CHAPTER 3

EXPERIMENTAL METHODS AND ANALYSIS

3.1 CHEMICALS AND MATERIALS

Analytical grade aniline, pyrrole, 4, 4′-diaminodiphenyl sulfone (DDS), 4, 4′-diaminodiphenyl ether (DDO), ammonium persulfate (APS), hydrochloric acid (HCl), nitric acid (HNO₃) and sulfuric acid (H₂SO₄) were purchased from Merck-India. Aniline and pyrrole monomer was purified at a temperature over the boiling point of their respective monomer by distillation to remove any impurities and oligomers. DDS was recrystallized from ethanol to yield white crystals (melting point 178-179°C). DDO was recrystallized from aqueous methanol (m.p. 188-190°C). The solvents N-methyl 2-pyrrolidone (NMP) and methanol (Merck) were purified, using standard procedures. For the preparation of oxidized MWCNT, commercial multi-walled carbon nanotubes (MWCNT) (purity ≥ 95 weight%, 20-40 nm in diameter, lengths of 10-50 µm) were used. To introduce hydrophilic functional groups onto the MWCNT surface, 100 mL of 1:3 (v/v) concentrated nitric acid/sulfuric acid was added and refluxed at 60°C for 10 h. The resultant solid was washed thoroughly with deionized water until the pH value was about 6 and then the black solid was filtered and dried overnight. PbSO₄, NiSO₄.6H₂O, and 3CdSO₄.8H₂O were procured form Aldrich-Sigma Chemical, India. All the chemicals and reagents used for experiments and analysis were of analytical grade.
3.2 METAL SOLUTIONS

The concentration of metal ion solutions were prepared by dissolving known quantity of PbSO\textsubscript{4}, NiSO\textsubscript{4}.6H\textsubscript{2}O and 3CdSO\textsubscript{4}.8H\textsubscript{2}O in an appropriate amount of distilled water. The desired (100 to 500 mg/L) test solutions of heavy metal ions were prepared by subsequent dilutions of the stock solution. The pH of each test solution was adjusted to the required value, by adding either 1N NH\textsubscript{4}OH or 1N CH\textsubscript{3}COOH.

3.3 SYNTHESIS AND SCHEMATIC REPRESENTATION OF NANOCOMPOSITES

3.3.1 Synthesis of Polymer Nanocomposites

3.3.1.1 Synthesis of polyaniline/o-MWCNT nanocomposite (PANI/o-MWCNT)

A PANI/o-MWCNT nanocomposite was synthesized by \textit{in-situ} chemical oxidative polymerization. All the solutions were prepared in de-ionized water having resistivity of \~18M\textOmega.. In a typical procedure, multi-walled carbon nanotubes were oxidized via sonication in 100 mL of 1:3 (v/v) concentrated nitric acid/sulfuric acids at 60°C for 10 h. With the resultant oxidized multi-walled carbon nanotubes (o-MWCNT) 1 wt % of aniline was dispersed in 50 mL of 1M HCl solution, sonicated for half an hour and then poured into 0.05 mol of aniline in the presence 50 mL of aqueous solution of HCl (0.05 mol) in 250 mL round bottomed flask and cooled down to 0-5 °C. The polymerization was started by drop wise addition of the oxidant solution containing 0.05 mol of APS dissolved in 50 mL of aqueous solution of HCl pre-cooled at 0-5°C. The polymerization was allowed to proceed at room temperature for 5 h with continuous stirring. Dark colored precipitate of the polymer nanocomposites thus obtained was separated by
filtration, washed with aqueous solution of HCl followed by de-ionized water and finally dried in an oven at 45°C for about 24 h to remove moisture/water.

