CHAPTER 3
RESEARCH METHODOLOGY / MATERIAL AND METHODS

In this chapter, experimental details including preparation and activation of adsorbent, adsorption model and physico-chemical techniques employed for studying the characteristics of adsorbent as well as adsorption process are given.

3.1 Materials
The chemicals and reagents used in the study were purchased from Modern Scientific Instrument company, Agra. The chemicals and reagents used in the present study such as Potassium Iodide, Iodine crystals, Sodium Thiosulphate, Starch as an indicator, Potassium Dichromate \( \{K_2Cr_2O_7\} \), Ferrous Ammonium Sulphate \( \{Fe(NH_4)_2 SO_4\} \), Silver Sulphate, Pheanthroline, Ferrous Sulphate, Mercuric Sulphate, Concentrated Sulphuric acid, Concentrated phosphoric acid, Sodium Carbonate for the preparation of adsorbent and adsorbate were of AR Grade. Analytical grade of Sodium hydroxide and hydrochloric acid were used for pH adjustment. Distilled and Deionized water were used for dust and impurity removal. Cutting oil (act as coolant in machining operations) was IPOL Aqua cut 125 manufactured by IPOL lubricants, Mumbai, India were purchased and used for the preparation of oil-water emulsion which is further used as effluent (WCFs). Some Agro-waste material such as de-oiled mustard cake, pomegranate peel waste, pumpkin seed waste were collected from local market/area for preparation of adsorbents.

3.2 Adsorbate Preparation
Commercial metal cutting fluid used in this study is IPOL Aqua Cut 125 manufactured by IPOL lubricants, Mumbai, India. This is an emulsifiable coolant which prevents rusting of work piece, machine tool beds and provides even surface for working. The fluid generated by the use of this coolant or cutting oil in machining processes, is called waste cutting fluids (WCFs) present in machining
waste water. Therefore, we have used prepared oil in water emulsion instead of real waste effluent for examining the adsorption of cutting oil from aqueous solution. Oil in water emulsions of 0.5-3.0% concentration range were prepared by making the solution of required volume percent (v/v %) of oil with deionized water up to 1000 ml in a round bottom flask. For stabilization of emulsion it must be blended in an electric mixer at a high speed with 20000rpm for 15-20 min. Finally the oil in water emulsions were appeared milky white and having pH 8-9. The density of oil at 30°C was 0.824g/cm³ determined by weighing a known volume of oil in a pycnometer. Viscosity of oil was 0.033pa.s measured according to ASTM D445. According to the company’s manual the ash % wt. of Aqua Cut 125 cutting oil is 0.865 measured by ASTM D482.

3.3 Adsorbent Preparation
The various agro-waste materials such as Pomegranate peel, Pumpkin Seed waste, De-oiled mustard cake were collected from local market.

3.3.1 Preparation of Pomegranate peel Activated Carbon
Pomegranate peel (PGP) was cut into small pieces, wash with distilled and then deionized water for removal of dirt, water soluble bio-molecules. The pieces of PGP were then dried in sunlight after that in an air oven at 100°C for 2-3 hr. until the residual moisture was completely evaporated and showed constant weight. After drying PGP pieces were grounded to a fine powder and made homogeneous through 90-300μm sieve and retained the 100μm sieve and preserved in desiccators for activation process. There are two methods for activation of raw material which increases remarkably the surface area of the adsorbents: Physical activation, Chemical activation
Here we use the chemical activation process for the activation of PGP. Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride and zinc chloride 25%). Then, the raw material
is carbonized at lower temperatures (450–900 °C). It is believed that the
carbonization / activation step proceeds simultaneously with the chemical activation.
We have preferred chemical activation over physical activation owing to the lower
temperatures and shorter time needed for activating material. Therefore, dried PGP
material were treated with concentrated H$_2$SO$_4$ or concentrated H$_3$PO$_4$ acid in the
ratio 1: 2.8 by weight and kept in an air oven at 185°±5°C for 24 h. The carbonized
material was cooled and washed several times with deionized water. After washing it
was soaked in 1% NaHCO$_3$ solution for 12h for removal of residual acid and again
washed with deionized water until the pH<7 was reached. Then the material was
dried at 105°±5°C for 7-8h up to constant weight and labelled as PGAC for further
adsorption procedure.

