CHAPTER 3

MATERIALS AND METHODS

This chapter gives the details of the materials and reagents used in order to achieve the aims and objectives of this study and deals with the adsorption of four different types of dyes namely acid red 114, basic green 4, direct brown 2 and reactive blue 2 on the adsorbent obtained from plastic waste activated carbon (PWAC). The present studies are performed under batch mode operation.

3.1 DYE SOLUTION CHARACTERISTICS

Dyes are used as the commercial salts without any further purification. Colour index classification of these dyes and their structural formula are given in Table 3.1. Wastewater from a common effluent treatment (Textile) plant is used for testing / comparing with the synthetic laboratory wastewater adsorption studies.
Table 3.1 Classification of the dyes and their structures

<table>
<thead>
<tr>
<th>S. No</th>
<th>Name of the dye</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acid Red 114</td>
<td><img src="image" alt="Acid Red 114 Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$: 514 nm CI: 23635</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Basic Green 4</td>
<td><img src="image" alt="Basic Green 4 Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$: 616 nm CI: 42000</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Direct Brown 2</td>
<td><img src="image" alt="Direct Brown 2 Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$: 587 nm CI: 22311</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Reactive Blue 2</td>
<td><img src="image" alt="Reactive Blue 2 Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$: 614 nm CI: 61200</td>
<td></td>
</tr>
</tbody>
</table>
3.2 ADSORBENTS

3.2.1 Collection of Adsorbents

The collection of the mostly used raw materials from municipal plastics waste near by the Gobi area, Erode District, Tamilnadu. They can be described given as below.

3.2.1.1 Used polypropylene waste

Polypropylene (plastic disposable containers, food storage containers, straws, syringes) were collected and cut into small flakes by a shredder and the flakes were used in the pyrolysis experiments.

3.2.1.2 Used polyethyleneterephthalate waste

Polyethyleneterephthalate (water bottles, medicine jars and biscuit trays) were collected and cut into small pieces by a shredder, used in the pyrolysis experiments.

3.2.1.3 Used polyvinylchloride waste

Polyvinylchloride (plumbing pipes and fittings, roof sheeting, cosmetic containers, cable insulation materials) were collected and used for the pyrolysis experiments.
### 3.2.2 Identification of the Plastic Waste

<table>
<thead>
<tr>
<th>Plastic waste name</th>
<th>DSC Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (a)</td>
<td><img src="image1.png" alt="Graph" /></td>
</tr>
<tr>
<td>PET (b)</td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td>PVC (c)</td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Figure 3.1 Identification selected plastic waste materials**
The identification of the waste plastics was confirmed by DSC analysis. The melting of the waste polymer material is found to be around 161.38 °C which ensures the samples to be polypropylene. Similarly the melting point of plastic waste segregated materials around 243.7 °C and 248.35 °C gives an idea about they were PET and PVC respectively. This idea achieved nearer to their pure polymer matrix melting points. The little variation in melting points of these polymeric waste materials with that of virgin polymers may be due to degradation of polymers by sunlight, the purpose used etc.

3.2.3 Preparation of Activated Carbon from Waste Plastics

The above identified plastic wastes materials are washed with water and dried. The dried wastes were pulverized into small pieces, pyrolysed and used for the preparation of activated carbons by various processes described in the following sections.

3.2.4 Catalyst

Three types of catalysts were used in this experiment, i.e., HZSM-5, HUSY and HMOR. Catalysts (mostly zeolites) have been used in order to improve the conditions of the pyrolysis to yield more useful products and lower the pyrolysis temperatures. In order to evaluate the catalyst and the product selectivity pattern, it is essential to estimate not only the total acidity but also to quantify the number of Bronsted and Lewis sites and their strength. The relative acidity of the reactant molecule as well as the quantitative distribution of the type of different acid sites will determine the catalytic activity. Reports are available on the relationship between the acidity of zeolites and their catalytic activity (Achilias et al. 2007, Kaminsky et al. 2007 and Elordi et al. 2009).
3.2.4.1 HZSM-5

The HZSM-5 zeolite is an active catalyst in several reactions such as alkylation, isomerization, disproportionation and cracking. Acidity is one of the most important characteristics of zeolites that make them catalytically active. The catalyst HZSM-5 contains Lewis and Bronsted acid sites (Achilias et al. 2007).

3.2.4.2 HUSY

HUSY zeolite was effective in converting plastic waste into useful chemicals such as char, gas and aromatic hydrocarbons during fast pyrolysis. The yield of liquid and the selectivity to produce the desired products can be controlled by tuning the acidity and pore size of the catalyst (Lin & Yang 2007).

3.2.4.3 HMOR

HMOR is a zeolite that has high thermal and acid stability. HMOR is used as a catalyst for important reactions, such as hydrocracking, alkylation, hydroisomerization, reforming, dewaxing and production dimethylamines. HMOR has also been used in the adsorptive separation of liquid or gas mixtures (Lin & Yen 2005 and Lee et al. 2002).