Scheme 3.1 Synthesis of PANI/o-MWCNT nanocomposite

3.3.1.2 Synthesis of polypyrrole/o-MWCNT nanocomposite (Ppy/o-MWCNT)

A PPy/o-MWCNT nanocomposite was synthesized by in-situ chemical oxidative polymerization. All the solutions were prepared in de-ionized water having resistivity of ~18MΩ. In a typical procedure, multi-walled carbon nanotubes were oxidized via sonication in 100 mL of 1:3 (v/v) concentrated nitric acid/sulfuric acids at 60°C for 10 h. To the resultant oxidized multi-walled carbon nanotubes (o-MWCNT), 1 wt % of pyrrole was added and dispersed in 50 mL of 1M HCl solution, sonicated for half an hour and then poured into 0.05 mol of pyrrole in the presence of 50 mL of aqueous HCl solution in 250 mL round bottom flask and cooled down to 0-5 °C. The polymerization was started by drop wise addition of the oxidant solution containing 0.05 mol of APS dissolved in 50 mL of aqueous solution of HCl pre-cooled at 0-5°C. The polymerization was allowed to
proceed at room temperature for 5 h with continuous stirring. Black colored precipitate of the polymer nanocomposite thus obtained was separated by filtration, washed with aqueous solution of HCl followed by de-ionized water and finally dried in an oven at 45°C for about 24 h to remove moisture/water.

Scheme 3.2 Synthesis of PPy/o-MWCNT nanocomposite

3.3.2 Synthesis of Copolymer Nanocomposites

3.3.2.1 Synthesis of poly(aniline-co-diaminodiphenyl sulfone)/o-MWCNT nanocomposite (PANI-co-DDS/o-MWCNT)

A PANI-co-DDS/o-MWCNT nanocomposite was synthesized by in-situ chemical oxidative polymerization. All the solutions were prepared in de-ionized water having resistivity of ~18MΩ. In a typical procedure, the oxidized multi-walled carbon nanotubes (o-MWCNT) 1 wt % of aniline was dispersed in 50 mL of 1M HCl solution and sonicated for half an hour and then poured into aniline (0.05 mol) and 4, 4'-diaminodiphenyl sulfone (0.05 mol) monomer solution in the presence 100 mL of aqueous solution of HCl (0.05 mol) in 250 mL round bottom flask and cooled down to 0-5°C. The
above mixture was sequentially magnetic stirred in an ice bath for an hour to make the mixture dispersed homogeneously. The polymerization was started by drop wise addition of the oxidant solution containing 0.05 mol of APS dissolved in 50 ml of aqueous solution of HCl pre-cooled at 0-5°C. The polymerization was allowed to proceed at room temperature for 5 h with continuous stirring. Dark colored precipitate of the copolymer nanocomposite (PANI-co-DDS/o-MWCNT) thus obtained was separated by filtration, washed with aqueous solution of HCl followed by de-ionized water and finally dried in an oven at 45°C for about 24 h to remove moisture/water.

Scheme 3.3 Synthesis of PANI-co-DDS/o-MWCNT nanocomposite

3.3.2.2 Synthesis of poly(pyrrole-co-diaminodiphenyl sulfone)/o-MWCNT nanocomposite (PPy-co-DDS/o-MWCNT)

A PPy-co-DDS/o-MWCNT nanocomposite was synthesized by in-situ chemical oxidative polymerization. All the solutions were prepared in de-ionized water having resistivity of ~18MΩ. In a typical procedure, the oxidized multi-walled carbon nanotubes (o-MWCNT) 1 wt % of pyrrole was added and dispersed in 50 mL of 1M HCl solution and sonicated for half an
hour and then poured into pyrrole (0.05 mol) and 4, 4′-diaminodiphenyl sulfone (0.05 mol) monomer solution in the presence 100 mL of aqueous HCl solution in 250 mL round bottom flask and cooled down to 0-5°C. The above mixture was sequentially magnetic stirred in an ice bath for an hour to make the mixture dispersed homogeneously. The polymerization was started by drop wise addition of the oxidant solution containing 0.05 mol of APS dissolved in 50 ml of aqueous solution of HCl pre-cooled at 0-5°C. The polymerization was allowed to proceed at room temperature for 5 h with continuous stirring. Dark colored precipitate of the copolymer nanocomposite (PPy-co-DDS/o-MWCNT) thus obtained was separated by filtration, washed with aqueous solution of HCl followed by de-ionized water and finally dried in an oven at 45°C for about 24 h to remove moisture/water.

