2. Materials

Montmorillonite obtained from Fluka, Switzerland was used as starting clay for the preparation of Zr-PILC. The chemicals used in the study were of analytical grade. Humic acid, tannic acid, phenol, $p$-chlorophenol, $p$-nitrophenol and zirconyl chloride were obtained from Fluka, Switzerland while NaCl, HCl, and NaOH were provided by E.Merck, India. The basic dyes namely methylene blue (MB), crystal violet (CV) and rhodamine B (RB) are used as commercial salts and were purchased from Fluka, Switzerland. The coconut husk used for the preparation of activated carbon was obtained from a local coir industry.

2.2. Instruments and Apparatus

Infrared spectroscopy was used to determine the surface functional groups of the, clays and carbon. The spectra of the samples were recorded on a Perkin-Elmer FTIR-180 Spectrophotometer in the wavelength range of 400 – 4000 cm$^{-1}$ in KBr. The scanning electron microscopy was taken using Philips microscope (model – XL – 30 CP). The X-ray diffraction study of natural clay was done on Philips diffraction unit (model-1710). The elemental (CHN) analysis of humic acid and tannic acid was carried out using an Erlo-Carba model CHN
analyzer. The surface area (BET) measurements of the adsorbents were obtained from N2 adsorption at 77 K using Quantasorb surface area analyzer (model-QS-7). A micrometric mercury Porosimeter (model-9310) was used to determine the porosity of the adsorbents. The surface charge of the adsorbents was determined using potentiometric method. The density of the adsorbents was estimated using specific gravity bottle.

All the glasswares were of borosil class-A types and thoroughly cleaned with chromic acid followed by rinsing with distilled water before each experiments. The pH measurements were made using a Systronics made µ-processor (model-362) pH meter (India). The estimation of the adsorbates in the supernatant solution was done using UV-Visible spectrophotometer (Shimadzu, model-1601). A temperature controlled water bath shaker (Remi, model-G-16, India) with a temperature variation of ± 1.0 °C was used for equilibrium studies.

2.3. Adsorbents

2.3.1. Preparation of zirconium pillared clay

Montmorillonite (Mte) was first converted to Na-form by treating the clay several times with 1.0 M NaCl and then washed with deionised water. The cation exchange capacity (CEC) of the clay in Na\(^+\) form equals 0.86 meq/g as determined by the BaCl\(_2\) method [240]. Zirconium pillared clay was synthesized by pillaring of Na-Mte with zirconyl chloride, as described by Dyer [241]. In this work, 20.0 g of Na-Mte was added to 600 mL of 0.1 M zirconyl chloride solution. The suspension was refluxed for 6 h at a constant temperature of 90 °C. The resultant slurry was then stirred for 24 h, filtered and washed free of chloride with distilled water and tested with 0.1 M AgNO\(_3\). The product,
zirconium pillared clay (Zr-PILC) was dried at 100 °C and sieved to obtain –80+230 mesh size particle (Average diameter 0.096 mm).

2.3.2. Preparation of humus pillared clay

Humic acid (HA) was impregnated on Zr-PILC at pH 3.0 using the batch adsorption technique reported by earlier workers [242,243]. The adsorption was conducted at a solid (g)/liquid (mL) ratio of 0.5/100 for different concentrations of HA solutions. Contact time was 24 h, i.e., the time necessary to reach adsorption equilibrium. After attaining equilibrium, the suspension was filtered and washed with 0.01 M NaClO₄ followed by deionised water. The adsorbent was dried at 60 °C for 24 h. Here after the humus pillared clay is designated as HA-Zr-PILC.

