3.1 Preparation of the Neem Leaf Powder

The preparation of the adsorbent, Neem Leaf Powder (NLP), included the following steps:

(i) Mature Neem leaves were collected from a number of tall Neem trees (District Morigaon, Assam, India) and were brought to the laboratory in plastic bags.

(ii) The leaves were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature in a shade.

(iii) The leaves were then further dried in an air oven at 333-343 K for 30 h when the leaves became crisp and brittle.

(iv) The crisp leaves were ground in a mechanical grinder to obtain a fine powder. The powder was sieved and fractionated using a series of sieves. The 53 – 74 μm fraction was separated and taken as the adsorbent.

(v) This fraction (53 – 74 μm) was washed several times with double distilled water till the washings were free of color and turbidity.

(vi) The washed powder was dried for several hours at room temperature and was preserved in glass bottles.

3.2 Characterization of the Neem Leaf Powder

3.2.1 Acidity of the NLP

The NLP was found to be weakly acidic in character in its reaction with water. The powder was mixed with water to obtain a 10 % slurry (10 g NLP in 100 mL double distilled water) and the pH was read with a pH-meter. The slurry had a pH of 5.6.

3.2.2 Determination of the Surface Area

(i) BET Method. The NLP sample was sent to the Centre for Environment and Safety, DRDO, New Delhi for determination of its surface area by the well-known BET method. Determination of the surface area of the powder paused the problem of
degassing because it burned as the temperature was raised. The degassing temperature had to be limited to 373 K, and applying the BET procedure, the method yielded a value of $\sim 1.3 \text{ m}^2 \text{ g}^{-1}$ only for the specific surface area of the powder. This value is much less compared to the specific surface area of the conventional activated carbon powders.

(ii) **Dye Adsorption Method.** This method is based on adsorption of the dye, Methylene Blue, on the adsorbent (Phelps and Harris, 1967; Pham and Brindley, 1970; Percival and Lindsay, 1997). In this method, the fully hydrated material is exposed to progressively increasing concentrations of a dilute Methylene Blue solution (25, 30, 40, 50, 60 and 70 mg/L) under continuous agitation and kept for 24 hours in contact with the dye solution. The amount of dye adsorbed on unit mass of NLP at equilibrium ($q_e \text{ mg/g}$) is determined for each dye concentration ($C_e \text{ mg/L}$) at equilibrium by spectrophotometrically measuring the amount of Methylene Blue remaining in the solution after adsorption. The amount of the dye adsorbed per unit mass (g) to form a complete monolayer is determined from Langmuir isotherm, i.e by plotting $C_e/q_e$ vs. $C_e$ as in equation (3)

$$
C_e/q_e = (1/bq_m) + (1/q_m) C_e \tag{3}
$$

the slope of which gives the Langmuir Monolayer Capacity, $q_m$. The specific surface area ($s_g$) is then obtained from the relation:

$$
s_g = M_f \times A_m \times N_A
$$

where $M_f =$ number of meq of Methylene Blue adsorbed per 100 g of material, $A_m =$ surface area of the Methylene Blue molecule (1.30 x $10^{-18}$ m$^2$/molecule), and $N_A =$ Avogadro Number (= 6.023 x $10^{20}$ molecules per meq). $M_f$ can be found from $q_m$. The Methylene Blue adsorption method gives the total surface area whereas the BET method only measures the external surface area.

The average monolayer capacity for methylene blue adsorption on Neem leaf powder was measured to be 8.76 mg/g, which yielded a value of 21.45 m$^2$/g for the specific surface area of the Neem Leaf Powder.
3.2.3 SEM Study of Surface Topography

Scanning Electron Microscopy (SEM) is an important tool to study the surface topography of a solid material. SEM imaging yields better results than optical microscopy because of better resolution and enhanced depth of field. The principle of the method involves focusing an electron beam with the help of electromagnetic lenses to the specimen in an evacuated chamber. The beam is then rastered over the specimen in synchrony with the beam of a cathode ray display screen. The inelastically scattered secondary electron emission from the specimen, which is determined to a large extent by the topography of the surface, is used to modulate the brightness of the cathode ray display screen resulting in the formation of an image of the surface. However, if the specimen surface consists of both topographic and compositional differences, image formation results from both inelastically scattered secondary electrons and elastically back-scattered electrons, and the image interpretation becomes very complicated (Macur et al., 1996).

