CHAPTER - IV

SUMMARY AND CONCLUSIONS
IV. SUMMARY AND CONCLUSIONS

Water is the most ubiquitous chemical substance needed by all plants, animals and human being to survive. In general, human body consists of two thirds of water by weight. Brain, blood and lungs are made up of 95, 82 and 90 % of water respectively. Drinking enough quantity of water transports important nutrients to our body and also removes harmful toxins from our body.

Of all the pollutants, colour is the first contaminant to be recognised because of its visibility to human eye. Colour is mainly obtained by using dye which is the major ingredient of the textile, paper and plastic industries where it is used in order to colour their products. Among these industries, textile industries consume more amount of water. The consumption of water for processing one kilogram of textile goods varies from 10 to 300 lit depending on the nature of the fiber, form of textile goods and the processing to be carried out. Hence, textile industry is one of the largest producers of waste water.

Activated carbons have shown greater potential in dye removal due to properties such as large surface area, micro porous structure and high adsorption capacity. The high cost of activated carbon induces the search for cheaper materials mainly from biological origin or waste materials. It has been proved that ligno-cellulosic biomasses serve as attractive resources in the preparation of carbonaceous materials involved in adsorption processes. The eco-friendly nature of ligno-cellulosic biomasses, their availability and low cost are some of the main advantages of these resources, which make them a suitable pre-cursor in the preparation of activated carbon.

A large amount of waste materials were generated in our day today activities from the natural and synthetic sources. Industrialisation is unavoidable for the economical development throughout the world. Solid wastes were accumulated on the
earth surface and thereby causing severe effects to the living organism. Disposal of large amounts of recurring industrial waste is a big problem for the pulp and paper industries and there is need for a rational alternative to utilize these wastes into a wealth material. So keeping this in mind, solid waste such as bagasse, eucalyptus hybrid (lignin) and de-inked pulp sludge were selected for the present study which is derived from most of the paper industries. A large number of activated carbons have been prepared for the water treatment applications. Activated carbons derived from naturally available waste materials would be of great concern as they are eco friendly. Therefore, natural wastes such as soybean hull and *Ailanthus exelsa* were also selected as precursor for carbon. Thus, these solid wastes have been converted as activated carbons (ACs) using H$_3$PO$_4$ as an activating chemical to increasing the surface area and thereby increasing the adsorption capacity.

Systematic studies have been carried out and compared the adsorption capacities of these carbons. A large of dyes is involved in the manufacturing of textile and paper industries. RhB and AO7 are being commonly used and hence RhB and AO7 were selected for the optimisation of the selected adsorbents. All carbons prepared from the selected plant and industrial wastes were shown higher adsorption efficiency owing to the presence of hydroxyl groups.

Systematic studies of batch adsorption were carried out for the prepared activated carbons viz., DIPSAC, BAC, LAC, AEAC and SBHAC. Characterisation of these carbons was also studied by using FTIR, SEM with EDAX and XRD analysis. These carbons have shown higher sorption capacity owing to their large surface area and hence proved to be a good adsorbent and abundance and its low cost make them promising. The details of the results are discussed in this chapter.
Wastewater treatment using photocatalyst is a very recent technique applied in the industrial wastewater treatment. The photocatalysts are used to convert UV energy to electro chemical energy capable of destroying organic waste in the process of decontamination of water. ZnO has been found to be an excellent catalyst in photocatalytic degradation of dyes owing to large number of active sites and it can be captured to absorb the visible light. As almost all the carbons shown the comparable sorption capacity, DIPSAC has been selected just to showcase the photocatalytic experiment of RhB and AO7.

The main objectives of the present study are,

- To prepare and characterize the low cost activated carbons from industrial and natural biowastes viz., Bagasse, Eucalyptus hybrid, Deinked pulp sludge, soybean hull and also leaves of Ailanthus exelsa for decolourisation
- To study the suitability of prepared Bagasse, Eucalyptus hybrid, Deinked pulp sludge, soybean hull and Ailanthus exelsa carbons for the removal of two commonly used dyes viz., RhB and AO7
- To optimize suitable conditions like contact time, dose, pH, temperature, initial dye concentration for the best sorptive capacity of the prepared adsorbents in the removal of dyes
- To carry out the isotherm, kinetics and thermodynamics studies and to establish the mechanism of dye removal capacity of the sorbents by adsorption method
- To investigate the photocatalytic degradation of RhB and AO7 using ZnO as a co-sorbent in the presence of the best adsorbent identified in our study under identical conditions
To optimize various conditions like irradiation time, dosage, pH, co-ions, initial concentration, light intensity etc., for the maximum removal of dyes

To propose the rate of photocatalytic degradation of dyes by Langmuir-Hinshelwood kinetics

Chapter I explores the causes of Rhodamine B and Acid Orange 7 pollution in water and their impacts on the environment and human beings. It also analyzes the various methods available for removal of RhB and AO7. A thorough review on the mechanism of adsorption of the dyes on various types of adsorbents reported in literature has been done. Survey of Literature revealed that the use of activated carbons in the removal of dyes is very scanty. This chapter also gives an idea about the photocatalytic decolourization of the dyes taken up for the study.