Scheme 3.4 Synthesis of PPy-co-DDS/o-MWCNT nanocomposite
3.3.2.3 Synthesis of poly(aniline-co-diaminodiphenyl ether)/o-MWCNT nanocomposite (PANI-co-DDO/o-MWCNT)

A PANI-co-DDS/o-MWCNT nanocomposite was synthesized by in-situ chemical oxidative polymerization. All the solutions were prepared in de-ionized water having resistivity of ~18MΩ. In a typical procedure, The oxidized multi-walled carbon nanotubes (o-MWCNT) 1 wt % of aniline was added and dispersed in 50 mL of 1M HCl solution, sonicated for half an hour and then poured into 0.05 mol of aniline and 4, 4′-diaminodiphenyl ether (0.05 mol) in the presence 100 mL of aqueous HCl solution in 250 mL round bottom flask and cool down to 0-5°C. The above mixture was sequentially magnetic stirred in an ice bath for an hour to make the mixture dispersed homogeneously. The polymerization was started by drop wise addition of the oxidant solution containing 0.05 mol of APS dissolved in 50 ml of aqueous HCl solution and pre-cooled at 0-5°C. The polymerization was allowed to proceed at room temperature for 5 h with continuous stirring. Dark colored precipitate of the copolymer nanocomposite (PANI-co-DDO/o-MWCNT) thus obtained was separated by filtration, washed with aqueous HCl solution followed by de-ionized water and finally dried in an oven at 45°C for about 24 h to remove moisture/water.

![Scheme 3.5 Synthesis of PANI-co-DDO/o-MWCNT nanocomposite](image-url)
3.3.2.4 Synthesis of poly(pyrrole-co-diaminodiphenyl ether)/
o-MWCNT nanocomposite (PPy-co-DDO/o-MWCNT)

A PPy-co-DDO/o-MWCNT nanocomposite was synthesized by
*insitu* chemical oxidative polymerization. All the solutions were prepared in
de-ionized water having resistivity of ~18MΩ. In a typical procedure, The
oxidized multi-walled carbon nanotubes (o-MWCNT) 1 weight percentage of
pyrrole was dispersed in 50 mL of 1M HCl solution, sonicated for half an
hour and then poured into 0.05 mol of pyrrole and 4, 4’-diaminodiphenyl
ether (0.05 mol) monomer solution in the presence 100 mL of aqueous HCl in
250 mL round bottom flask and cool down to 0-5°C. The above mixtures
were sequentially magnetic stirred in an ice bath for an hour to make the
mixture dispersed homogeneously. The polymerization was started by drop
wise addition of the oxidant solution containing 0.05 mol of APS dissolved in
50 ml of aqueous HCl solution and pre-cooled at 0-5°C. The polymerization
was allowed to proceed at room temperature for 5 h with continuous stirring.
Dark colored precipitate of the copolymer nanocomposite (PPy-co-DDO/o-
MWCNT) thus obtained was separated by filtration, washed with aqueous
solution of HCl followed by de-ionized water and finally dried in an oven at
45°C for about 24 h to remove moisture/water.
Scheme 3.6 Synthesis of PPy-co-DDO/o-MWCNT nanocomposite

3.4 CHARACTERIZATION AND EXPERIMENTAL METHODS

3.4.1 ATR-IR Spectroscopy

Attenuated total reflectance Infrared Spectroscopy (ATR-IR) method allows one to characterize vibrations in molecules by measuring the absorption of light of certain energy that correspond to the vibrational excitation of the molecules from lower to higher state. For this purpose thesis, were recorded on a Perkin Elmer, Spectrum Two spectrophotometer in the range 4000–400 cm⁻¹.
3.4.2 Raman Spectroscopy

Raman spectroscopy provides an extremely useful tool for the study of polyaniline and its copolymers. Raman spectra of this and related polymers are usually rich in bands which correspond to a wide variety of vibration modes characteristic for these species. Moreover, many Raman bands are highly sensitive to both the redox state, and the degree of protonation of polymer backbone. For the purpose of this thesis, the Raman spectra were recorded on Bruker RFS27 operating with 1064 nm line of Nd: YAG Laser source in rock solid interferometer in the range of 100–700 cm\(^{-1}\) using liquid nitrogen cooled germanium detector with the resolution of 4 cm\(^{-1}\).