Surface topography of the Neem Leaf Powder was observed with Scanning Electron Microscopy (SEM) at the Regional Sophisticated Instruments Centre (RSIC), North Eastern Hill University, Shillong, India (Scanning Electron Microscope, JEOL JSM 35CF). In the present study, since NLP is a nonconducting sample, it was studied by sputtering a thin conducting coating of gold to avoid electrical charging of the sample during bombardment with the electron beam. Sample size was approximately 1 cm.

Electron micrographs (Plates 3.1 to 3.22) were taken of the following specimens:

a) The Neem Leaf Powder (NLP),

b) NLP after adsorption of Cr(VI),

c) NLP after adsorption of Cd(II),

d) NLP after adsorption of Pb(II),

e) NLP after adsorption of an equimolar mixture of Cd(II) and Pb(II),

f) NLP after adsorption of Methylene Blue,

g) NLP after adsorption of Congo Red, and

h) NLP after adsorption of Brilliant Green.

The adsorption was carried out by keeping a specimen of NLP in a 1000 ppm solution of the metal ion/dye for 24 hours, separating the adsorbent by filtration and drying the same at 333 – 343 K in an air oven.
a) **SEM photographs of pure NLP:** Plate 3.1 (x 4000) indicates that the NLP consists of innumerable particles of different shapes and sizes. Some of the particles may be quite small while some others may be as big as 10 μm in diameter. All the particles have broken edges with steps and kinks contributing to the uneven topography (Plate 3.2 for a single big particle, x 20000, Plate 3.3 for the edge of a big particle, x 18000).

b) **SEM of Cr(VI)-adsorbed NLP:** SEM images, presented in Plates 3.4 and 3.5 (single particle) show the particles to be shaded, but firm conclusion could not be made.

c) **SEM of Cd(II)-adsorbed NLP:** SEM images, presented in Plates 3.6 (magnification x 4000), 3.7 (single particle, magnification x 20000) and 3.8 (edge of a single particle, magnification 18000) again show darkening of the particles perhaps due to coverage by Cd-salt.

d) **SEM of Pb(II)-adsorbed NLP:** SEM images, presented in Plates 3.9 (magnification x 4000), 3.10 (single particle, magnification x 20000) and 3.11 (edge of a single particle, magnification 18000) are similar to those obtained after adsorption of Cd(II) showing darkening of the particles perhaps due to masking by Pb-salt.

e) **SEM of Pb(II) and Cd(II) coadsorbed NLP:** SEM images, presented in Plates 3.12 (x 4000) and 3.13 (single particle, x 20000) again show clearly dark patches on the NLP particles after adsorption from an equimolar mixture of Pb(II) and Cd(II).

f) **SEM of Methylene Blue-adsorbed NLP:** SEM images, presented in Plates 3.14 (x 4000), 3.15 (single particle, x 20000) and 3.16 (edge of single particle, x 18000) show masking of the particles with dark patches over the NLP particles after adsorption of the dye, Methylene Blue.

g) **SEM of Congo red-adsorbed NLP:** SEM images, presented in Plates 3.17 (x 4000), 3.18 (single particle, x 20000) and 3.19 (edge of single particle, x 18000) show clearly that the NLP particles are masked with dark patches due to the dye after adsorption of Congo Red.
Plate 3.1: SEM image of the surface of NLP particles (x 4000)

Plate 3.2: SEM image of a single big NLP particle (x 20000)
Plate 3.3: SEM image of the edge of a single big NLP particle (x 18000)

Plate 3.4: SEM image of Cr(VI) adsorbed NLP (x 4000)
Plate 3.5: SEM image of Cr(VI) adsorbed NLP particle (x 20000)

Plate 3.6: SEM image of Cd(II)-adsorbed NLP (x 4000)
Plate 3.7: SEM image of Cd(II)-adsorbed NLP single particle (x 20000)

Plate 3.8: SEM image of Cd(II)-adsorbed NLP single particle edge (x 18000)
Plate 3.9: SEM image of Pb(II)-adsorbed NLP particles (x 4000)

Plate 3.10: SEM image of Pb(II)-adsorbed NLP single particle (x 20000)
Plate 3.11: SEM image of Pb(II)-adsorbed NLP single particle edge (x 18000)

Plate 3.12: SEM image of Pb(II), Cd(II)-adsorbed NLP (x 4000)
Plate 3.13: SEM image of Pb(II), Cd(II)-adsorbed NLP single particle (x 20000)