3.3.2 Preparation of Pumpkin SeedwasteActivated Carbon
Pumpkin seed were first dehulled manually and the waste (seed hull) was first wash
with distilled and then deionized water for removal of dirt, water soluble bio-
molecules and then cut into small pieces. The pieces of PSW were then dried in
sunlight after that in an air oven at 100°C for 2-3 hr. until the residual moisture was
completely evaporated and showed constant weight. After drying PSW pieces were
grounded to a fine powder and made homogeneous through 90-300μm sieve and
retained the 100μm sieve and preserved in desiccators for activation process. There
are two methods for activation of raw material which increases remarkably the
surface area of the adsorbents: Physical activation, Chemical activation

Here we use the chemical activation process for the activation of PSW. Prior to
carbonization, the raw material is impregnated with certain chemicals. The chemical
is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide,
sodium hydroxide, calcium chloride and zinc chloride 25%). Then, the raw material
is carbonized at lower temperatures (450–900 °C). It is believed that the
carbonization / activation step proceeds simultaneously with the chemical activation.

We have preferred chemical activation over physical activation owing to the lower
temperatures and shorter time needed for activating material. Therefore, dried PSW
material were treated with concentrated H$_2$SO$_4$ or concentrated H$_3$PO$_4$ acid in the
ratio 1: 2.8 by weight and kept in an air oven at 185º±5ºC for 24 h. The carbonized material was cooled and washed several times with deionized water. After washing it was soaked in 1% NaHCO₃ solution for 12h for removal of residual acid and again washed with deionized water until the pH<7 was reached. Then the material was dried at 105º±5ºC for 7-8h up to constant weight and labelled as PSAC for further adsorption procedure.

3.3.3 Preparation of De-oiled Mustard cake Activated Carbon

De-oiled mustard cake was crushed into small pieces. Then material was washed with distilled water continuously and then with deionized water for removal of dirt particles and water soluble bio-molecules. After thoroughly washing material were dried in sunlight until the moisture was partially evaporated and was further dried in hot air oven at 70-100ºC for 3-4h until the residual moisture was completely evaporated showed constant weight. The activated carbon of agro-waste materials were produced by using the method reported elsewhere (Ramakrishnan et al., 2009). The dried material was grounded to a fine powder and made homogeneous through 90-300μm sieve and retained the 100μm sieve and preserved in desiccators for the activation use. They were carefully labelled as as DMC.

Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride and zinc chloride 25%). Then, the raw material is carbonized at lower temperatures (450–900 ºC). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. We have preferred chemical activation over physical activation owing to the lower temperatures and shorter time needed for activating material. Therefore, dried raw material were treated with concentrated H₂SO₄ or concentrated H₃PO₄ acid in the ratio 1: 2.8 by weight and kept in an air oven at 185º±5ºC for 24 h. The carbonized material was cooled and washed several times with deionized water. After washing it was soaked in 1% NaHCO₃ solution for 12h for removal of residual acid and again washed with deionized water until the pH<7 was reached. Then the material was
dried at 105°C±5°C for 7-8h up to constant weight and labelled as DMAC for further adsorption procedure.

3.4 Characterization of adsorbent
The rate of the removal of pollutants from wastewater using adsorbent is significantly affected by the physico-chemical nature of the adsorbent. Hence the relevant physico-chemical characteristics of activated carbons of agro-waste materials were measured by following methods. The detailed physical characteristics of adsorbents are given in Table 3.1.

3.4.1 Moisture Content
Thermal drying method was used in the determination of moisture content of the samples. Dried activated carbons of amount 1.0 g were weighed three times and placed in clean weighed crucible. The crucibles were placed in an oven and dried at 105°C to constant weight for 4h according to the method of Rengaraj et al., (2002). The percent moisture content (%MC) was computed as follows:

\[
\text{Moisture (％)} = \frac{\text{loss in weight on drying (g)}}{\text{initial sample weight}} \times 100
\]

3.4.2 Carbon Yield
The total yields were determined after sample processing in terms of raw material mass. The dried weight (W_o) of each pre-treated sample was determined using Metler balance and the carbon yield as:

\[
Y(％) = \frac{W}{W_o} \times 100
\]

Where, Y = Carbon yield (％); w = dried weight of AC prepared; W_o = pre-treated sample used in the carbonization and activation processes.