3.2.5 Pyrolysis

The pyrolysis reaction can be carried with and without catalyst. If without catalyst, it is termed as thermal cracking and in the presence of catalyst, it is termed as catalytic pyrolysis. Thermal pyrolysis involves the degradation of the polymeric materials by heating them to a very high temperature.
The heating should be carried out in the absence of oxygen to make sure that no oxidation of the polymer takes place. The production of value added products obtained in the temperature ranges between 400 ºC to 900 ºC. The products formed include a carbonized char (solid residues) and a volatile fraction. A portion of the volatile fraction can be condensed to give possibly paraffins, isoparaffins, olefins, naphthenes, aromatics and while the remaining is a noncondensable materials having high calorific value gas. The products formed and their precise composition depends on the type of the plastic waste and the process conditions. In catalytic cracking the same process is carried out in the presence of catalyst. The prominent advantage of this method is that the presence of catalyst lowers reaction temperature and time. Another added advantage is that in thermal cracking a broad variety of products are formed by the breaking of the polymeric chain. While in catalytic degradation, the degradation product distributions are mostly lighter hydrocarbons. From the economic point of view, usage of catalyst reduce the cost further will make this process more attractive. Due to feasibility and efficiency reasons in the present work, catalytic pyrolysis method is adopted for the synthesis of char. The importance of this work lies in comparing the performance of various commercially used industrial catalysts like HZSM-5, HUSY and HMOR for the pyrolysis of municipal waste segregated polypropylene (PP), polyethyleneterephthalate (PET) and polyvinylchloride (PVC). The process is optimized by selecting the most suitable catalyst based on the yield and adsorption properties of the activated carbon obtained.

3.2.5.1 Pyrolysis experimental setup

The pyrolysis setup used in this experiment is a tubular reactor as shown in the Figure 3.2. It consists of a reactor made of quartz tube (length-145 mm, internal diameter- 37 mm and outer diameter- 41 mm), in which
nitrogen gas pass through at one end and an outlet tube at other end for obtaining the volatile/gas/oil products of the reaction. The pyrolysis reactor was a tubular furnace equipped with quartz tube, tubular furnace and a temperature controlled system (Figure 3.2) externally heated by an electrical furnace.

Before the experiments, 40 gm of the mixture of plastic waste and catalyst was loaded in quartz tube and the reactor was purged with nitrogen gas for 10 min, at a flow rate of 300 mL/min to remove oxygen and air. The sample was placed in a silica crucible in the centre of the quartz tube of the furnace and pyrolysis began when the tubular furnace was heated to the desired pyrolysis.

Figure 3.2 Schematic diagram for the pyrolysis unit

3.2.5.2  Thermal pyrolysis

The municipal solid waste segregated plastic mixture used for the pyrolysis experiment was composed of approximately 20% polypropylene (PP), 40% polyvinyl chloride (PVC), 40% polyethyleneterephthalate (PET) was placed in the tubular reactor and heated at 10 °C/min up to 600 °C for 1
hour in N$_2$ atmosphere. 12% carbon yield was obtained after the pyrolysis and carbon char was powdered with mortar and then washed with 200 ml of concentrated hydrochloric acid by using magnetic stirrer for 1h to remove the inorganic impurities. Finally the residue rinsed with distilled water until the filtrate pH becomes 7. The final char was dried in a hot air oven at 110 °C and it was left to cool over night.

Table 3.2 Thermal pyrolysis of waste plastics

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp ºC</th>
<th>% Char</th>
<th>% Oil</th>
<th>% Gas</th>
<th>% Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>600</td>
<td>6.7</td>
<td>74.1</td>
<td>15.5</td>
<td>3.7</td>
</tr>
<tr>
<td>PET</td>
<td>600</td>
<td>9.5</td>
<td>28.2</td>
<td>55.7</td>
<td>6.6</td>
</tr>
<tr>
<td>PVC</td>
<td>600</td>
<td>10.3</td>
<td>20.7</td>
<td>61.6</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Table 3.2 shows the thermal pyrolysis yields three different commercial waste polymers such as polypropylene (PP), polyethyleneterephthalate (PET) and polyvinylchloride (PVC) at 600 ºC in the presence of nitrogen atmosphere. The higher percentage of char yield was obtained from waste PP, PVC and PET.

3.2.6 Catalytic Pyrolysis

The product yields of solid, liquid and gaseous products obtained from pyrolysis of plastic waste depends on many parameters such as composition of the waste mixture, temperature, type of catalyst, catalyst and plastics ratio, resistance time in the reactor, type of the reactor and heating rate.
The use of catalyst allows modifying the process to produce a highly porous material with higher surface area which provides a higher market value. Moreover, process temperature can be reduced by the use of catalyst and promotes decomposition speed, which reduces the energy consumption (Lin and Yang 2007). The most widely used catalysts HZSM-5, HMOR and HUSY which are selected on the basis of their acid strength and surface characteristics.

3.2.6.1 Catalytic pyrolysis with HZSM-5

The plastic mixture used for the experiment was composed of 38% polyethyleneterepthalate (PET), 38% polyvinyl chloride (PVC), 19% polypropylene (PP) and 5% HZSM-5 (catalyst was obtained from a Sud-Chemie India Pvt. Ltd) were placed in the tubular reactor and heated at 10 °C per min to 600 °C for 1h in N₂ atmosphere. 10.2% carbon yield was obtained after the pyrolysis and residues was powdered with mortar and then washed with 200 ml of concentrated hydrochloric acid by using magnetic stirrer for 1h to remove the existing inorganic impurities. Finally the residue rinsed with distilled water until the filtrate pH becomes 7. The final char was dried in a hot air oven at 110 °C and it was left to cool over night.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temp ºC</th>
<th>% char yield</th>
<th>% oil yield</th>
<th>% gas yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>600</td>
<td>7.5</td>
<td>75.3</td>
<td>17.2</td>
</tr>
<tr>
<td>PET</td>
<td>600</td>
<td>10.7</td>
<td>32.2</td>
<td>57.1</td>
</tr>
<tr>
<td>PVC</td>
<td>600</td>
<td>11.6</td>
<td>22.5</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Table 3.3 Catalytic pyrolysis of the plastic waste with HZSM-5
Table 3.3 shows the yield of char, oil and gas from the pyrolysis of the individual plastics with catalyst under nitrogen atmosphere, where the samples were heated at 10 °C min⁻¹ to the final temperature of 600 °C and held at 600 °C for 60 min. The reaction of polypropylene (95 % wt) and HZSM-5 catalyst (5% wt) produced a high conversion of oil product at 75.3 wt%, 17.2 wt% gases and 7.5 wt% of char. Similarly, the pyrolysis of polyethyleneterephthalate used instead of PP under the above condition and yields 10.7 wt% of char, 32.2 wt% of oil and 57.1 wt% gases and polyvinylchloride yields 11.6 wt% of char, 22.5 wt% of oil and 65.9 wt% gases.