The amount of HA loaded in Zr-PILC was determined by the following procedure. The filtrate and washings were collected in 1000 mL flask and made up to the mark. The amount of unadsorbed HA was determined using UV-visible spectrophotometer at a wavelength of 400 nm. The maximum amount of HA loaded in the Zr-PILC was calculated and found to be 51.87 μmol/g Zr-PILC. The amount of HA in the adsorbent calculated by this method was further confirmed by quantifying the HA after desorption from HA-Zr-PILC. HA retained in the Zr-PILC was completely desorbed with 250 mg of sodium dodecyl sulphate in 100 mL of 0.1 M NaOH solution [244]. Absorbance of the solution was measured at 400 nm. The surfactant did not interfere with spectrophotometric determination of HA.

In order to find out whether there is any leakage of HA from HA-Zr-PILC during the adsorption experiments, the supernatant
solutions were analysed for HA. It was observed that there was no leakage of HA from the adsorbent in a range of 2.0 – 8.0. However at a higher pH range of 8.5-11.0, a small amount of HA (6-14%) leached out from HA-Zr-PILC. Since the wastewaters containing dyes are always acidic in nature and the optimum pH range for wastewater treatment is below 8.5, the small amount of HA leaching at a higher pH may not create any problem.

2.3.3. Preparation of activated carbon

The coconut husk (CH) was ground, washed with distilled water to remove dirt and fine particles (< 0.096 mm), and dried at 80 °C for 4 h. About 50 g of CH was placed in a purpose-made graphite tube and placed at the center of the Matri (India) made furnace. Steam, produced by a steam generator, entered the graphite tube at a rate of approximately 3 mL/min (liquid water). The sample was then heated at 10 °C/min to 600 °C and held at that temperature for 1 h. After allowing the furnace to cool to room temperature the carbonized material was washed with 0.1 M HCl and then with distilled water. The washed product was then dried in an oven at 100 °C until constant weight and cooled. The yield of the activated carbon was found to be 42% of the original material. The adsorbent was ground and the particles having the average diameter of 0.096 mm (-80+230 mesh) was collected and kept in desiccator for subsequent use.

2.4. Characterization Methods

The adsorbent materials used in the present study were routinely characterized to get the structural information. The various properties
such as specific surface area, functional groups (FTIR spectrum), elemental composition, porosity, cation exchange capacity, moisture content, $pH_{zpc}$ and apparent density were determined using standard techniques. The properties are very useful for explaining the surface properties, adsorption mechanism and adsorption capacities of various adsorbents.

2.4.1 Surface area

The surface area of the adsorbents were determined using the $N_2$ gas adsorption with a Quantasorb Surface area analyzer (QS/7) using BET equation.

2.4.2. Porosity

The pore volumes are estimated using mercury porosimeter.

2.4.3. Elemental composition

The CHN analysis was performed using an Erlo-Carba model CHN analyzer. The percentage of oxygen content was calculated as the difference between 100.0% and the sum of the percentages of C, H, and N.

2.4.4. Cation exchange capacity

About 0.1 g of the adsorbent was transferred into a 100 mL stoppered bottle containing 50 mL of NaCl solution having different concentrations. The solution was agitated constantly on a water bath shaker at 30 °C and samples were taken only after 24 h. The amount of sodium ions in the supernatant solution was measured spectrophotometrically. The amount of sodium ions adsorbed on to the
adsorbent was calculated from the difference between the initial \( (C_0) \) and the remaining \( (C_c) \) metal concentrations in solutions.

2.4.5. Zero point charge

Acid/base potentiometric titration was also carried out to obtain the zero point charge \( (\text{pH}_{zpc}) \). The titrations were made in 0.001, 0.01, and 0.1 M NaNO\(_3\). The amount of adsorbents used in each titration was 0.1 g. Titrations were performed by adding standard solutions of HNO\(_3\) (0.1 M) and NaOH (0.1 M) using calibrated micropipettes. The different amounts of acid or base were added to each bottle. The bottles were then placed on a shaker and allowed to obtain equilibrium for over two days. They were filtered after shaking was finished. These procedures were repeated for different ionic strengths of the NaNO\(_3\) solution. After the equilibrium period, the pH recorded after a stable value was obtained using an Elico pH/mv meter. Blank samples containing NaNO\(_3\) was also titrated. The net surface charge density \( \sigma_o \) was calculated using the equation

\[
\sigma_o = \frac{F}{A} \left( C_A - C_B + \frac{[\text{OH}^-] - [H^+]}{A} \right)
\]