3.4.3 Iodine Number
Many carbons preferentially absorb small molecules. Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg/g (typical range 500–1200 mg/g). It is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine.
from solution. It is equivalent to surface area of carbon between 900 m²/g and 1100 m²/g. It is the standard measure for liquid phase applications. The iodine number was tested according to Gimba et al. (2007). A stock solution was prepared containing 2.7 g of iodine crystals and 4.1 g of potassium iodide per litre. The prepared stock solution was standardized using a standardsolution of sodium thiosulphate. Into a 100 cm³ volumetric flask, 0.5 g of the activated carbon and 10 cm³ of 5% v/v hydrochloric acid was introduced. The flask was swirled until the carbon was wetted. Then 100 cm³ of the stock iodine solution was added and agitated at a fast speed, using an electric shaker for a period of 60 min. The mixtures were filtered through a sintered glass crucible. An aliquot portion (20 ml) was titrated with 0.1 M sodium thiosulphate using starch as indicator. The concentration of iodine adsorbed by the activated carbon at room temperature was calculated as amount of iodine adsorbed in milligrams by the following equation:

\[
\frac{m g}{g} = \frac{B - S}{B} \times \frac{V M}{W} \times 253.81
\]

Where, B and S are the volumes of thiosulphate solution required for blank and sample titrations respectively. W is the mass of activated carbon sample, M is the concentration of the iodine solute, 253.81 is the atomic mass of iodine and V is 20 ml aliquot.

### 3.4.4 Pore (Void) Volume Determination

Each activated carbon sample of 1 g was immersed in water and boiled for 15 min. in order to displace air from the pores. The samples were superficially dried and reweighed. The pore volume was calculated as increase in weight divided by the density of water at 20°C using equation:

\[
PoreVolume = \frac{\text{increase in weight}}{\text{density of water}}
\]

### 3.4.5 Bulk Density

A cylinder and an aluminium plate were each weighed. A sample of activated carbons were put into the cylinder and reweighed. The samples were transferred into the aluminium plate and put into an oven so as to dry it to constant weight at a
temperature of 105°C for 1h. The weight of the dried samples was taken again after drying. A clean dry well corked density bottle was weighed. The bottle was filled with water, corked and reweighed, small quantities of samples of activated carbons were taken and ground to powder, sieved using 106μm and gradually put into the bottle with little amount of water and weighed again. The bulk density and dry density were calculated using the following expressions:

\[
\text{Bulk density} = \frac{\text{mass of wet sample}}{\text{mass of volume}}
\]

\[
\text{Dry density} = \frac{\text{mass of dry sample}}{\text{volume of cylinder}}
\]

### 3.4.6 Surface Area

Surface area for adsorbents were determined by B.E.T. method using low temperature N\(_2\) gas adsorption. Brunauer et al. (1938) derived an equation known as B.E.T equation by applying the Langmuir treatment to the concept of multilayer physical adsorption of gas molecules. By adsorption of N\(_2\) gas on adsorbent (activated carbons), the surface area of adsorbent can be obtained with the help of this equation. The B.E.T equation is:

\[
\frac{\frac{P}{V(P_0 - P)}}{V m C} = \frac{1}{V m C} + \frac{C - 1}{V m C} \frac{P}{P_0}
\]

Where, \(V\) = the volume of gas adsorbed at the pressure \(P\)

\(V_m\) = the volume adsorbed when the surface of the adsorbent is covered with a single layer of molecules

\(C\) = constant approximately equal to \(e^{(E_1 - E_L)RT}\)

\(E_1\) = the heat evolved in the adsorption of the first layer of gas molecules

\(E_L\) = the heat of condensation of the gas to liquid

### Table 3.1 Quantitative characterization of prepared activated carbons for the present study

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>PSAC</th>
<th>PGAC</th>
<th>DMAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Content</td>
<td>5.2%</td>
<td>2%</td>
<td>5.7%</td>
</tr>
<tr>
<td>Carbon Yield</td>
<td>34%</td>
<td>39%</td>
<td>3%</td>
</tr>
</tbody>
</table>
### Table 3.1: Relevant physico-chemical characteristics of adsorbents