### 3.2.6.2 Catalytic pyrolysis with HUSY

The plastic mixture used for the experiment was composed of 38% polyethyleneterephthalate (PET), 38% polyvinyl chloride (PVC), 19% polypropylene (PP) and 5% HUSY (catalyst was obtained from a Sud-Chemie India Pvt. Ltd) were placed in the tubular reactor and heated at 10 °C per min to 600 °C for 1h in N₂ atmosphere. 3% carbon yield was obtained after the pyrolysis and carbon char powdered with mortar and then washed with concentrated hydrochloric acid by using magnetic stirrer for 1h to remove the existing inorganic impurities. Finally, the residue rinsed with distilled water until the filtrate pH becomes 7. The final char was dried in a hot air oven at 110 °C and it was left to cool over night.

On the pyrolysis of waste plastics such as PP, PET and PVC individually, with HUSY catalyst ratio of 19:1 at 600 °C in the presence of N₂ atmosphere, the product yields were observed. Polypropylene yields 5.6 wt% of char, 60.8 wt% of oil and 33.6 wt% gases, polyethyleneterephthalate yields
8.3 wt% of char, 28.5 wt% of oil and 63.2 wt% gases and polyvinylchloride yields 9.4 wt% of char, 16.9 wt% of oil and 73.7 wt% gases.

Table 3.4 Catalytic pyrolysis of the plastic waste with HUSY

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temperature °C</th>
<th>% carbon yield</th>
<th>% oil yield</th>
<th>% gas yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>600</td>
<td>5.6</td>
<td>60.8</td>
<td>33.6</td>
</tr>
<tr>
<td>PET</td>
<td>600</td>
<td>8.3</td>
<td>28.5</td>
<td>63.2</td>
</tr>
<tr>
<td>PVC</td>
<td>600</td>
<td>9.4</td>
<td>16.9</td>
<td>73.7</td>
</tr>
</tbody>
</table>

3.2.6.3 Catalytic pyrolysis with HMOR

The plastic mixture used for the experiment was composed of 38% polyethyleneterephthalate (PET), 38% polyvinyl chloride (PVC), 19% polypropylene (PP) and 5% HMOR (catalyst was obtained from a Sud-Chemie India Pvt. Ltd) were placed in a tubular reactor and heated at 10 °C per min to 600 °C for 1h in N₂ atmosphere. 5% carbon yield was obtained after the pyrolysis and carbon char was powdered with mortar and then washed with concentrated hydrochloric acid for by using magnetic stirrer for 1h to remove the existing inorganic impurities. Finally the residue rinsed with distilled water until the filtrate pH becomes 7. The final char was dried in a hot air oven at 110 °C and it was left to cool over night.

On the pyrolysis of plastic’s waste such as PP, PET and PVC with HMOR catalyst ratio 19:1 individually at 600 °C in the presence of N₂ atmosphere. Polypropylene yields 5.1 wt% of char, 57.3 wt% of oil and 37.6 wt% gases, polyethyleneterephthalate yields 7.7 wt% of char, 25.8 wt% of
oil and 66.5 wt% gases and polyvinylchloride yields 8.4 wt% of char, 12.5 wt% of oil and 79.1 wt% gases.

Table 3.5 Catalytic pyrolysis of the plastic waste with HMOR

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Temperature °C</th>
<th>% carbon yield</th>
<th>% oil yield</th>
<th>% gas yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>600</td>
<td>5.1</td>
<td>57.3</td>
<td>37.6</td>
</tr>
<tr>
<td>PET</td>
<td>600</td>
<td>7.7</td>
<td>25.8</td>
<td>66.5</td>
</tr>
<tr>
<td>PVC</td>
<td>600</td>
<td>8.4</td>
<td>12.5</td>
<td>79.1</td>
</tr>
</tbody>
</table>

3.2.6.4 Choice of catalyst

This research work was aimed to investigate the catalytic cracking of PP, PET and PVC in a tubular reactor using HZSM-5, HUSY and HMOR with nitrogen as fluidizing gas. Zeolite catalysts show advantages of high catalytic activity, shape selectivity, strong acidity and stability at elevated temperatures. They are used for a many reactions such as alkylation, cracking, aromatization and isomerization of hydrocarbons. The high energy conversion of plastic waste to carbon char successfully achieved by HZSM-5, HMOR and HUSY catalyst. The high % of char yield was obtained for HZSM-5 catalyst compared with HUSY and HMOR catalyst. The high percentage of plastic waste char was then carbonized by reported activation processes to produce activated carbon for the treatment of industrial wastewater stream.

Greater product selectivity was observed with HZSM-5 as catalyst with higher percentage of the char product. Differences observed in product yields and product distributions under similar reaction conditions can be attributed to the microstructure of catalysts. Valuable products such as char,
oil and gaseous products were produced by low temperatures and short contact time by using HZSM-5 catalyst.