Chapter II deals with the experimental methods to analyze RhB and AO7 dyes and characterization techniques adopted to characterize the activated carbons prepared and procedure adopted to carry out the adsorption and photocatalytic studies.

Chapter III presents the methods of preparation and characterization of various activated carbons for the removal of RhB and AO7 dyes from aqueous solution. The results obtained from the studies for removal of RhB and AO7 dyes are given under the following divisions.

- Removal of Rhodamine B and Acid Orange 7 dyes using De-inked pulp sludge activated carbon
- Removal of Rhodamine B and Acid Orange 7 dyes using Bagasse activated carbon
- Removal of Rhodamine B and Acid Orange 7 dyes using Lignin activated carbon
✓ Removal of Rhodamine B and Acid Orange 7 dyes using Soy-bean hull activated carbon

✓ Removal of Rhodamine B and Acid Orange 7 dyes using Ailanthus excelsa leaves activated carbon

✓ Photodegradation of Rhodamine B and Acid Orange 7 dyes using ZnO and De-inked pulp sludge activated carbon under UV irradiation

Chapter IV presents the contribution of the researcher for the removal of RhB and AO7 dyes from water by adsorption and photocatalytic method which forms the concluding part of the work.

Conclusions

In chapter 3, under results and discussion of the dye removal capacity, optimum conditions for dye removal, mechanism of dye removal, suitable isotherm and kinetic models are discussed in detail for the sorption of RhB and AO7 on each carbon. The photocatalytic degradation studies using the photocatalyst in the presence and absence of carbon are also well explained. Here an overview of all the sorption studies related to dye removal is presented. The merits and demerits and their suitability for RhB and AO7 dyes removal are discussed in detail.

✓ Removal of Rhodamine B and Acid Orange 7 dyes using De-inked pulp sludge activated carbon

This chapter deals with the results obtained in the adsorption studies on the removal of RhB and AO7 from aqueous solution using De-inked pulp sludge activated carbon (DIPSAC).

In the case of RhB dye, the percentage removal by DIPSAC was found to be 90.02 %. The contact time for maximum percentage removal of RhB dye was found to be 60 min using DIPSAC. At low pH, the percentage of RhB dye removal was found to be...
higher. The equilibrium data obtained for RhB sorption onto DIPSAC were successfully fitted to the Freundlich isotherm model. The values of thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$) supported the spontaneous and exothermic nature of the RhB adsorption onto DIPSAC. Subsequently, the kinetic data were well described by the pseudo-second-order model.

The percentage removal of AO7 dye was found to be 90.12% at 60 min of contact time using DIPSAC. As pH increases, the percentage of anionic AO7 dye removal were found to decrease with DIPSAC, i.e., at pH 2, the removal percentage was found to be maximum. The equilibrium data obtained for AO7 sorption onto DIPSAC successfully fitted to the Freundlich isotherm model. The values of thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$) supported the spontaneous and exothermic nature of the AO7 adsorption onto DIPSAC. Consequently, the kinetic data were well described by the pseudo-second-order model. HCO$_3^-$ has significant effect on the adsorption of RhB and AO7 on DIPSAC. Electrostatic attraction was involved between adsorbents and adsorbates.

The DIPSAC, being a waste material, could be an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

✓ **Removal of Rhodamine B and Acid Orange 7 dyes using Bagasse activated carbon (BAC)**

This chapter discuss the preparation and characterization of BAC for the removal of RhB and AO7 from aqueous solution. Sugarcane bagasse was washed thoroughly with distilled water and taken for the preparation of activated carbon by using H$_3$PO$_4$ solution at 500 °C for 30 min. The percentage removal of BAC for the dyes RhB and AO7 determined were found to be 90.50 and 92.90% at 303 K respectively. The results of the analysis clearly establish that the equilibrium data agree well with
Freundlich isotherm model than the Langmuir model for the sorption of RhB and AO7 on BAC. Statistical analysis of RhB and AO7 sorption on BAC suggests the dominance of physisorption process. The sorption process is spontaneous and exothermic for RhB and AO7 sorption on BAC. The kinetics of sorption of both dyes on BAC followed pseudo-second-order and the sorption process was controlled by the pattern of both particle and intra-particle diffusion model.