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>PGAC</th>
<th>PSAC</th>
<th>DMAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine Number</td>
<td>348</td>
<td>745</td>
<td>263</td>
</tr>
<tr>
<td>Pore volume/porosity</td>
<td>0.352cm$^3$/g</td>
<td>87.80%</td>
<td>36.6%</td>
</tr>
<tr>
<td>Surface Area</td>
<td>567.75m$^2$/g</td>
<td>820m$^2$/g</td>
<td>28.2m$^2$/g</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>0.782g/ml</td>
<td>0.346g/cm$^3$</td>
<td>0.869g/ml</td>
</tr>
</tbody>
</table>

On plotting a adsorption curve between $P/V(P_0-P)$ vs. $P/P_0$ by using B.E.T equation, from the slope and intercept, the value of $V_m$ can be obtained. From the known molecular diameter and assuming close packing in the unimolecular layer, the surface area of the adsorbent can be calculated.

Agricultural waste materials such as Pomegranate peel waste, Pumpkin seed waste and De-oiled mustard cake have been used as raw material for the preparation of activated carbons such as PGAC, PSAC and DMAC respectively as adsorbents in the present study. The relevant physico-chemical characteristics of these adsorbents including bulk density, particle size, surface area and other morphological characteristics have been evaluated experimentally for all the above mentioned adsorbents used in this work.

The physical characteristics of all the prepared adsorbents studied are given in table 3.1. The iodine number and porosity of activated carbons are inter-related. For high surface area carbons (>900m$^2$/g), the iodine number is numerically similar to the BET surface area measurements, whereas for low surface area active carbons, the above correlation of surface area with iodine number falls away. The results obtained here are consistent with this statement. A high degree of iodine number indicates a higher surface area and large micro-porous structure (Gergova et al., 1993). Therefore, it can be predicted that pomegranate peel activated carbon (PGAC) will prove to be better adsorbent than other two. Carbon yield percentage decreases in the order Pomegranate peel activated carbon > Pumpkin seed waste activated carbon > De-oiled mustard cake activated carbon and will also having decreasing adsorption capacity.

### 3.5 Proximate and ultimate analysis
Proximate and ultimate analysis was used to characterize the activated carbon. Experimental techniques regarding Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermo gravimetric studies were also done.

### 3.5.1 X-Ray Diffraction Study

X-Ray diffraction study (XRD), a structural determining method in which powder diffraction diagram, produced by a crystalline substance, is characteristics of that substance. The powder method can be used as a means of identification of crystals as well as relative orientations of the individual crystals. The scattering power of an atom for X-ray depends on the number of electrons it possesses. Thus the position of the diffraction beams from a crystal depends only on the size and shape of the repetitive unit of a crystal and the wavelength of the incident X-ray beam. The intensities of the diffracted beams depend on the type of atoms in the crystal and the location of the atoms in the fundamental repetitive unit cell. No two substances, therefore, have absolutely identical diffraction patterns when one considers both the direction and the intensity of all diffracted beams. However, some similar, complex organic compounds may have almost identical patterns. The diffraction pattern is thus a fingerprint of a crystalline compound and the crystalline components of a mixture can be identified individually (Willard et al., 1986).

Any non-crystalline solid or liquid with short-range molecular order and no long-range molecular order will give rise to an X-Ray amorphous powder pattern e.g. glassy material. A number of general material properties can be determined through direct analysis of the X-ray amorphous powder pattern. Due to the nature of random packing in the solid state, a randomly packed material will give X-ray amorphous halos.

X-ray diffraction study for nature of prepared activated carbons from agro-waste materials was carried out using Philip’s Analytical Instrument (40 kW/30 mA) from 0° to 80° (2θ) ranges.

Researchers worked on X-ray diffraction analysis of activated carbons, concluded that predominantly amorphous solid having large internal surface area and pore
volume (Nurul, 2007). It found that activated carbon showed very disordered microcrystalline structure in which graphitic microcrystals are randomly oriented (Mohamed et al., 2010). Fig. 3.1, Fig.3.2 and Fig 3.3 illustrate the XRD pattern of the prepared activated carbons PGAC, PSAC and DMAC respectively. In Fig. 3.1, two weak diffraction maxima indicated that the content of ordered crystalline phase is negligible and the present cellulose in Pomegranate Peel is broken by sulfuric acid to form amorphous carbon (PGAC) and showed broad asymmetric peaks corresponding to $2\Theta \sim 21.5^\circ$ and $2\Theta \sim 27^\circ$.

