation. Also the slope value ranged from 0.6 to 0.9 was got from the logarithmic plot of peak current vs. scan rate. These factors revealed that the oxidation reaction was controlled by adsorption. The fractional an values calculated from the slope of the plot peak potential vs. log scan rate was found to be fractional in all pH which confirmed the irreversibility of the reaction. From the chronocoulometry the number of electrons transferred was calculated to be two and the rate of the electron transfer was faster in the optimum pH 1.0. From the controlled potential coulometric studies the diffusion coefficient value was calculated.

CHAPTER IV
Spectral behaviour of reactive dyes

In this chapter, the UV-VISIBLE spectroscopy and FTIR spectroscopy and in situ spectroelectrochemical studies of the selected dyes were discussed. The UV-VIS spectral studies were carried out using UV-VIS spectrophotometer JASCO model and FTIR spectral studies were done using a Perkin-Elmer 783 spectrophotometer.

The in situ spectroelectrochemical behaviour of reactive dye solutions was studied. The spectroelectrochemical cell used incorporates a central ‘multi-electrode’ three-electrode system. Pt wire gauze as a working electrode, Ag/AgCl as reference electrode and platinum foil as counter electrode. CH Instruments electrochemical workstation 760C was used for bulk electrolysis (with coulometry) experiment. USB 4000 ocean optics probe UV-VIS spectrometer was used for the absorption studies. The sample solution is oxidized and UV-VIS spectroelectrochemistry monitors changes in the UV-visible spectra as potentials were applied to the working electrode in the cell.
Also the studies were carried out at different time intervals at a constant applied potential. From this study it is concluded that at certain applied potential, the selected reactive dyes undergo disintegration during anodic oxidation to smaller organic molecules having aromatic rings. At longer duration the complete decolourisation is also observed.

CHAPTER V
Electrochemical studies of reactive dyes on clay modified electrode

This chapter discusses the electrochemical behaviour of all the five reactive dyes selected for this investigation on glassy carbon electrode modified by a multilayer film of sodium montmorillonite (NaMM/GCE) using various voltammetric techniques. Cyclic voltammetric studies of RB 19 were carried out at an optimized pH 13.0. Two anodic peaks and one cathodic peak were observed in the cyclic voltammogram. The main anodic peak with high current response was considered for further studies and the effect of scan rate and concentration was studied. From the calibration plots, it may be considered that the oxidation of reactive blue 19 was irreversible and controlled by diffusion. The controlled potential coulometry and chronocoulometry experiments were conducted and it was seen that the same mechanism was followed as in the case of bare glassy carbon electrode.

Similar CV studies were carried out for reactive red 2 at an optimum pH of 1.0 and only one prominent anodic peak was observed. Plots of peak current versus scan rate resulted in slight curved line whereas the same with square root of scan rate resulted in a straight line. The slope value from the plot of log peak current vs. log scan rate was below 0.5. These factors suggest diffusion controlled anodic reaction. The absence of reversible counter part and the fractional transfer coefficient value conclude the irreversible nature of oxidation. The chronocoulometry and controlled potential...
coulometry indicate the number of electrons transferred to be two and hence the same mechanism discussed with GCE holds good here also.

Electrochemical behaviour of reactive orange 4 was observed at an optimum pH of 1.0 with clay modified electrode. The cyclic voltammogram showed two anodic peaks of which the anodic peak 1 with high current response was considered for further analytical studies. The correlation studies represent the over all reaction to be irreversible and diffusion controlled. Peak current showed an increasing trend with increase in concentration. Chronocoulometric and controlled potential coulometric experiments were carried out and the reactions proceed with the same mechanism proposed for the bare glassy carbon electrode. Considering the reactive yellow 107, similar behaviour as in the case of glassy carbon electrode was observed. Hence, it may be considered that the oxidation reactive yellow 107 followed an irreversible diffusion controlled mechanism.

Similar to the previous cases, the cyclic voltammetry, chronocoulometry and controlled potential coulometry were carried out for reactive black 5 using clay modified electrode. From the correlation studies, the oxidation was found to be irreversible and adsorption controlled with two electron transfer. A comparison between the GCE and NaMM GCE was also discussed in this chapter.

CHAPTER VI

Electrochemical studies of reactive dyes on polypyrrole modified electrode

In this chapter, a conducting polymer polypyrrole modified electrode was used for the investigation of the selected samples. The following table details the salient points discussed in this chapter.
CHAPTER VII

Electrochemical studies of reactive dyes on PEDOT modified electrode

This chapter presents the voltammetric studies of the five reactive dyes using PEDOT modified glassy carbon electrode. As in the previous chapter, the electrochemical studies were carried out at optimum pH values. This electrode showed very good response compared to other electrode systems for the dyes reactive orange 4, reactive yellow 107 and reactive black 5. The results observed in this chapter are shown in the following table.