3.4.3 DRS UV Spectroscopy

DRS UV-vis spectroscopy is a versatile and useful technique for studying the molecular structure and conformation of conducting polymers. The particular absorption bands arising from a polymer samples are indicative the nature of the polymer, the extent of both electronic and proton doping, the oxidation state of polymer as well as polymer chain conformation. The absorbance spectra in Diffuse Reflectance Spectroscopy (DRS UV-vis) of powdered samples were recorded on a Shimadzu UV-2450 spectrophotometer over the range of 190–800 nm using barium sulfate as reference.

3.4.4 X-ray Diffraction Spectroscopy

The X-ray diffraction (XRD) patterns of polymer nanocomposites were recorded on a PANalytical X’Pert Pro X-ray diffractometer using CuK\(\alpha\) as the radiation source. The diffraction patterns were recorded in the 2\(\theta\) range from 10 to 80° in steps of 0.02° with a count time of 20 s at each point. The average particle size was determined from the diffraction peak using the
Scherrer formula, \( D = \frac{K\lambda}{\beta \cos \theta} \), where \( D \) is the average particle size (nm), \( K \) is the Scherrer constant, \( \lambda \) is the wavelength of X-ray source, \( \beta \) is the full width at half-maximum and \( \theta \) is the Bragg’s angle.

### 3.4.5 Thermogravimetric Analysis

The Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the composition of the materials and to predict their thermal stability at temperatures up to 800°C. Thermogravimetric analysis was determined using a Perkin Elmer SII (Diamond Series) model under nitrogen atmosphere in the temperature range of 30–800°C at a heating rate of 20°C min\(^{-1}\).

### 3.4.6 Scanning Electron Microscopy and EDX Analysis

Scanning electron microscopy is a powerful tool for studying the surface morphology and micro/nano structures of o-MWCNT doped polymers and its copolymer nanocomposites. The surface morphology of the polymer nanocomposites were examined by scanning electron microscope after gold coating using SEM-JEOL, JSM-5600 model. Cressington 108 auto sputter coater was used for coating. The accelerating voltage of SEM was 20 kV.

The Energy Dispersive X-ray spectrometry (EDX) provides the crystalline and elemental composition information about a material from a few nano meter depth of the material surface via the electron Back Scattered Detection (BSD) system attached with a microscope.
3.4.7 Transmission Electron Microscopy and SAED Pattern Analysis

Transmission electron microscopy is versatile and useful technique for studying surface morphology and particle size of conducting polymer and its nanocomposites. In this thesis, Transmission electron microscopic (HR-TEM) images were recorded using JEOL; JEM 2100 electron microscope operated at an accelerating voltage of 150 kV. The selective area electron diffraction pattern (SAED) provides the crystalline domains and presence of elemental composition in polymer and its copolymer nanocomposites.

3.4.8 Atomic Absorption Spectrometry analysis

The concentration of metal ions such as Pb, Ni, Cd etc. after the attainment of equilibrium in the solutions before and after treatment was calculated by AA6300 Atomic absorption spectrometer (AAS) (Shimadzu, Japan) with different pH solution measured with a Hanna pH meter using a combined glass electrode and the pH was maintained using 1N NH₄OH or 1N CH₃COOH solutions.