![Fig. 3.1. X-Ray diffraction pattern of PGAC](image)
Fig. 3.2. X-Ray diffraction pattern of metal PSAC
Fig. 3.3. X-Ray diffraction pattern of DMAC

In Fig 3.2., the activated carbon PSAC exhibited broad peak at around $2\Theta$~25° reveals the breaking of chemical bonds in organic compounds present in material and condensing into active compounds (Lua et al., 2004). In Fig. 3.3., the appearance of a broad peak at $2\Theta$~24° indicated that the silica present in DMAC was amorphous in nature (Mopoung, 2008). It was concluded that XRD patterns for each activated carbons indicated a shape of typical amorphous carbon.

The XRD analyses show that the activated carbon prepared from Pomegranate peel, Pumpkin seed waste and De-oiled mustard cake were clearly formed in amorphous state. Metal cutting oil was adsorbed on these activated carbons. This statement was supported by the XRD patterns of activated carbon after adsorption of cutting oil show in Fig. 3.4, Fig.3.5 and Fig.3.6. From these figures the nature of adsorbents remain amorphous same as earlier whereas the position of broad peaks show the different and increased value of $2\Theta$. XRD pattern shows in Fig.3.4 the broad peak of oil loaded PGAC have $2\Theta$~22° & $2\Theta$~42.5° and Fig. 3.5 shows peak at $2\Theta$~26° in PSAC after oil adsorption. The oil loaded DMAC in Fig.3.6 shows a little deviation in nature of adsorbent with a sharp peak at $2\Theta$~27° reveals the partial crystalline nature of adsorbent.
Fig. 3.4. X-Ray diffraction pattern of metal cutting oil loaded PGAC

Fig. 3.5. X-Ray diffraction pattern of metal cutting oil loaded PSAC
3.5.2. Fourier Transform Infrared Radiation (FTIR) Spectral Study

FTIR is one of the most widely used tools for the detection of functional groups in pure compounds and mixtures. IR spectrum of solid sample is obtained in minute quantities using a few mg of the compound together with KBr pallets. Organic compound absorb electromagnetic energy in the infrared region of the spectrum. Infrared radiation does not have sufficient energy to cause the excitation of electrons; however, it causes atoms or groups of atoms of organic compound to vibrate faster about the covalent bonds which connect them. The position of the infrared absorption band is specified in frequency unit by wave number (cm\(^{-1}\)). Each dip in a spectrum called a band or peak represents absorption of IR at that frequency by the sample. A 100% transmittance means no adsorption and if all the radiations are absorbed the transmittance is 0% (Kalsi, 2004).

The infrared region 4000cm\(^{-1}\)-400cm\(^{-1}\) is useful for structural information of organic compounds. This region is split into two parts, 4000cm\(^{-1}\)-1300cm\(^{-1}\) the high frequency part i.e. the functional group region and the low frequency part 1300cm\(^{-1}\)-650cm\(^{-1}\) i.e. the fingerprint region.
Fourier Transform Infrared Spectra (KBr pallets) of AC and oil loaded AC was measured in a Perkin Elmer Spectrum version 10.03.05 instrument using potassium bromide (KBr) pellet for wavelength ranged from 4000 to 400 cm$^{-1}$. FT-IR spectra were obtained with dried powdered samples recorded as KBr disks on a Perkin Elmer Spectrum version 10.03.05 Fourier Transform Infrared Spectrophotometer. Approximately 1mg samples were mixed in a matrix of KBr (100 mg) and pressed to form pellets.

