Chapter – IV

Experimental Technique
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EXPERIMENTAL TECHNIQUE

4.1. Procurement of the adsorbent

Plaster of Paris, available at commercial shop has been procured. This is activated at 400°C in a muffle furnace for 5 hours. It is then cooled, ground well to fine powder and stored in desiccator. The activated plaster of Paris was sieved well using the sieves of desired particle size range. The activated plaster of Paris is abbreviated as activated POP and it is applied as an adsorbent for the removal of selected metal ions and dyes.


The adsorbent selected in the present investigation, activated POP is characterized for particle size, apparent density, moisture content, ash content, water soluble matter and pH using the procedures detailed below:

4.2.1. Particle size

The particle size of the activated POP was measured using the Carl Zeiss Light microscope (Axiostar Plus). In order to determine the particle sizes of the activated POP, the ocular micrometer with a dimension of 10x was attached. Each division in the scale of the ocular micrometer is 0.01mm. The length and breadth of the each particle were measured using the ocular micrometer scale. By application of multiplication factors, the size of the particles was calculated.
4.2.2 Apparent density

A 100 mL graduated cylinder was weighed accurately. For the determination of apparent density, sufficient amount of the activated POP was transferred to constant tapping and filled up to the 50 ml mark. After filling the graduated cylinder with the activated POP, it was weighed accurately. The apparent density was computed by splitting up the weight of activated POP by 50.

4.2.3. Moisture content

About 10 g of the activated POP was weighed in a petri dish. The dish was placed in an air oven maintained at 105 ±5°C for about 4 hrs. The dish was covered, cooled in a desiccator and weighed. Heating, cooling and weighing were repeated at 30-minute intervals until the difference between the two consecutive weighing was less than 5 mg.

\[
\text{Moisture content (percent by mass)} = \frac{100(M - X)}{M}
\]

Where, M is mass in grams of the activated POP taken for test and X is the mass in grams of the activated POP after drying.

4.2.4. Ash content

Two grams of the POP variety under examination was weighed accurately into a tarred porcelain crucible. The crucible and its contents were placed in an air oven at 105 ± 5°C for about 4 hrs. The moisture content was established as described above and the contents were ignited in an electric muffle furnace at a temperature of 1000°C for about 3 hrs. The process of
heating and cooling was repeated until the difference between two consecutive weighing was less than 5 mg.

\[
\text{Ash on dry basis (percent by mass)} = \frac{M_1 \times 100}{M \left(100 - X\right)}
\]

Where, ‘\(M_1\)’ is mass of the ash in grams. ‘\(M\)’ is the mass of the activated POP taken for test in grams and ‘\(X\)’ is the percentage of moisture content present in the activated POP taken for test.

4.2.5. Matter soluble in water

Ten grams of the activated POP of known moisture content were weighed accurately and transferred into a one-liter beaker. About 100 mL of distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes after the flame was extinguished. The activated POP was then allowed to settle and the supernatant liquid was filtered through a Gooch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 100 mL of water each time. The combined filtrate was concentrated to less than 100 mL over a water bath, cooled and made up to 100 mL mark in a volumetric flask. Exactly 50 mL of the concentrate was transferred to a china dish, evaporated to almost dryness on a boiling water bath and finally dried in an electric oven maintained at 105 ± 5°C, cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30 min intervals, until the difference between two consecutive weighing was less than 5 mg.
Matter soluble in Water (%) = \frac{M \times 100 \times 2}{M_1 \times 100 (100 - X)}

Where, ‘M’ is the mass of the residue in grams. ‘M₁’ is the mass of the activated POP taken for test in grams and ‘X’ is the percent of moisture present in the activated POP.

4.2.6. pH

One gram of the dried activated POP was weighed and transferred into a one-liter beaker. 100 mL of freshly boiled and cooled water (adjusted to pH 7.0) was added and heated to boiling. After digesting for 10 min, the solution was filtered while it was hot, rejecting the first 20 mL of the filtrate. The remaining filtrate was cooled to room temperature and the pH was determined using an Elico model digital pH meter.