The sorption of RhB on BAC was on higher side at pH 4 due to the reason that RhB readily enters into the pore structure of the carbon surface, whereas at pH beyond 4, the zwitterionic form of RhB in water aggregated to form a dimer, which was unable to enter into the pore. The greater aggregation of the zwitterions is due to the attractive electrostatic interaction between the carboxyl and xanthane groups of the dye.

The dye sorption capacity of BAC was found to increase in acidic pH of both dye solutions and to decrease in alkaline medium. The sorption of AO7 on BAC is governed by electrostatic attraction which could be explained as the surface adsorbs anions favourably at lower pH due to the presence of H⁺ ions, whereas the surface is active for the adsorption of cations at higher pH is due to the deposition of OH⁻ ions.

Since BAC is abundant and cheap, it could be employed as low cost activated carbon for removal of dyes viz., RhB and AO7.

✓ Removal of Rhodamine B and Acid Orange 7 dyes using Lignin activated carbon (LAC)

This chapter reported the preparation and characterization of LAC for the removal of RhB and AO7 dyes from aqueous solution.

The black liquor, a recycled by-product of the pulping of Eucalyptus hybrid, was acidified to pH 2 to 3 with sulphuric acid by precipitation method. The precipitated solids containing lignin were dried. Lignin, washed with de-ionized water
prior to the experiments was shaken in an end-over-end shaker for 12 h and filtered. The solid obtained was oven-dried at 45 °C for one day and it was used for the preparation activated carbon by using H$_3$PO$_4$.

LAC was used for the removal of RhB and AO7 from aqueous solution by batch mode. It was found that the removal of RhB and AO7 by the LAC was highly pH dependent and it was mainly attributed to weak electrostatic interaction between the dye molecules and the solid surface. The equilibrium was reached within 120 min. Compared to other anions, bicarbonate anion has significantly altered both RhB and AO7 removal efficiency. The equilibrium data of the sorption process were well described by the Freundlich isotherm model. The values of ΔG°, ΔH° and ΔS° revealed that the adsorption of RhB and AO7 on to LAC was a spontaneous and endothermic process in nature. Pseudo-second-order kinetic model was found to be the best at describing the adsorption process.

The initial pH of the solution has played a vital role in the adsorption process. The maximum removal of RhB and AO7 occurred at pH 7 and pH 2, respectively. The higher r values obtained for both particle and intra-particle diffusion models suggest that LAC follow both the models on dye sorption.

As the activated carbon prepared from Lignin is inexpensive and effective, it could be used as low cost activated carbon for the removal of dyes viz., RhB and AO7.

✓ **Removal of Rhodamine B and Acid Orange 7 dyes using Soy-bean hull activated carbon (SBHAC)**

Soybean hull, reported to be enriched with isoflavones was used in the preparation of activated carbon by using activating agent H$_3$PO$_4$ and the activated carbon was examined for the removal of RhB and AO7 from their aqueous solutions. Batch experiments were carried out to examine the adsorption of RhB and AO7 onto
the SBHAC as a function of pH, dosage, contact time and initial concentration. The maximum percentage removal of SBHAC for RhB and AO7 were 84.81 and 86.42 %, respectively.

The equilibrium was reached within 60 min. Compared to other anions, chloride anion significantly altered the RhB and AO7 removal efficiency. The equilibrium data of the sorption process were well described by the Freundlich isotherm model than the Langmuir and D–R isotherm model. The negative values of $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ revealed that the adsorption of RhB onto SBHAC was a spontaneous and exothermic process in nature while the sorption of AO7 by SBHAC was spontaneous, endothermic and favourable. Pseudo-second-order kinetic model was found to be the best at describing the adsorption process.

Besides, the results indicated that the SBHAC adsorbent is capable for the removal of RhB and AO7 with high affinity and capacity indicating its potential use as a low cost adsorbent in near future.