Table 3.1 Common load parameters and requirements of AAS for heavy metal ions study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Requirements</th>
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</thead>
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<td>S.R.Width</td>
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</tr>
<tr>
<td>Lamp mode</td>
<td>BGC-D₂</td>
</tr>
<tr>
<td>Burner light</td>
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</tr>
<tr>
<td>Burner angle</td>
<td>0°</td>
</tr>
<tr>
<td>Flame type</td>
<td>AirC₂H₂</td>
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<tr>
<td>Flame gas limit</td>
<td>1.8 L/min (C₂H₂)</td>
</tr>
<tr>
<td>Support gas limit</td>
<td>15 L/min (Air)</td>
</tr>
<tr>
<td>Parameters</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Hollow cathode lamp</td>
<td>L233-82NQ</td>
</tr>
<tr>
<td>Maximum current peak</td>
<td>15 mA</td>
</tr>
<tr>
<td>Minimum current peak</td>
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<tr>
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</tr>
<tr>
<td>Most sensitive line</td>
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</tr>
</tbody>
</table>

### 3.5 BATCH ADSORPTION STUDIES

Batch adsorption experiments were carried out in a series of stoppered conical flasks. A weighed amount (20 mg) of adsorbents (PANI-co-DDS/o-MWCNT, PPy-co-DDS/o-MWCNT, PANI-co-DDO/o-MWCNT, PPy-co-DDO/o-MWCNT, PANI/o-MWCNT and PPy/o-MWCNT) was introduced into conical flasks (250 mL) containing various concentration with 20 mL aqueous solutions of three metal ions such as Pb(II), Ni(II) and Cd(II). Then the conical flask were shaken at room temperature using a horizontal bench shaker (Orbitek-Teqip-ACT/EQ/454) for a prescribed time to attain the equilibrium. The aliquot solutions were filtered using Whatmann 42 filter paper and the concentration of each metal ions were determined by AAS method. Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one. All the experiments were performed in duplicate and the mean values are presented. The metal ions removal percentage (A %), the amount of metal ions adsorbed per unit mass of adsorbent at time t (q, mg g⁻¹) and the amount of metal ions adsorbed per unit
mass of adsorbent at equilibrium \( (q_e, \text{mg g}^{-1}) \), were calculated from the following equations:

\[
A\% = \frac{C_o - C_e}{C_o} \times 100
\]  

(3.1)

where \( C_o \) and \( C_e \) (mg L\(^{-1}\)) are the initial and final concentrations of metal ion solutions, respectively.

### 3.5.1 Effect of Solution pH onto Metal Ion Adsorption

The effect of pH on the adsorption capacity of adsorbent such as PANI-co-DDS/o-MWCNT, PPy-co-DDS/o-MWCNT, PANI-co-DDO/o-MWCNT, PPy-co-DDO/o-MWCNT, PANI/o-MWCNT and PPy/o-MWCNT onto metal ions (Pb(II), Ni(II) and Cd(II)) was investigated, using a 20 mL of fixed concentration of metal ion solution (100 mg/L) with a fixed amount of adsorbent dose (20 mg) at the optimum pH for 60 min at 35°C. The samples were then agitated in a horizontal bench shaker at 150 rpm at different solution pH in the range of 2-10. After reaching equilibrium time, the solutions were filtered through Whatmann 42 filter paper and the filtrate was analyzed as mentioned above to determine the metal ion concentration.

### 3.5.2 Effect of Adsorbent Dosage

The study of the effect of adsorbent dose is necessary to observe the maximum adsorption with the minimum possible amount of adsorbent. The effects of adsorbent dosage of as synthesized adsorbent were varied from 20 to 100 mg under optimized pH of 6.0. The other parameters such as initial metal ion concentration, contact time and agitation speed were kept constant at 100 mg/L, 60 minutes and 150 rpm respectively. The samples were kept in
shaker for equilibrium to reach. The sample solution was then filtered and the filtrate was analyzed in the usual manner for determining metal ion concentration.

3.5.3 Effect of Contact Time

The adsorption equilibrium time between the adsorbent and metal ion concentration plays an important role for designing batch adsorption experiments. The effect of contact times of Pb(II), Ni(II) and Cd(II) ions on to the synthesized polymer nanocomposites such as PANI-co-DDS/o-MWCNT, PPy-co-DDS/o-MWCNT, PANI-co-DDO/o-MWCNT, PPy-co-DDO/o-MWCNT, PANI/o-MWCNT and PPy/o-MWCNT were studied at 10 minutes time intervals from 5 to 60 minutes. Keeping all other optimized parameters such as initial metal ion concentration, pH, adsorbent dose and contact time has to be viewed. The samples were agitated for equilibrium in a thermostat shaker. The filtrates were analyzed for the metal ions using AAS.