### 3.2.7 Identification of Polymer Mixture Ratios

Attempts made to identify the best ratio of mixture that to be used for the cracking of plastic waste particularly into char and other products. The proportions of the plastics in the mixture were established based on the composition of real waste samples.

#### Table 3.6 Identification of ratio of the plastic waste into char conversion

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Char yield %</th>
<th>Oil yield %</th>
<th>Gas yield %</th>
<th>Residue%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP: PET: PVC 20:30:50</td>
<td>9.1</td>
<td>43.6</td>
<td>36.7</td>
<td>10.6</td>
</tr>
<tr>
<td>PP: PET: PVC 40:40:20</td>
<td>8.0</td>
<td>45.2</td>
<td>38.1</td>
<td>8.7</td>
</tr>
<tr>
<td>PP: PET: PVC 20:50:30</td>
<td>9.1</td>
<td>35.2</td>
<td>48.4</td>
<td>7.3</td>
</tr>
<tr>
<td>PP: PET: PVC 50:30:20</td>
<td>8.8</td>
<td>46.8</td>
<td>36.2</td>
<td>8.2</td>
</tr>
<tr>
<td>PP: PET: PVC 20:50:20</td>
<td>8.1</td>
<td>36.6</td>
<td>46.4</td>
<td>8.9</td>
</tr>
<tr>
<td>PP: PET: PVC 20:40:40</td>
<td>12.4</td>
<td>34.8</td>
<td>50.3</td>
<td>3.2</td>
</tr>
<tr>
<td>PP: PET: PVC 60:20:20</td>
<td>8.5</td>
<td>55.8</td>
<td>28.7</td>
<td>7.0</td>
</tr>
</tbody>
</table>

From the Table 3.7, it is optimized the best composition of the material converted to char was found to be in the ratio that to be of the plastic waste material like PP: PET: PVC (20:40:40) respectively.
3.2.7.1 Optimization of the catalyst and waste plastic material ratio

The catalysts are used in various ratios with feed to find out the optimum range at which maximum yield occurs. The main objective of this study is to investigate the effect of catalyst amount, reaction temperature, and weight ratio of waste plastics to catalyst in tubular reactor, based on the results of yields and of yield distributions of char, liquid and gaseous product.

The pyrolysis temperature for achieving good conversion is reduced drastically and as the catalyst/plastics ratio is increased; the pyrolysis temperature can be further lowered. The experiments were conducted by using different feed plastics to catalyst ratios of 19:1, 18:2, 17:3 and 16:4. All these ratios required different temperature conditions and the char, liquid and gaseous products yield varied for all these conditions.

Table 3.7 Identification of ratio of the plastic waste and Catalyst into char conversion

<table>
<thead>
<tr>
<th>Precursor &amp; Catalyst ratio (600 °C)</th>
<th>Char yield %</th>
<th>Oil yield %</th>
<th>Gas yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP: PET: PVC: HZSM-5 19:38:38:5</td>
<td>10.2</td>
<td>49.2</td>
<td>40.2</td>
</tr>
<tr>
<td>PP: PET: PVC: HZSM-5 20:35:35:10</td>
<td>9.3</td>
<td>53.1</td>
<td>36.6</td>
</tr>
<tr>
<td>PP: PET: PVC: HZSM-5 20:40:25:15</td>
<td>8.5</td>
<td>50.4</td>
<td>40.2</td>
</tr>
<tr>
<td>PP: PET: PVC: HZSM-5 20:30:30:20</td>
<td>7.9</td>
<td>41.8</td>
<td>50.3</td>
</tr>
<tr>
<td>PP: PET: PVC: HZSM-5 10:30:30:30</td>
<td>7.5</td>
<td>34.1</td>
<td>48.4</td>
</tr>
</tbody>
</table>

Different composition of char product is obtained for different catalyst and its different ratio with plastic feed. The char obtained is highest
for a particular ratio at a particular temperature. This is the optimum range for
the particular catalyst. It is seen that HZSM-5 give the maximum solid
product and it is the minimum ratio of catalyst (19:1) for the best optimized
product. The quality of product obtained is also better in case of catalytic
cracking.

3.2.7.2 Optimization of the temperature, catalyst and waste plastic
material ratio

The pyrolysis experiments are conducted by using mixture of
waste plastics such as PP, PET and PVC as the raw material with the selected
catalyst HZSM-5. The plastic mixture is pyrolysed catalytically using at
various temperature ranges of 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and
900 °C.

Table 3.8 Optimization of the temperature, catalyst and waste plastic
material ratio

<table>
<thead>
<tr>
<th>Catalytic pyrolysis Temperature (PP: PET: PVC: HZSM-5 19:38:38:5)</th>
<th>Char Yield</th>
<th>Methylene blue number</th>
<th>Iodine number</th>
<th>Phenol number</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>15.8</td>
<td>212.7</td>
<td>423.4</td>
<td>20.28</td>
</tr>
<tr>
<td>500</td>
<td>12.5</td>
<td>248.5</td>
<td>471.1</td>
<td>22.53</td>
</tr>
<tr>
<td>600</td>
<td>10.2</td>
<td>330.2</td>
<td>565.4</td>
<td>25.21</td>
</tr>
<tr>
<td>700</td>
<td>9.8</td>
<td>315.6</td>
<td>521.9</td>
<td>23.74</td>
</tr>
<tr>
<td>800</td>
<td>9.3</td>
<td>306.5</td>
<td>481.2</td>
<td>22.87</td>
</tr>
<tr>
<td>900</td>
<td>8.6</td>
<td>276.3</td>
<td>452.8</td>
<td>21.04</td>
</tr>
</tbody>
</table>
The products obtained by different composition and the product yield are different for different temperatures. According to the physico-chemical characteristic study of the char obtained, 600 °C is the optimum temperature for pyrolysis to produce carbon adsorbents.