Fig.3.7, Fig.3.8, Fig.3.9, Fig.3.10 illustrate the functional groups and surface properties of the adsorbent by FTIR spectrum. The spectra of the adsorbents are as evidenced by the presence of a large number of peaks. The peaks obtained at 3428cm$^{-1}$, 3418cm$^{-1}$, 3424cm$^{-1}$ in following Figures indicate the presence of O-H group. In fact on hydrogen bonding the frequency of O-H stretching is broadened and lowered to around 3300cm$^{-1}$ as compared to free O-H group which gives a sharp absorption peak as high as 3600cm$^{-1}$ (Kalsi, 2004). The peaks in the range 3000cm$^{-1}$ – 2840cm$^{-1}$ represent the absorption arising due to C-H stretching. Peaks at 2959cm$^{-1}$ due to –CH$_3$ asymmetric stretching vibrations, 2926cm$^{-1}$ due to –CH$_2$ asymmetric stretching vibrations and 2856cm$^{-1}$ due to –CH$_2$ symmetric stretching arise. Peaks at 1458cm$^{-1}$, 1447cm$^{-1}$ in Fig.3.9, Fig.3.10 are due to –CH$_2$ symmetric bending and –CH$_3$ asymmetric bending. The peaks in the range 1630-1600cm$^{-1}$ of H-O-H bending mode show the presence of lattice water in adsorbent and N-H bending vibrations of primary amines is observed with the peak at 1628cm$^{-1}$. 
The most characteristic absorption of poly-nuclear aromatics results from C-H out of plane bending vibrations of αβ-substituted naphthalene of 4 adjacent hydrogens at 759cm\(^{-1}\) – 742cm\(^{-1}\) frequency. These bands can be correlated with the number of adjacent hydrogen atoms on the ring. Strong absorption due to asymmetrical C-O-C stretching in vinyl ethers occurs in the 1228cm\(^{-1}\) with a strong symmetrical band at 1041cm\(^{-1}\) or 1042cm\(^{-1}\) (1075-1020cm\(^{-1}\) range) (Silverstein et al., 1981). 1072cm\(^{-1}\) – 1040cm\(^{-1}\) wave number is associated with the C-O stretching due to presence of cellulose, hemicellulose and lignin content in the activated carbon (Adebejo et al., 2004).
Fig. 3.8. FTIR Spectrum of Pomegranate peel Activated Carbon

Fig. 3.9. FTIR Spectrum of PSAC adsorbent
The FTIR spectra of adsorbents (PGAC, PSAC and DMAC) after metal cutting oil adsorption are shown in Fig. 3.11, Fig. 3.12 and Fig.3.13. Each and every spectrum
contains the peaks at $1123\text{cm}^{-1}$ because of asymmetrical C-O-C stretching. The presence of peak at $1273\text{cm}^{-1}$ shows C-O-C asymmetric stretching of aryl alkyl ether group and the peak at $1382\text{cm}^{-1}$ shows the aldehydic C-H bending vibration.

Fig. 3.12. FTIR of metal cutting oil loaded PSAC adsorbent
The carboxylate ion of a carboxylic acid gives rise to 2 bands: a strong asymmetric stretching band near 1650-1550 cm\(^{-1}\) (at 1629 cm\(^{-1}\)) and a weaker symmetrical stretching band near 1400 cm\(^{-1}\). C-N stretching band of primary amide also occurs near 1400 cm\(^{-1}\), this reveals the attachment of amido group at the surface. The presence of peak at 1458 cm\(^{-1}\) and 743 cm\(^{-1}\) are due to CH\(_2\) deformation and C-H out of plane bending. Possibility of benzoates absorb at 1729 cm\(^{-1}\) due to conjugation of an aryl group or other unsaturation with the carbonyl group causes this C=O stretch to be lower than normal frequency. A weak peak visible at 2359 cm\(^{-1}\) corresponds to the stretching vibration of the C-O for carbon mono-oxide or carbon dioxide derivatives.

The results shows that some peaks are shifted and new peaks are also appeared. The differences in peak position and intensity in the spectra suggested the attachment of new functional groups of metal cutting oil adsorbed at the surface of adsorbents.

3.5.3. Scanning Electron Micrograph (SEM) Analysis

SEM technique in the present study is used to determine the surface structure and texture of the used sample before and after adsorption of metal cutting oil. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology or texture, chemical composition, crystalline structure and orientation of materials making up the sample and a two dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques. The SEM is also capable of performing analyses of selected point locations on the sample, this approach is especially useful in quantitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientations. Sample preparation can be minimal or elaborate for SEM analysis, depending on the nature of the samples and the data required. Minimal preparation includes acquisition of a sample that will fit into the SEM
chamber and some accommodation to prevent charge build-up on electrically insulating samples. Most electrically insulating samples are coated with a thin layer of conducting material, commonly carbon, gold, or some other metal or alloy. The choice of material for conductive coatings depends on the data to be acquired; carbon is most desirable if elemental analysis is a priority, while metal coatings are most effective for high resolution electron imaging applications. Alternatively, an electrically insulating sample can be examined without a conductive coating in an instrument capable of "low vacuum" operation.