Plate 3.14: SEM image of Methylene Blue-adsorbed NLP (x 4000)
Plate 3.15: SEM image of Methylene Blue-adsorbed NLP single particle (x 20000)

Plate 3.16: SEM image of Methylene Blue-adsorbed NLP single particle edge (x 18000)
Plate 3.17: SEM image of Congo Red-adsorbed NLP particles (x 4000)

Plate 3.18: SEM image of Congo Red-adsorbed NLP single particle (x 20000)
Plate 3.19: SEM image of Congo Red-adsorbed NLP single particle edge (x 18000)

Plate 3.20: SEM image of Brilliant Green-adsorbed NLP particles (x 4000)
Plate 3.21: SEM image of Brilliant Green-adsorbed NLP single particle (x 20000)

Plate 3.22: SEM image of Brilliant Green-adsorbed NLP single particle edge (x 18000)
h) **SEM of Brilliant Green-adsorbed NLP**: SEM images, presented in Plates 3.20 (x 4000), 3.21 (single particle, x 20000) and 3.22 (edge of single particle, x 18000) again show clearly the adsorption of the dye on the NLP particles indicated by the presence of dark patches following adsorption of Brilliant Green.

The topography of the NLP as revealed by the SEM study shows that the adsorbent powder consists of non-uniform, irregular-shaped particles. The particles have large number of steps and defects, and the edges are highly broken. Adsorption of the metals [Cr(VI), Cd(II) and Pb(II)] and the dyes [Methylene Blue, Congo Red and Brilliant Green] is clearly revealed by masking of some of the particles by dark patches over them. This further reveals that adsorption takes place preferentially over certain locations and the adsorbate does not form a uniform layer over the whole surface. The crevices and the steps have been found to be more active in adsorption.

**3.2.4 Identification of Surface Functional Groups with IR spectroscopy**

IR spectroscopy is one of the major tools used for obtaining information on functional groups on a solid surface. The principle of IR spectroscopy is based on molecules vibrating with specific frequencies associated with internal vibrations of groups of atoms. These frequencies occur in the IR region of the electromagnetic spectrum, i.e. ~ 200 to ~ 4000 cm⁻¹. When a sample is placed in a beam of IR radiation, the sample absorbs all radiations corresponding to those of molecular vibrational frequencies, and transmits all other frequencies. Identification of functional groups is possible because differences in the chemical structure give rise to characteristic vibrations and yield unique IR spectra, known as the ‘fingerprint’ spectra. The Fourier transform infrared spectrometer (FTIR) employs an interferometer instead of a monochromator.

In the present work, FTIR measurements were taken with a Perkin Elmer Spectrum RX I spectrometer (range 4000 – 400 cm⁻¹) using ‘nujol’ method for sample introduction. The NLP samples were kept in an oven at 333 – 343 K overnight for getting rid of moisture, allowed to cool to room temperature in a dessiccator and then, a tiny amount was spread on a nujol film between two KBr windows. The spectra obtained were given in Fig. 3.1 to 3.8 for the following samples respectively:
a) Neem Leaf Powder (NLP),
b) NLP after adsorption of Cr(VI),
c) NLP after adsorption of Cd(II),
d) NLP after adsorption of Pb(II),
e) NLP after adsorption of an equimolar mixture of Cd(II) and Pb(II),
f) NLP after adsorption of Methylene Blue,
g) NLP after adsorption of Congo Red, and
h) NLP after adsorption of Brilliant Green.

The principal IR bands obtained for each sample are presented in Table 3.1 and Table 3.2. The spectra for the 8 different NLP samples are very much similar with only a few differences as can be seen from the peak tables. However, it is to be noted that the IR spectra show the presence of the following functional groups on the NLP surface:

- a) -OH (3600 cm\(^{-1}\)),
- b) -NH\(_2\) (3357 cm\(^{-1}\)),
- c) >C=N− (1607 – 1631 cm\(^{-1}\)),
- d) =C=O, =C=N< and =C=O− (1000 – 1214 cm\(^{-1}\)),
- e) >C=O, >C=C< (1607 – 1687 cm\(^{-1}\)),
- f) >C=S (1143 – 1154 cm\(^{-1}\)).