The waste plastic was subjected to various conditions of reactions which results in thermal cracking and catalytic cracking by different catalyst. The plastic mixture was catalytically cracked by using HZSM-5 as the catalyst, it gave quite good quantity and quality of char products. The highest yield was obtained when the mixture of plastic waste to catalyst ratio was 19:1, temperature of 600 °C and 60 minutes process time. From the Table 3.8, it can be observed that as the catalyst ratio increases, the char yield decreases.

3.2.8 Carbonization Procedures

3.2.8.1 KOH activation process

KOH activation was used to prepare activated carbon from PP, PET, PVC and HZSM-5 catalyst pyrolysed char. The raw material was carbonized at 600 °C in nitrogen atmosphere and the carbon yield was 50 wt. %. The carbonized sample is then activated by KOH in a mass ratio of 1:2 under nitrogen stream at 850 °C. The obtained solid was washed with 1M HCl solution and distilled water to reduce decomposed fragments and then dried at 110 °C for 24 hours. The final activated carbons were ground and passed through a desired sieve meshes and sieved to 75-180, 180-250, 250-355 μm size (Linan et al. 2010).
3.2.8.1.1 ZnCl₂ activation process

As per the chloride activation method described, sufficient quantities of plastic waste char are soaked well with 10% zinc chloride solution of 5 litres capacity respectively so that the solutions get well adsorbed for a period of 24 hour. At the end of 24 hour the excess zinc chloride are decanted off and dried. Then activated carbons are prepared as described in the steam activation method after the impregnation. On cooling, the excess ZnCl₂ on activated carbon particles are leached out by immersing it in 1M HCl solution for about 24 hours. It is then repeatedly washed with hot distilled water until all the chloride had disappeared from the wash water (silver nitrate method). The material is subsequently oven dried and stored in airtight plastic containers (Kumar Ramakrishnan and Chinnaia Namasivayam 2009).

3.2.8.1.2 Sulphuric acid process

Activated carbon is prepared by reacting plastic waste char materials with concentrated sulphuric acid. Initially studies are made using 50g of plastic waste char was mixed with 200 gm of sulphuric acid. When the reaction subsided, the mixture is left in an air oven maintained at 140-160 °C for a period of 24 hours. At the end of this period, the product is washed with large volume of water to remove free sulphuric acid and dried at 110 °C. It is found that the residue after washing exhibit adsorptive and ion exchange properties when used in wet state (Rengaraj et al. 1999).
3.2.8.1.3 CO₂ activation process

In physical activation, the char was placed in a quartz tube in CO₂ atmosphere. The activated carbon was prepared by heating stainless steel reactor 10 °C/min temperature rising up to 900 °C through tubular furnace.

![Diagram of ACs Conversion](image)

**Figure 3.3 Diagram of ACs Conversion**

At 900 °C the char was activated for 2 hours and allowed to cool in N₂ atmosphere (Linan et al. 2010). In this carbon dioxide activation method, the reaction involved between carbon atom and the oxidizing gas. It is this reaction that gives rise to the pore creation and development of the char structure. Since physical activation uses gaseous activation agents and does not produce waste water this method is considered to be an environmental friendly technology. The obtained activated carbon was further characterized by characterization analysis.

3.3 CHARACTERIZATION OF THE ADSORBENT

3.3.1 Determination of Zero Point Charge (pH\text{zpc})

The adsorbent (100 mg) suspension (particle size, 75-150 μm) is prepared in 50 ml solution of NaNO₃ electrolyte of concentration, approximately 10⁻³M. Aliquots of suspension are adjusted to different pH values with dilute HNO₃ and NaOH solutions. After one hour equilibration,
the initial pH values are measured. Then 1.0 g of NaNO₃ is added to each aliquot to bring final electrolyte concentration of electrolyte to about 0.45M. After an additional one hour agitation, final pH is measured. The results are plotted with ΔpH (final pH – initial pH) against final pH. The pH at which ΔpH = 0 yielded pHᵪₑ (Rajeshwar et al. 2012).

3.3.2 Surface Area of Activated Carbon

A specific surface area of PWAC was analyzed according to the Brunauer, Emmett and Teller (BET) method. The BET surface area of the activated carbon (Sᵥₑₚₑ) was obtained from N₂ adsorption isotherm at 77 K with sorbitometer (NOVA 1000, Quanta chrome instrument). The surface area was calculated from the nitrogen adsorption isotherms by assuming the area of nitrogen molecule to be 0.16 nm². Based on these data, the manufacturer’s software provides the pore characteristics viz., the total pore volume (Vᵥₑₚₑ) by the BJH theory, micro and meso pore size by both t plot method and BJH method respectively.

3.3.3 Pore Structure

The phenomena of adsorption and porosity are inseparable. Porosity is usually characterized by pore volume and pore size distribution (PSD). The pore size is generally specified as a pore width. The single value of pore width is meaningless without definition of the pore shape.

In practice, it is usually an effective pore width: an available inner diameter of tubular pores or a distance between the opposite walls in slit shaped pores. In mesoporous and macroporous solids, the effective pore width is consistent with the thermodynamical requirements of capillarity, while in microporous solids it is a dimension controlling the entry of molecules of
particular size. Different pore sizes (micropores and mesopores) are traditionally treated separately, mainly due to a lack of mathematical models. Micropore PSD are traditionally evaluated using Dubinin–Radushkevich (D-R) method and the Horvath-Kawazoe (H-K) method. The mesopore PSD is obtained using the Barrett-Joyner-Halenda (BJH) method.