3.5.4 Effect of Metal Ion Concentration

The initial metal ion concentration plays an important role in the adsorption capacity. The effects of different initial metal ion concentration were carried out in the range of 100 mg/L to 500 mg/L of metal solutions at constant temperature. All other parameters such as solution pH, contact time, adsorption dosage and agitation were kept constant at pH 6, 60 minutes, 60 mg and 150 rpm respectively. After reaching equilibrium time, the solutions were filtered through Whatman 42 filter paper and the filtrate was analyzed using AAS to determine the metal ion concentration.
3.5.5 Adsorption Kinetics

The kinetic data obtained from the effect of contact time studies were utilized to test different adsorption kinetic models, using the pseudo first order equation (Lagergren 1898), pseudo-second order equation (Ho & McKay 1999) and Elovich kinetic model (Ho & McKay 2002). The amount of metal ion adsorbed onto the adsorbent at various time intervals was calculated, using the following relationship:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

(3.2)

where \( q_t \) is the amount of metal ion adsorbed onto the adsorbent at any time \( t \) (mg/g), \( C_t \) is the concentration of the metal ion solution at any time \( t \) (mg/L), \( V \) is the volume of the metal ion solution (L) and \( m \) is the mass of the adsorbent used (g).

3.5.5.1 Pseudo first order kinetic model

The kinetic of adsorption mechanism may be described by the pseudo first order (Equation 3.3). The linearized form of the model is generally expressed as follows:

\[ \log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \]  

(3.3)

where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the amounts of metal ions adsorbed at equilibrium and at time \( t \) (mg/g) respectively, and \( k_{ad} \) is the pseudo first order kinetic rate constant (min\(^{-1}\)). The values of \( q_e \) and \( k_{ad} \) were calculated from the slope and intercept of the line obtained by the plot of \( \log (q_e - q_t) \) versus \( t \).
3.5.5.2 Pseudo second order kinetic model

The kinetics of the adsorption process may also be described by the pseudo second order rate equation. The linearized form of the equation is expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

(3.4)

where \( k (g \text{ mg}^{-1} \text{ min}^{-1}) \) is the pseudo second order rate constant. The values of \( q_e \) and \( k \) were calculated from the slope and intercept of the line obtained by the plot of time (min) versus \( t/q_t \) (min \( \text{mg}^{-1} \text{ g} \)). The kinetic data for all three metal ions with polymer nanocomposites adsorbent were fitted and best fit was found.

3.5.5.3 Elovich kinetic model

The experimental data were applied to the Elovich kinetic model, which is given in the following equation;

\[
q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t
\]

(3.5)

where \( \alpha \) is the initial adsorption rate in mg/(g.min), and \( \beta \) (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption.
3.5.6 Adsorption Isotherms

Analysis of adsorption isotherm model by fitting the experimental data was a suitable method for finding out the design of adsorption system. The experimental data were fitted with two-parameter adsorption isotherm models: Langmuir, Freundlich and Redlich-peterson. The constant parameters of isotherm equations for this adsorption process were calculated by nonlinear regression analysis using MATLAB R2009a. The amount of metal ions adsorbed on to the adsorbent at equilibrium, $q_e$ (mg/g) was calculated by the following relationship:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3.6)$$

where, $C_o$ and $C_e$ (mg/L) are the initial and equilibrium metal ion concentrations respectively.

3.5.6.1 Langmuir isotherm

The Langmuir adsorption model mainly concern about saturation level of monolayer adsorption process and interaction between the adsorbent and heavy metal ion (adsorbate) that is completely homogeneous. The non-linear form of Langmuir adsorption isotherm model is given as:

$$q_e = \frac{q_mKLC_e}{1 + KLC_e} \quad (3.7)$$

where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_m$ is the maximum monolayer adsorption capacity (mg/g), $K_L$ is the Langmuir constant related to
the affinity of the adsorbate molecule to the polymer nanocomposite (L/mg) and \( C_e \) is the equilibrium concentration of metal ion solution (mg/L).