The results obtained from FTIR spectra of the Neem Leaf Powder are in conformity with the large number of constituents present in the Neem leaves. The leaves have also been shown to contain a number of fatty acids like oleic acid, stearic acid, palmitic acid, linoleic acid, etc., [Skellon et al., 1962]. The presence of polar groups on the surface [Ho et al., 2001a, Weber and Moris, 1963, Hall et al., 1966] has been shown to be responsible for considerable cation exchange capacity of a solid, which is therefore also likely in case of the Neem Leaf Powder.
Table 3.1: Prominent IR bands (cm\(^{-1}\)) of the Neem Leaf Powder before and after saturation with Cr(VI), Cd(II), Pb(II) and an equimolar mixture of Cd(II) and Pb(II).

<table>
<thead>
<tr>
<th>IR bands (cm(^{-1}))</th>
<th>NLP</th>
<th>NLP + Cr(VI)</th>
<th>NLP + Cd(II)</th>
<th>NLP + Pb(II)</th>
<th>NLP + Cd(II) + Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
</tr>
<tr>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
</tr>
<tr>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
</tr>
<tr>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
</tr>
<tr>
<td>2905.2</td>
<td>2905.2</td>
<td>2857.6</td>
<td>2857.6</td>
<td>2857.6</td>
<td>2857.6</td>
</tr>
<tr>
<td>2857.6</td>
<td>2857.6</td>
<td>2738.6</td>
<td>2738.6</td>
<td>2738.6</td>
<td>2679.0</td>
</tr>
<tr>
<td>2714.8</td>
<td>2679.0</td>
<td>2679.1</td>
<td>2679.1</td>
<td>1619.2</td>
<td>1619.2</td>
</tr>
<tr>
<td>2667.2</td>
<td>2381.6</td>
<td>2357.8</td>
<td>2369.7</td>
<td>1512.1</td>
<td>1512.1</td>
</tr>
<tr>
<td>2357.8</td>
<td>1631.1</td>
<td>1631.1</td>
<td>1607.3</td>
<td>1452.4</td>
<td>1452.4</td>
</tr>
<tr>
<td>1687.7</td>
<td>1500.0</td>
<td>1452.4</td>
<td>1512.1</td>
<td>1369.1</td>
<td>1369.1</td>
</tr>
<tr>
<td>1464.3</td>
<td>1452.6</td>
<td>1381.0</td>
<td>1452.4</td>
<td>1303.7</td>
<td>1303.7</td>
</tr>
<tr>
<td>1381.0</td>
<td>1369.3</td>
<td>1297.7</td>
<td>1381.0</td>
<td>1154.9</td>
<td>1154.9</td>
</tr>
<tr>
<td>1327.5</td>
<td>1214.0</td>
<td>1202.5</td>
<td>1309.6</td>
<td>1024.0</td>
<td>1024.0</td>
</tr>
<tr>
<td>1178.7</td>
<td>1190.8</td>
<td>1154.9</td>
<td>1154.9</td>
<td>964.5</td>
<td>964.5</td>
</tr>
<tr>
<td>1143.0</td>
<td>1143.2</td>
<td>1024.0</td>
<td>1035.9</td>
<td>869.1</td>
<td>869.1</td>
</tr>
<tr>
<td>1059.7</td>
<td>1000.4</td>
<td>970.3</td>
<td>1000.0</td>
<td>726.3</td>
<td>726.3</td>
</tr>
<tr>
<td>1000.0</td>
<td>964.5</td>
<td>845.3</td>
<td>875.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>738.2</td>
<td>726.3</td>
<td>714.4</td>
<td>738.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2: Prominent IR bands (cm\(^{-1}\)) of the Neem Leaf Powder before and after saturation with the dyes, Methylene Blue (MB), Congo Red (CR), and Brilliant Green (BG).