A detailed report of the pore structure in terms of pore size distribution is important as it may be used for the correlation and prediction of the carbon materials performance in industrial applications, as well as in the development of new porous materials. In this study, the pore size distribution of PWAC is studied by using H-K and BJH methods.

3.3.4 XRD and SEM Analysis

The surface morphology is studied using electron scanning micrographs and then recorded the image without sample coating by JOEL JSM-5600LV scanning electron microscope. The X-ray patterns were recorded under the scan rate of 0.1 °/min using SHIMADZU diffractometer system.

3.3.5 FTIR and Elemental Analysis

The PWAC sample is examined using Shimadzu IFS 66V FTIR. For analysis, the activated carbon is mixed with KBr pellets and an absorbance spectrum is recorded from 4000-400 cm\(^{-1}\). Elemental analysis of the carbon samples was carried out using Perkin Elmer PE2400 Series II elemental analyzer.
3.3.6 Thermogravimetric Analysis

The thermal stability of PWAC is evaluated by Thermogravimetric Analysis, (TGA) using TA Instruments Q500 HiRes TGA analyzer. Approximately, 5 mg to 10 mg of the samples is heated from 30 °C to 900 °C with the heating rate 10 °C per minute under controlled nitrogen atmosphere.

3.3.7 pH and Conductivity

10 g of carbon sample in 200 ml of distilled water is equilibrated for an hour by agitating at 200 rpm. The supernatant is analysed for pH and conductivity by Elico pH meter (model L1-120) and conductivity meter (model M-180) respectively (ISI 1977, Samson Maria Louis & Sudha 2013).

3.3.8 Moisture Content

5 g of carbon is placed in a petridish and heated in an oven at 110 °C for one hour. After heating and then the petridish is cooled in a dessicator and then weighed. Heating, Cooling and weighing is repeated at 30 minute intervals until the difference between the consecutive weighing is less than 5 mg the loss in weight gives the moisture content (ISI 1977, Samson Maria Louis & Sudha 2013).

Moisture content (%) by mass = \( \frac{100 - (M-x)}{M} \) \quad (3.1)

Where, \( M = \) Mass of the material for test (g)

\( X = \) Mass of the material after drying
3.3.9  **Ash Content**

About 1g of carbon is weighed accurately in a tarred porcelain crucible and placed in a hot air oven at 110 °C for about 5 hours. The crucible is removed from the oven and the contents are ignited in an electric furnace at a temperature of 800 °C for about 2 hours. The process of heating and cooling is repeated until the difference between two sequential weighing is less than 5 mg (ISI 1977, Samson Maria Louis & Sudha 2013).

Ash (on dry basis) % by mass= 10,000 \( \left( \frac{M_1}{M_2} (100-x) \right) \)  

where,  
\( M_1 = \) Mass of the ash(g)s  
\( M_2 = \) Mass of the material for test (g)  
\( X = \) percent moisture content present in the material used for test.

3.3.10  **Apparent Density**

A 50 ml graduated pycometer is weighed. For the determination of apparent density; a trip balance is used to fill the carbon in the cylinder. Sufficient amount of the carbon is poured with constant tapping and filled to the 50 ml mark. The shaker is attached to the balance able to adjusted so that the carbon filled the pycnometer is approximately 1ml/sec. After filling the graduated cylinder with carbon, it is weighed accurately. The apparent density is calculated by dividing the weight of the carbon by 50 (ISI 1977, Samson Maria Louis & Sudha 2013).

3.3.11  **Specific Gravity**

5g of oven dried carbon sample is placed in a small porcelain dish with about 50 ml of distilled water and the contents are heated to boil gently
for 3 minutes to expel the air. After cooling in a water bath to 10 °C the carbon suspension is transferred to a 100 ml pycnometer with the help of a small funnel, a wire and wash bottle. The pycnometer is filled with water and stoppered taking care not to leave any bubble in the container. The pycnometer is dried with a piece of cloth and weighed (Wc) (Wilde et al. 1992).

Specific Gravity = Weight of adsorbent (W_a) / Volume of displaced water (v)  
\[ (3.3) \]

where,  
\[ V = W_a + W_b + W_c / \text{Density of water (1.0)} \]

\[ W_b = \text{Weight of pycnometer with water (g)} \]

\[ W_c = \text{Weight of pycnometer with adsorbent suspension} \]

3.3.12 Decolourising Power

About 0.5 g of carbon material is transferred to a 100 ml conical flask and one ml of Methylene blue solution is added to the conical flask. The contents are shaking till the colour disappears. Again another one ml of methylene blue solution is added to the conical flask and shaking is continued. The process is repeated until the blue colour persists for at least ten minutes. Decolourizing power of carbon is indicate in terms of milligrams of MB adsorbed by one gram of carbon is given by (Wilde et al. 1992),

\[ \text{Decolourizing power (mg/g)} = 1.5 \times \frac{V}{M} \quad (3.4) \]

where,  
\[ V = \text{Volume of methylene Blue solution consumed (ml)} \]

\[ M = \text{Mass of material taken for the test (g)} \]
3.3.13 Ion-Exchange Capacity

About 2 g of carbon is weighed and taken in a beaker and sufficient amount of distilled water is added to cover the carbon. The slurry is carefully transferred to a burette. The column is never allowed to drain completely and the level of the liquid is maintained at about 1 cm above the carbon bed (Wilde et al. 1992).