The surface morphology of the AC before and after metal cutting oil adsorption was examined with a SEM (Model: Zeiss EVOMA 10). The samples were mounted onto a SEM holder with double-sided electrically-conducting carbon adhesive tabs to prevent the surface of the specimens when exposed to the electron beam. The samples were then coated with a silver foil, set at a voltage 20kV.

Fig. 3.14. SEM image of PGAC adsorbent
There are represented the SEM images of prepared activated carbon from Pomegranate peel waste (PGAC), Pumpkin seed waste (PSAC) and de-oiled mustard cake (DMAC) in the figure numbered Fig. 3.14, Fig.3.15 and Fig.3.16 respectively. The figures show clear fine pores and cavities visible within the microstructure of activated carbons and the well-developed pores in activated carbons possessed high surface area. These figures also showed that the external surfaces of these carbons are full of cavities and quite irregular as a result of activation. It is clear from the Fig.3.17, Fig.3.18 and Fig.3.19 of metal cutting oil loaded adsorbents (PGAC, PSAC and DMAC respectively), that the adsorbents have sufficient numbers of pores on a rough and snare type structure surface where the oil droplets are easily trapped and a layer of adsorbed cutting oil has spread over the surface of adsorbents. These figures also show that the numbers of cavities on the adsorbent surface are decreased after adsorption of metal cutting oil.

Fig.3.15. SEM image of PSAC adsorbent
Fig.3.16. SEM image of DMAC adsorbent
Fig. 3.17. SEM image of PGAC with adsorbed metal cutting oil
Fig. 3.18. SEM image of PSAC with adsorbed metal cutting oil
3.5.4. Thermal Gravimetric Analysis

The Thermal degradation behavior of the prepared activated material and the material after adsorption was studied using a Perkin Elmer thermal analyzer (TGA). This study will focus on the thermal characteristics of the sorbents in the form of kinetic parameters of the thermal degradation and also for desorption experiments. Experiments were conducted in the temperature range of 30°C- 995°C under a N₂ gas flow at 20ml/min and at scanning rate 10°C/min. Weight loss and the rate of weight change were measured against the time and temperature of the placed in a muffle furnace.

3.6 Adsorption Process

There are two type of adsorption process used.

1. Batch adsorption process
2. Continuous adsorption process

3.6.1 Batch Adsorption Process
Batch adsorption consists of contacting finely divided activated carbon with the adsorbate solution for a given period of time in a mixing vessel. The experiments of batch adsorption process were performed for the determination of adsorption isotherm of adsorbate solution onto the adsorbent in glass flask. The flasks were shaken at a constant rate, temperature, pH for sufficient time up to equilibrium takes place. We separate adsorbent from the vessel time to time and find out the equilibrium concentration of the adsorbate solution. The amount of metal adsorbed per unit mass is calculated as:

\[ Q_e = \frac{(C_i - C_e)V}{m} \]

Where \( C_i \) and \( C_e \) are the initial and equilibrium concentration of adsorbate solution, \( m \) is the mass of the adsorbent and \( V \) is the volume of the solution. Percent removal (%R) of adsorbate solution was calculated using the equation:

\[ \%R = \frac{(C_i - C_e)}{C_i} \times 100 \]

Some researchers have been reported adsorption of spilled oil, synthetic cutting fluid, spent cutting fluid, emulsified oil, mineral oil through batch adsorption process by using chitosan (Piyamongkala et al. 2008), SDS modified barley straw (Ibrahim et al. 2010), saw dust of mango rinds (Tiwari et al. 2009), cajan cajan (Tiwari et al. 2011), bentonite (Okiel et al. 2011), powdered activated carbon, lemon peel (Tembhurkar et al. 2012) etc.