<table>
<thead>
<tr>
<th>IR bands (cm(^{-1}))</th>
<th>NLP</th>
<th>NLP + MB</th>
<th>NLP + CR</th>
<th>NLP + BG</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
<td>3600.0</td>
</tr>
<tr>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
<td>3357.4</td>
</tr>
<tr>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
<td>3190.8</td>
</tr>
<tr>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
<td>2929.0</td>
</tr>
<tr>
<td>2905.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2857.6</td>
<td>2857.6</td>
<td>2857.6</td>
<td>2857.6</td>
<td>2857.6</td>
</tr>
<tr>
<td>2714.8</td>
<td>2738.6</td>
<td>2738.6</td>
<td>2738.6</td>
<td>2738.6</td>
</tr>
<tr>
<td>2667.2</td>
<td>2679.1</td>
<td>2679.0</td>
<td>2679.0</td>
<td>2679.0</td>
</tr>
<tr>
<td>2357.8</td>
<td>2381.6</td>
<td>2381.6</td>
<td>2381.6</td>
<td>2381.6</td>
</tr>
<tr>
<td>1687.7</td>
<td>1666.8</td>
<td>1631.1</td>
<td>1643.0</td>
<td>1643.0</td>
</tr>
<tr>
<td>1464.3</td>
<td>1464.3</td>
<td>1452.6</td>
<td>1464.3</td>
<td>1464.3</td>
</tr>
<tr>
<td>1381.0</td>
<td>1381.0</td>
<td>1381.0</td>
<td>1381.0</td>
<td>1381.0</td>
</tr>
<tr>
<td>1327.5</td>
<td>1333.4</td>
<td>1297.7</td>
<td>1321.5</td>
<td>1321.5</td>
</tr>
<tr>
<td>1178.7</td>
<td>1178.7</td>
<td>1154.9</td>
<td>1154.9</td>
<td>1154.9</td>
</tr>
<tr>
<td>1143.0</td>
<td>1047.8</td>
<td>1035.9</td>
<td>1024.0</td>
<td>1024.0</td>
</tr>
<tr>
<td>1059.7</td>
<td>1000.2</td>
<td>976.4</td>
<td>988.3</td>
<td>988.3</td>
</tr>
<tr>
<td>1000.0</td>
<td>738.0</td>
<td>833.4</td>
<td>857.3</td>
<td>857.3</td>
</tr>
<tr>
<td>738.2</td>
<td></td>
<td>774.1</td>
<td>785.7</td>
<td>785.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>714.4</td>
<td>726.3</td>
<td>726.3</td>
</tr>
</tbody>
</table>
Fig. 3.1: FTIR spectra of Neem Leaf Powder
Fig. 3.2: FTIR spectra of Neem Leaf Powder after adsorption of Cr(VI).
Fig. 3.3: FTIR spectra of Neem Leaf Powder after adsorption of Cd(II).
Fig. 3.5: FTIR spectra of Neem Leaf Powder after adsorption of Pb(II) and Cd(II).
Fig. 3.6: FTIR spectra of Neem Leaf Powder after adsorption of Methylene Blue.
Fig. 3.7: FTIR spectra of Neem Leaf Powder after adsorption of Congo Red
Fig. 3.8: FTIR spectra of Neem Leaf Powder after adsorption of Brilliant Green
3.2.5 Determination of the Surface elements

XRF analysis of the dried Neem leaf powder (Philips PW 1480, Rh anode and LiF 200 crystal analyzer at Sophisticated Instruments Facility, Gauhati University) shows the presence of Ca, Cu, Fe, K, and Mn. However, due to absence of suitable standard, quantitative estimation could not be done. The XRF spectrum of the dried Neem Leaf Powder is presented in Fig. 3.9.

3.2.6 Conclusions from the characterization study

The following conclusions may be made from the physicochemical characterization study of the Neem leaf powder:

a) The powder has an acidic reaction with water yielding a pH value of 5.6 for the 10% slurry.

b) It was not possible to determine the BET surface area of the powder due to difficulties with degassing during the measurement.

c) Methylene Blue adsorption method yielded a value of 21.45 m²/g for the specific surface area of the Neem Leaf powder.

d) SEM analysis of the Neem Leaf Powder showed the surface topography to be quite rough and non-uniform. The powder consists of irregular shaped particles of different sizes and in most cases, with broken edges. Steps and kinks are quite common on the surface of the particles.

e) Adsorption of both metal ions and dyes creates dark patches on the surface masking some of the surface sites but not all the sites as could be seen from the SEM photographs.

f) FTIR study of the NLP surface showed the presence of –OH, –NH₂, >C=N–, ≡C≡C=, ≡C≡N< and ≡C≡O, >C=O, >C=C<, and >C=S groups. These groups are likely to determine the interaction properties of the NLP surface.

g) The presence of the metals, Ca, Cu, Fe, K, and Mn, on the NLP particles is qualitatively established from the XRF measurements.
Fig. 3.9: XRF spectra of the Neem Leaf Powder