250 ml of a solution of 0.25 M sodium sulphate is allowed to drip into the column at a rate of 2 ml/min and the effluent is collected in 500 ml conical flask. When all the solution has passed through the column, the effluent is titrated against 0.1N sodium hydroxide solution using phenolphthalein as indicator. Ion exchange capacity of the bed in milliequivalents/gram is given by NV/W,

where,

\[ N = \text{Normality of the sodium hydroxide solution} \]
\[ V = \text{Volume in ml} \]
\[ W = \text{Weight of carbon} \]

3.3.14 Matter Soluble in Water

5 grams of the carbon material of known moisture content is weighed accurately and transferred to a one litter beaker. About 300 ml of distilled water is added and heated (up to boiling) with continuous stirring. Stirring is continued for 5 minutes after the flame is removed. The material is then allowed to settle. The supernatant is filtered through a gouch crucible fitted with an asbestos mat. The procedure is repeated thrice with the residue in the beaker using 300 ml of water each time. The combined filtrate is
concentrated to less than 100 ml of a water bath, cooled and made upto 100 ml mark in a volumetric flask.

Exactly 50 ml of the concentrate is transferred to a china dish in an electric oven, maintained at 100 ± 5°C, cooled in a dessicator and weighed. The procedure of drying and weighing is repeated at 30 minutes interval (ISI 1977).

Matter soluble in water (\%) = \frac{20,000 \times M_1}{M_2(100-X)} \hspace{1cm} (3.5)

where,

- \( M_1 = \) mass of the residue (g)
- \( M_2 = \) mass of the material taken for test (g)
- \( X = \) percent of moisture present in the material

3.3.15 Matter Soluble in Acid

5g of the carbon material of known moisture of known content is weighed accurately and transferred into a one litre beaker. Stirring is continued for 5 minutes after the flame is removed. The supernatant is filtered through a gouch crucible fitted with an asbestos mat. The procedure is repeated thrice with the residue in the beaker using 300 ml of acid each time. The combined filtrate is concentrated to lesser than 100 ml over a water bath, cooled and the contents are transferred to a china dish and evaporated to nearly dryness on a boiling water bath and finally dried in an electric oven, maintained at 100 ± 5°C, cooled in a dessicator and weighed. The procedure of drying and weighing is repeated at 30 minute interval, until the difference between the consecutive weighing is less than 5 mg (ISI 1977).

Acid soluble matter (\%) = \frac{20,000 \times A}{M(100-X)} \hspace{1cm} (3.6)

where,

- \( A = \) mass of the dried residue (g)
$M =$ mass of the material taken for test (g)

$X =$ percent of moisture present in the material

### 3.3.16 Phenol Adsorption Capacity

0.1 g of carbon is accurately weighed in a 100 ml conical flask and agitated for 3 hours with 25 mg / litre phenol. Absorbance is measured at 270 nm before and after the phenol (percent) removal is calculated (Economy & Lin 1976).

\[
\text{\% Removal} = \frac{B.T - A.T \times 100}{B.T}
\]  

(3.7)

where,  
\begin{align*}
B.T &= \text{Absorbance before treatment} \\
A.T &= \text{Absorbance after treatment}
\end{align*}

### 3.3.17 Determination of Oxygen Containing Functional Groups

About 1.0 g of the PWAC is kept in contact with 15 ml solution of NaHCO$_3$ (0.1M), Na$_2$CO$_3$ (0.05M) and NaOH (0.1M) for acidic groups and 0.1M HCl for basic groups respectively at room temperature for 2 days. Subsequently, the aqueous solutions are back titrated with HCl (0.1M) for acidic and NaOH (0.1M) for basic groups. The number and type of acidic sites are calculated by considering that (Boehm 2002 & Rajeshwar et al. 2012)

- NaOH neutralizes carboxylic, lactonic and phenol groups,
- Na$_2$CO$_3$ neutralizes carboxylic and lactonic groups and
- NaHCO$_3$ neutralizes only carboxylic groups.

Carboxylic groups are therefore quantified by direct titration with NaHCO$_3$. The difference between the groups titrated with Na$_2$CO$_3$ and those
titrated with NaHCO₃ is assumed to be lactones and the difference between
the groups titrated with NaOH and those titrated with Na₂CO₃ is assumed to
be phenol. Basic sites are determined by titration with HCl.

Neutralization points are known using pH indicator of
phenolphthalein solution for the titration of strong base and strong acid,
methyl red solution for weak base with strong acid and pH together. In order
to neutralize basic groups, remaining HCl in the solution is back titrated with
0.1M NaOH.

3.4 OPTIMUM CONDITIONS FOR THE PRODUCTION OF
ACTIVATED CARBON

In this study, efficiency and quality of the activated carbon are
preliminarily characterized by measuring both iodine and methylene blue
number. Iodine number can be used for estimation of the relative surface area
and measurement of porosity, the pores size greater than 1.0 nm in diameter.
Therefore, the iodine number is measured to evaluate the adsorptive capacity
of the produced activated carbon. In case of methylene blue number, it is also
one of the most widely recognized probe molecules for assessing the removal
capacity of the specific carbon for moderate size pollutant molecules
(≥1.5 nm) (Girgis 2002).