(52)

where \( \sigma_o \) is the surface charge density \( (\text{C/cm}^2) \), \( A \) is the surface area of the suspension \( (\text{cm}^2/\text{g}) \) \( C_A \) and \( C_B \) are the concentration of strong acid and alkali after each addition during the titration, \([H^+]\) and \([\text{OH}^-]\) are equivalents of \( H^+ \) and \( \text{OH}^- \) bound to the suspension surface \( (\text{eq/cm}^2) \).

2.4.6. Density

Densities of the adsorbents were calculated by picnometric method in which water and nitrobenzene were used as displacing liquids.
2.4.7. Chemical composition

The chemical analysis of the clay samples was performed. The studies revealed that clay contains silica and alumina as major constituents while other oxides of metals are present in lesser amounts.

2.4.8. Scanning electron microscopy

Scanning electron microscopy (SEM) is widely used to examine surfaces; resolution down to a few thousand angstroms is possible, depending on the nature of the sample. The surface is scanned by a focused electron beam, and the intensity of secondary electrons is monitored. Surface morphology of clay and modified clays were characterised by scanning electron microscope (SEM) method using Philips microscope (model-XL-30 CP). The samples were deposited on a brass stud from a well-dispersed dilute suspension. The surface of the pillared samples were made active to electron beam by depositing gold on the surface of the powder using an ion sputtering unit.

2.4.9. X-ray diffraction method

X-ray diffraction studies by the powder diffraction method making use of the Bragg equation can give us information about the crystallinity, chemical combination and interpretation of patterns in a particular material.

2.5. Methods

2.5.1. Adsorption experiments

The experimental conditions were optimized for the adsorption experiments by carrying out a few preliminary experiments. For this batch adsorption technique was used. Stock solutions of adsorbates were
prepared and the experimental solutions are prepared by diluting the stock solutions. Fifty mL of the experimental solutions mixed with 0.1 g of adsorbent in a stoppered bottle of 100 mL capacity was shaked at a fixed temperature in a water bath shaker for a period of time. After equilibration, the supernatant liquids were filtered and the adsorbate concentration was determined. The amount of adsorbate was estimated using UV-Visible spectrophotometer. The $\lambda_{\text{max}}$ of each adsorbate studied is given in Table 3.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic acid</td>
<td>350</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>270</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>662</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>591</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>554</td>
</tr>
<tr>
<td>Phenol</td>
<td>267</td>
</tr>
<tr>
<td>$p$-chlorophenol</td>
<td>279</td>
</tr>
<tr>
<td>$p$-nitrophenol</td>
<td>316</td>
</tr>
</tbody>
</table>

The effect of several parameters such as pH, initial concentration, contact time, agitation speed, temperature, particle size, ionic strength, and quantity of adsorbent on adsorption was studied. The pH was controlled by Systronics pH meter and adjusted by the addition of 0.1 M HCl and NaOH. Kinetic experiments were performed using different initial concentrations and at different temperatures. Adsorption isotherm experiments were also performed using the varying
concentration of adsorbates at a temperature range of 20-60 °C. The amount of adsorbed humic acid, tannic acid, phenolic compounds or dyes was calculated using the equation

$$q = \frac{(C_o - C_e) V}{m}$$ (53)

where q is the amount of adsorbate adsorbed onto unit amount of adsorbent (mg/g), C_o and C_e are the initial and equilibrium solution concentration (mg/L), respectively, V is the volume of aqueous phase (mL) and m is the mass of the adsorbent (g).