✓ Removal of Rhodamine B and Acid Orange 7 dyes using Ailanthus excelsa leaves activated carbon (AEAC)

This chapter investigated the preparation and characterization of AEAC for the removal of RhB and AO7 dyes from aqueous solution. Activated carbon, prepared from Ailanthus excelsa leaves by chemical activation method was used for removal of RhB and AO7. FTIR and SEM analysis confirmed the adsorption of RhB and AO7 onto AEAC. The influence of various parameters such as pH, dosage, co-ions, contact time and concentration on the removal of dyes selected for the study were also optimized. The percentage removal of AEAC towards RhB and AO7 were 91.26 and 92.54 %, respectively. The maximum sorption of RhB and AO7 by AEAC was found at pH 4 and pH 2, respectively. Electrostatic attraction was involved between adsorbent and
adsorbate. Cl⁻ ions had a significant effect on the adsorption of RhB and AO7 on AEAC.

The percentage removal of AEAC decreased with the increase in temperature which revealed the exothermic nature of the adsorption process and this feature was further supported by the thermodynamic data. The equilibrium data fitted well to the Freundlich isotherm model. The rate of sorption reaction of all the dyes follows pseudo-second-order kinetics, particle and intra-particle diffusion model. Only a few dye sorption studies using AEAC are available in the literature and hence this carbon could be studied for the removal of large varieties of dyes and could be employed for technology development.

Though the sorption of all the dyes on the respective carbons follows a uniform pattern the Percentage removal varies with respect to the nature of the sorbents and dye. Table 4.1 shows the results of Percentage removal of RhB and AO7 on various activated carbons.

**Table 4.1. Comparison of removal efficiency of prepared activated carbon**

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>Percentage removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RhB</td>
</tr>
<tr>
<td>DIPSAC</td>
<td>90.02</td>
</tr>
<tr>
<td>BAC</td>
<td>90.50</td>
</tr>
<tr>
<td>LAC</td>
<td>90.60</td>
</tr>
<tr>
<td>SBHAC</td>
<td>84.81</td>
</tr>
<tr>
<td>AEAC</td>
<td>91.26</td>
</tr>
</tbody>
</table>
Photodegradation of Rhodamine B and Acid Orange 7 dyes using ZnO and De-inked pulp sludge activated carbon (DIPSAC) under UV irradiation

This chapter explores the results obtained in the photocatalytic studies on the removal of RhB and AO7 dyes using ZnO and Co-sorbent like DIPSAC under UV light irradiation.

Zinc oxide is renowned to be one of the important photocatalysts owing to its unique advantages viz., low cost, high photocatalytic activity, high stability and non-toxicity. Accordingly, ZnO has attracted a great deal of attention for its use as a catalyst in the photooxidation of organic pollutants. Photocatalytic degradation is found to be efficient, economical and eco-friendly. As these carbons enhance the photocatalytic activity of catalysts by means of inhibiting the recombinations of electron/hole pairs, the photocatalytic degradation method could make use of these carbons.

The photodecolourization of RhB and AO7 dyes using ZnO under UV light at optimized experimental conditions was found to be comparatively low with ZnO + DIPSAC/UV. Hence, the studies were limited for ZnO + DIPSAC/UV system due to its higher capacity when compared to the ZnO/UV alone. In the case of RhB dye, the percentage of decolourization using ZnO and ZnO + DIPSAC under UV irradiation was found to be 98.0 and 99.2 %, respectively. The irradiation time for maximum decolourization of RhB was found to be 60 min using ZnO and ZnO + DIPSAC.

The percentage of decolourization of AO7 dye by ZnO and ZnO + DIPSAC under UV irradiation was found to be 80.0 and 99.2 %, respectively. The irradiation time for maximum decolourization of AO7 was found to be 30 min.

The percentage of photodecolourization of RhB dye was found to be higher in both acidic and alkaline pH, as RhB is known to be cationic dye having acidic colligator. The percentage of photodecolourization of AO7 dye was found to be higher at pH 2.
The decolourization of both dyes was mainly affected by the irradiation time, catalyst dosage, pH, light intensity, co-ions, as well as with the initial dye concentration. The photodegradation of all the dyes followed pseudo-first-order kinetics which fitted the Langmuir–Hinshelwood model.

**Table 4.2. Percentage removal of RhB and AO7 on ZnO and ZnO + DIPSAC**

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>Percentage removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RhB</td>
</tr>
<tr>
<td>ZnO/UV</td>
<td>98.0</td>
</tr>
<tr>
<td>ZnO + DIPSAC/UV</td>
<td>99.2</td>
</tr>
</tbody>
</table>

The percentage of decolourization of RhB and AO7 dye using ZnO + DIPSAC/UV was found to be 99.2 and 99.2 % respectively which is also higher than ZnO/UV at optimized conditions.