### 3.6.2 Continuous adsorption process

The present investigations are used continuous adsorption process. A column or a bed of adsorbent is used to study the adsorption of metal cutting fluids at various parameters like bed height, influent concentration and flow rate. The continuous adsorption process includes three different patterns (in Fig 3.1):

- Fixed bed or expanded bed adsorption
- Moving bed adsorption
- Fluidized bed adsorption
3.6.2.1 Fixed bed adsorption

This is the most common type of adsorption column for wastewater treatment. The fixed bed adsorption processes consist of a solid mass as adsorbent packed inside a column to separate one or more components from wastewater as it flows downward through the packed bed. Separation in a fixed bed is an unsteady-state rate controlled process, i.e., the conditions at any particular point within the fixed bed vary with time. Fixed bed adsorption including removal of dissolved organic compounds from wastewater is also called Percolation. The downflow fixed bed adsorption column also acts as a depth filter for particles that can be contained in the waste water. These adsorption columns also have the facilities for backwashing (Karunarathne et al., 2013).

Steps involved in fixed bed column adsorption

As the waste water moves through a fixed bed of carbon, the pollutant to be adsorbed will move from the waste water to the carbon bed. Several steps are involved in the overall adsorption process of a single molecule of pollutant (Treybal et al., 1968, Weber et al., 1972).

Mass transfer step: Mass transfer from the bulk of the wastewater to the surface of the carbon particle through the boundary layer around the particle.
Diffusion step: internal diffusion through a pore.

Adsorption step: adsorption on to the surface of the particle.

Adsorption is a transient process. The amount of material adsorbed within a bed depends both on position and time. As fluid enters the bed, it comes in contact with the first few layers of absorbent. Solute adsorbs, filling up some of the available sites. Soon, the adsorbent near the entrance is saturated and the fluid penetrates farther into the bed before all solute is removed. Thus the active region shifts down through the bed as time goes on.

The fluid emerging from the bed will have little or no solute remaining, at least until the bulk of the bed becomes saturated. The break point occurs when the concentration of the fluid leaving the bed spikes as un-adsorbed solute begins to emerge. The bed has become ineffective. Usually, a breakpoint composition is set to be the maximum amount of solute that can be acceptably lost, typically something between 1 - 5 %.

As the concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region. This mass transfer zone moves down the bed until it "breaks through". The shape of the mass transfer zone depends on the adsorption isotherm (equilibrium expression), flow rate, and the diffusion characteristics. Usually, the shape must be determined experimentally.

The wave front may change shape as it moves through the bed, and the mass transfer zone may broaden or diminish. Unfavorable and linear isotherms tend to broaden. Favorable Langmuir and Freundlich isotherms may broaden at first, but quickly achieve a constant pattern front, an asymptotic shape. This means that the mass transfer zone is constant with respect to both position and time.
Fig. 3.21. Flow diagram of Continuous adsorption process within the fixed bed column

3.6.2.2 Factors affecting the fixed bed adsorption process

- Particle size
- Diameter of column
- Flow rate of incoming wastewater or residence time
- Height of adsorption bed
- Pressure drop
• Time required achieving breakthrough
• Time of exhaustion

3.7 Experimental set-up for continuous adsorption procedure

![Flow diagram of experimental set up of fixed bed adsorption system](image)

Fig. 3.22. Flow diagram of experimental set up of fixed bed adsorption system

All column experiments were conducted in a Pyrex glass column of 30mm inner diameter and 200mm long, in a downward flow of the oil in water emulsion with peristaltic pump (at 25°C fixed temperature) for monitoring the flow rates. A measured quantity of adsorbent was placed in column at different filter bed heights (36mm and 80mm). Prior to each experiment, distilled water was passed through the column to remove impurities and air bubbles. Oil concentration in effluent was measured as a function of time with varying operating conditions such as different flow rates (25ml/min, 50ml/min), varying influent concentrations (pH 8-9) and amount of adsorbent for thorough study of adsorption process.

3.8 Measurement of oil concentration

We already have the oil concentrations before adsorption as we have prepared the emulsion but the oil concentrations in the effluent were determined by COD analysis, using reactor digestion method [29] and calibrated on ELICO Double beam SL 210 UV Vis Spectrophotometer.
Percent of removal of oil from emulsion (%) = \( \frac{\text{changes in concentration}}{\text{initial concentration}} \times 100 \)