3.5.6.2 Freundlich isotherm

The Freundlich isotherm mainly describes the adsorption on heterogeneous surfaces, which means the interaction between adsorbed molecules, and the application of the Freundlich equation, also suggests that the sorption energy exponentially decreases on completion of the adsorptioanal centers of an adsorbent. The non-linear form of Freundlich adsorption isotherm model is given as:

\[
q_e = K_f C_e^{1/n}
\]  

(3.8)

where \( K_F \) is the Freundlich constant ((mg/g)(L/mg)\(^{1/n}\)) related to the bonding energy and \( n \) is a measure of the deviation from linearity of adsorption (g/L). The significance of \( n \) value is as follows: \( n = 1 \) indicates the adsorption is linear; \( n < 1 \) indicates the adsorption is a chemical process and \( n > 1 \) indicates the adsorption is a physical process.

3.5.6.3 Redlich-Peterson isotherm

Redlich-Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich model which incorporates three parameters into an empirical equation and can be applied either in homogeneous or heterogeneous system due to its versatility. It approaches Freundlich isotherm model at high concentrations and is in accordance with the low concentration limit of the ideal Langmuir condition. The equation is given as:
where $q_e$ is the amount of adsorbate in the sorbent at equilibrium (mg/g), $C_e$ is the equilibrium concentration (mg/L); $K_R$ is the Redlich-Peterson isotherm constant (L/g), $\alpha_R$ is the Redlich-Peterson isotherm constant (L/mg), and $\beta$ is the exponent which lies between 0 and 1. The Redlich-Peterson isotherm exponent which lies between 0 and 1 has two limiting behaviour: Langmuir form for $\beta$=1 and Freundlich form for $\beta$=0.

### 3.6 ADSORPTION THERMODYNAMICS

In environmental engineering exercise, both energy and entropy factors must be considered, in order to determine what process will occur spontaneously. Gibb’s free energy change ($\Delta G^\circ$) is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature, if $\Delta G^\circ$ is a negative value. The thermodynamic parameters of Gibbs free energy ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) for the adsorption processes are calculated using the following equations for the temperature range of 303-333 K:

\[
K_c = \frac{C_{ae}}{C_e} 
\]  

\[
\Delta G^\circ = -RT \ln K_c 
\]  

\[
\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} 
\]

where $K_c$ is the equilibrium constant, $C_e$ is the equilibrium metal ion concentration in solution (mg/L), $C_{ae}$ is the amount of metal ions adsorbed on
the adsorbent per liter of solution at equilibrium (mg/L), R is the gas constant (8.314 J/mol.K) and T is the temperature (K).

### 3.7 BATCH DESORPTION STUDIES

To investigate the desorption ability of adsorbed metal ions from the synthesized polymer nanocomposites adsorbent, desorption experiments were carried out for important application in the field of heavy metal removal from wastewater. Because of the development of good quality adsorbent, the regeneration ability is an important key factor. The spent adsorbent such as PANI-co-DDS/o-MWCNT, PPy-co-DDS/o-MWCNT, PANI-co-DDO/o-MWCNT, PPy-co-DDO/o-MWCNT, PANI/o-MWCNT and PPy/o-MWCNT were treated with 50 mL of 0.2 N H₂SO₄, HCl and CH₃COOH solution for an hour and the solution was filtrated, and the filtrate was evaluated to determine the metal recovery by the AAS. The acid washed adsorbent was again washed with water to remove the acid present on the adsorbent surface, and was reused for further five cycles. The metal ion desorbed from the spent polymer nanocomposites adsorbent was calculated using Eqn.

\[
\text{% Desorption} = \left( \frac{\text{Amount released to solution (mg/L)}}{\text{Total adsorbed}} \right) \times 100
\]  

(3.13)