The effect of pH on adsorption was studied using two initial concentrations of adsorbates. The pH of each samples was adjusted between 2.0 and 9.0 using different standard solutions (0.001, 0.01, 0.1, 1.0 and 2.0 M) of HCl and NaOH. The pH-adjusted solutions were kept for an agitation time of 4 h in a water bath shaker having a constant speed of 200 rpm at 30 °C. The residual adsorbate concentration of each sample was measured. The optimum pH for the adsorption process was confirmed from the above experiment.

The effect of ionic strength on the adsorption of phenolic compounds was studied with different ionic strengths of 0.001, 0.005, 0.01, 0.05 and 0.1 M and at a fixed initial concentration of adsorbate. 0.1 g of adsorbent was added to stoppered bottles containing 50 mL of adsorbate solution with different ionic strengths. The solution was agitated for 4 h. The residual adsorbate concentration was estimated.

The effects of equilibrium time and initial concentration for the adsorption of phenolic compounds and dyes were performed by the following experiments. A known amount of adsorbent (0.1 g) was placed
in a 100 mL stoppered flask containing 50 mL solution. The pH was adjusted to the optimum value. The samples were shaken in a temperature controlled water bath shaker. Samples were then drawn from the flask at predetermined time intervals and residual adsorbate concentration was determined using spectrophotometric method. From this, various kinetic parameters can be calculated by kinetic equations.

Adsorption isotherm study were conducted by batch technique. About 0.1 g of the adsorbent was added to the stoppered bottles, which contain 50 mL of varying concentration of adsorbates. pH of the solution was kept at optimum value. The sample bottles were shaken continuously in a water bath shaker for the equilibrium time, after which samples were taken and filtered. Adsorbent loadings were calculated from the mass balance after initial and residual concentrations had been determined.

In order to determine the competition among various binary solution mixtures, batch experiments were performed using 50 mL combined solution containing varied concentration of dyes with 0.1 g of the adsorbent in 100 mL stoppered flask. The contents were shaken over a water bath shaker with a constant speed of 200 rpm at pH 6.0 and 30 °C. Samples were withdrawn at appropriate intervals of time, filtered and the filtrate was analyzed for dyes using the following equations

\[
C_A = \frac{K_{B_2}d_1 - K_{B_1}d_2}{K_{A_1}K_{B_2} - K_{A_2}K_{B_1}} \tag{54}
\]

\[
C_B = \frac{K_{A_1}d_2 - K_{A_2}d_1}{K_{A_1}K_{B_2} - K_{A_2}K_{B_1}} \tag{55}
\]
where subscripts A and B represent components in a binary solute system. $K_{A_1}$, $K_{B_1}$, $K_{A_2}$, and $K_{B_2}$ are the calibration constants for components A and B at $\lambda_1$ and $\lambda_2$, respectively. $d_1$ and $d_2$ are the optical densities at $\lambda_1$ and $\lambda_2$ respectively.

2.5.2. Desorption study

The spent adsorbent was thoroughly washed with deionised water. Desorption studies on spent adsorbent were carried out using 50 mL distilled water having different pH values. The pH of the solution was adjusted to different values and agitated for 6 h at 30 °C. Prior to desorption the adsorbent was washed with distilled water to remove any unadsorbed adsorbate. After agitation, the supernatant solution was filtered and estimated. The percentage desorption was determined at different pH values.

2.5.3. Test with industrial wastewater

The suitability of the adsorbent material for treating phenolic wastewaters was tested using oil refinery industry effluents. Effluent was collected from the local oil refinery and was characterized using standard methods. Batch operation technique was performed for this study. 50 mL of synthetic or industrial wastewater was treated with varying amount of adsorbent in a water bath shaker at constant speed and temperature. After attaining equilibrium, the suspensions were filtered and the concentrations of phenols in the filtrates were measured using spectrophotometer. From this the adsorbed amount of phenol was determined.