<table>
<thead>
<tr>
<th>Reactive dyes</th>
<th>pH</th>
<th>Redox response</th>
<th>Nature of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue 19</td>
<td>13.0</td>
<td>Two anodic peaks and one cathodic peak</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
<tr>
<td>Red 2</td>
<td>1.0</td>
<td>Two anodic peaks and one cathodic peak</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
<tr>
<td>Orange 4</td>
<td>1.0</td>
<td>Two anodic peaks and one cathodic peak</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
<tr>
<td>Yellow 107</td>
<td>1.0</td>
<td>One anodic peak</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
<tr>
<td>Black 5</td>
<td>1.0</td>
<td>Two anodic peaks and one broad cathodic peak</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
</tbody>
</table>
CHAPTER VIII

Electroanalytical determination of selected reactive dyes using bare glassy carbon and modified glassy carbon electrodes

This chapter discussed the stripping voltammetry, which is one of the most important and significant methods to determine trace level species. Differential pulse voltammetric studies and square wave stripping voltammetric studies were carried out for the selected reactive dyes to develop a sensitive determination procedure. The stripping studies were carried out at pH 1.0 for all the dyes except reactive blue 19 for which the optimum pH is 13.0. The optimization of the parameters was carried out on glassy carbon electrode. After fixing all the parameters, the concentration dependence was studied on GCE as well as on the modified electrodes. The optimum experimental conditions arrived in DPSV is listed in the following table.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>oxidation process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow 107</td>
<td>1.0</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
<tr>
<td>Black 5</td>
<td>1.0</td>
<td>Irreversible, diffusion controlled two electron oxidation process</td>
</tr>
</tbody>
</table>

The choice of the working electrode was discussed in this chapter. The polypyrrole modified electrode was found to be suitable for the electrochemical studies of reactive blue 19 and reactive red2 whereas the PEDOT modified electrode was suitable for the reactive orange 4, reactive yellow 107 and reactive black 5.
The optimization of accumulation parameters and stripping parameters in the square wave stripping voltammetry are listed in the following table.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Optimum Value of Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{acc} ) (mV)</td>
</tr>
<tr>
<td>RB 19</td>
<td>100</td>
</tr>
<tr>
<td>RR 2</td>
<td>100</td>
</tr>
<tr>
<td>RO 4</td>
<td>150</td>
</tr>
<tr>
<td>RY 107</td>
<td>400</td>
</tr>
<tr>
<td>RB 5</td>
<td>600</td>
</tr>
</tbody>
</table>

After optimizing the parameters, the concentration dependence was studied using all the four electrodes for all the five samples. From the results obtained it can be considered that square wave stripping voltammetric studies using PEDOT/GCE was sensitive in the determination of Reactive Orange 4, Reactive yellow 107 and Reactive Black 5. And the SWSV studies using PPY/GCE was sensitive in the determination of Reactive Red 2. Regarding the dye Reactive Blue 19, the differential pulse stripping voltammetric studies using the Polypyrrole modified electrode was found to be more...
sensitive. Using the suitable working electrode and technique the real sample analysis was also done for the effluent got from the lab scale dying of cotton fabrics with the selected dyes.

CHAPTER IX

Electrochemical treatment of reactive dyes

This chapter deals with the electrochemical treatment of the five selected reactive dyes using batch static electrolytic cell. Graphite anode was chosen for the study. Stainless steel mesh was used as the cathode and saturated calomel electrode as reference electrode. The optimum quantity of electricity required was found out, where maximum COD reductions were achieved. The influence of pH on the electrolysis was studied by carrying out experiments at various pH values ranging from 1.0 to 13.0. The samples were drawn at constant intervals for the analysis. From the results, the optimum pH for significant removal of dye was chosen and further studies were done only at this pH. Experiments were carried out at various current densities from 1.0 to 5.0A/dm² and the corresponding cell potentials and electrode potentials were measured as a function of time with reference to SCE. The optimum current density was found out from the results. The power consumption was also calculated. The stability of the electrode was studied. COD values were determined for the samples collected at intervals and the percentage of COD reduction was calculated. UV-VIS spectral studies of the dye and the determination of percentage absorbance reduction were carried out to ascertain the removal of dye during electrolysis. The optimum conditions obtained are presented in the following table. A possible mechanism of destruction is proposed. The conclusions derived from the electrochemical treatment of the five dyes prove the technical feasibility of the application of electrochemical processes to the treatment of dyeing industrial effluent streams.
Optimum conditions and results obtained in electrochemical treatment of reactive dyes

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>Current density (A/dm²)</th>
<th>Max. % of COD reduction</th>
<th>Max. % of absorbance reduction</th>
<th>% current efficiency</th>
<th>Power consumption KWhr/Kg of COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB 19</td>
<td>7.0</td>
<td>4.0</td>
<td>96.34</td>
<td>97</td>
<td>54.2</td>
<td>5.2</td>
</tr>
<tr>
<td>RR 2</td>
<td>7.0</td>
<td>3.0</td>
<td>93.75</td>
<td>96</td>
<td>47.9</td>
<td>4.0</td>
</tr>
<tr>
<td>RO 4</td>
<td>7.0</td>
<td>3.0</td>
<td>95</td>
<td>97</td>
<td>54.4</td>
<td>4.0</td>
</tr>
<tr>
<td>RY 107</td>
<td>1.0</td>
<td>3.0</td>
<td>98</td>
<td>96</td>
<td>62.4</td>
<td>4.2</td>
</tr>
<tr>
<td>RB 5</td>
<td>7.0</td>
<td>4.0</td>
<td>96</td>
<td>98</td>
<td>54.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

CONCLUSION

Thus this investigation results in establishing the redox mechanism of the selected reactive dyes on GCE, NaMM/GCE, PPY/GCE and PEDOT/GCE systems and proposing suitable electroanalytical method for the determination of these selected dyes. It discusses the spectral behaviour of the selected reactive dyes. It also suggests suitable electrochemical treatment procedure for the selected dyes.