3.4.1 Adsorption of Iodine

The iodine number of activated carbon is obtained on the basis of
the Standard Test Method; ASTM Designation D4607-86 by titration with
sodium thiosulphate (Haimour & Emeish 2006). The concentration of iodine
solution is thus calculated from volume of sodium thiosulphate used and
volume dilution factor.
The prepared activated carbon is characterized by its adsorptive capacity of iodine, which is referred to as iodine number. The iodine number is defined as the milligrams of iodine adsorbed by 1 g of carbon when the iodine concentration of the residual filtrate is 0.02 N (Robinson & Hansen 1978). The procedure of the iodine number determination procedure is as follows:

- A dry sample of the activated carbon is weighed and added to 10 ml of 5% HCl acid and then mixed until the carbon sample is wetted then the mixture is boiled for 30 minutes then cooled.
- 100 ml of standardized iodine solution of normality N1 is added to the mixture and the contents are shaken for 30 minutes and then filtered through Whatmann No. 42 filter paper.
- A volume of 50 ml of the filtrate is titrated with standardized 0.1 N sodium thiosulfate solution and using starch as indicator.
- The amount of iodine adsorbed = N1*100 - N2*V*110/50 g mol. (3.8)
- The iodine number of the activated carbon is then calculated by using the following equation:

\[ \text{Iodine Number} = \frac{X}{m} A \] (3.9)

Where A is the obtained correction factor after the calculation of the residual filtrate normality, m the weight of activated carbon in grams, X is the weight of adsorbed iodine in milligrams and is given by:

\[ X = \{(N_1 - 100) - [(N_2 - V - 110)/50]\} 126.93 \] (3.10)
Where, $N_1$ is the normality of iodine solution, $N_2$ is the normality of thiosulfate solution and $V$ is the volume of thiosulfate solution used for titration.

The percentage yield of activated carbon is calculated as:

$$\% \text{Yield} = \frac{\text{weight of the final product}}{\text{weight of the impregnated powder} - \text{weight of the used reagent impregnated}}$$

(3.11)

### 3.4.2 Adsorption of Methylene Blue

By batch experiment, methylene blue (MB) solution is mixed with activated carbon and shaken (200 rpm) at room temperature. After the reaction completed, the solutions are filtered and the concentrations of methylene blue solution are then determined by an Agilent 8453 UV-Vis spectrophotometer (Germany) at 663 nm. The equilibrium adsorption capacities ($q_e$) of the activated carbon are determined based on adsorbate mass balance using equation (Rajeshwar et al. 2012).

$$q_e = \frac{(C_0 - C_e)V}{M}$$

(3.12)

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of the dye (mg/L), respectively, $V$ is the volume of the aqueous solution (L) and $M$ is the mass of activated carbon used (g).

### 3.5 Determination of Dye Concentration

The dye adsorbed adsorbent after equilibrium time is separated by centrifugation and the quantity of dye adsorbed is determined by using a UV-Visible spectrophotometer, spectronic 21D model, in the respective $\lambda_{\text{max}}$ of
each dye. The percentage of dye adsorption is calculated from the absorbance value before and after treatment.

The quantity of the dyes adsorbed is determined by the following equation (Hitchcock et al. 1983).

\[
Q_e = (C_o - C_f) V/ W
\]

3.6 MEASUREMENT OF PH

A digital pH meter (Elico) is used for the pH measurement. The pH meter is standardized by using potassium hydrogen phthalate (pH 4.01) and sodium borate (pH 9.18) as buffers.

3.7 ESTIMATION OF PARTICLE SIZE OF ADSORBENTS

Sieve analysis is done by electronic sieve machine (Lynx) M/s Lawrence & Mayo, India. 1 kg of the sample is taken into it and shacked exactly for 5 sec. Test sieves of desired mesh size is used for this purpose. Particles left in mesh is taken and weighed. This is repeated three times and the mean value is taken. Test sieves of different mesh size are obtained from Geologists Syndicate Limited, Calcutta, West Bengal, India.
3.8 ISOTHERM STUDIES

Batch experiments are so designed as to cover equilibrium studies. A 100 ml dye solution of various concentrations 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150, mg/litre) are prepared and each is treated with 1g of the adsorbent and equilibrated for a period of 24 hours with stirring. The different parameters such as temperature and particle size are varied with constant pH of 6.5.

3.9 KINETIC STUDIES

A 100 ml dye solution of concentration 20 mg/L is treated with 1 g of the adsorbent materials over a period of time with constant stirring. The following parameters are studied to elucidate the kinetics of adsorption.

**Effect of initial concentration:** 20 mg/L, 40 mg/L and 60 mg/L at constant temperature (30 ºC), pH (6.5) and particle size (75-180 microns).

**Effect of temperature:** 30 ºC, 45 ºC and 60 ºC at constant pH (6.5) and particle size (75-180 microns).

**Effect of pH:** 5, 6.5 and 8 at constant temperature (30 ºC) and particle size (75-180 microns).

**Effect of adsorbent particle size:** 75-180 microns, 180-250 microns and 250-355 microns at constant temperature 30 ºC and pH 6.5.

**Desorption studies:** For this one gram of the dye adsorbed material is treated with 100 ml of double distilled water, desorbing agents like H$_2$SO$_4$, NaOH (0.5 N, 1N and 2.0 N) and 50% CH$_3$COOH respectively and possible desorption is studied keeping all other parameters constant.
3.10  ERROR ANALYSIS

The optimization provides method for determining isotherms and kinetics parameter values. Error function assessment is used to evaluate the fit of the isotherms and kinetics to the experimental results. In this study eight linear error functions such as sum squares errors (SSE), sum of absolute error (EABS), average relative error (ARE), linear chi-square test ($\chi^2$), root mean square error (RMSE), Marquardt’s percent standard deviation (MPSED), hybrid fractional error function (HYBRID) and F-Test is operated and it’s fitness to the experimental results were analysed.