4.3. Materials
4.3.1. Reagents

All the chemicals used in the present research work were of analytical reagent grade and doubly distilled water was utilized for preparing experimental solutions.

4.3.2. Preparation of double distilled water

The doubly distilled (DD) water was prepared by distilling the distilled water over alkaline potassium permanganate in an all glass Pyrex apparatus.
4.3.3. Cleaning of glassware

The cleaning of glassware was done by soaking the glassware in a detergent solution followed by keeping them in chromic acid for a period of 48 hours. This glassware was then rinsed with DD water prior to use.

4.4. Preparation of experimental solutions

4.4.1. Preparation of heavy metal ion solutions

The heavy metal ions chosen for the adsorption studies in the present work are iron(III), copper(II), nickel(II) and chromium(VI). The Stock solutions (1000 mg/L) of Fe(III), Cu(II), Ni(II) and Cr(VI) were prepared by dissolving required amount of metal salt in one liter of DD water. The weights of the respective salts taken are listed in the table (Table 4).

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Formula of metal salt</th>
<th>Weight (g) of metal salt in one liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (III)</td>
<td>FeNH₄(SO₄)₂·12H₂O</td>
<td>8.634</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>CuSO₄</td>
<td>3.9290</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Ni(NH₄)₂(SO₄)₂·6H₂O</td>
<td>6.6990</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>K₂Cr₂O₇</td>
<td>2.8288</td>
</tr>
</tbody>
</table>

4.4.2. Preparation of dye solutions

The dyes employed in the adsorption studies in the present investigation are methylene blue [MB], rhodamine B [RDB] and malachite green [MG]. Stock solutions (1000 mg/L) of the dyes were prepared by dissolving required amount...
of the respective dye in one liter of DD water. The weights of the respective dyes taken are listed in the table (Table 5).

**Table 5**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Weight (g) of dye in one litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>1.0000</td>
</tr>
<tr>
<td>RDB</td>
<td>1.0000</td>
</tr>
<tr>
<td>MG</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

4.4.3. Preparation of 5% \( \text{K}_4[\text{Fe(CN)}_6] \)

About 5g of potassium ferrocyanide was accurately weighed and dissolved in 100 mL of \( \text{H}_2\text{O} \).

4.4.4. Preparation of 2% KCNS

About 2g of potassium thiocyanate was accurately weighed and dissolved in 100 mL of \( \text{H}_2\text{O} \).

4.5. Adsorption studies

4.5.1. Batch equilibration method

All experiments were carried out at 30°, 40°, 50° and 60°C temperature in batch-mode. Batch-mode process was taken because of its ease and reliability [Hema Krishna and Gilbert, 2014]. The batch-mode experiments were conducted using Erlenmeyer glass flask of 100 mL capacity. Prior to each experiment, a predetermined amount of activated POP was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure equal mixing. Each flask was filled with a known volume of sample
before commencing stirring such as metal ion and dye solution with an initial concentration of 25 mg/L to 250 mg/L, the flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion and dye was measured by using Elico make UV-Visible double beam spectrophotometer.

4.5.2. Effect of variable parameters

4.5.2.1. Dosage of activated POP

The various doses (10 to 250 mg / 50 mL of the activated POP) were chosen and they mixed with the metal ion and dye solution and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

4.5.2.2. Initial concentration of metal ion or dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of metal ions and MB dye ranging from 25 to 125 mg/L and MG & RDB dyes ranging from 50 to 250 mg/L by keeping all other factors were kept constant.

4.5.2.3. Contact time

The effect of period of contact between the adsorbent (activated POP) and adsorbate on the removal of the metal ions and dyes was determined in a single cycle by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.
4.5.2.4. Initial pH

Adsorption experiments were carried out at a wide range of pH of the solution i.e. 2-10. The acidic and alkaline pH of the medium was maintained by adding the required amounts of dilute hydrochloric acid or sodium hydroxide solutions. While carrying out the experiments, the parameters like particle size of the activated POP, metal ion or dye concentration, dosage of activated POP, the concentration of other ions and temperature were kept constant.

4.5.2.5. Other ions

A specific metal ion and dye in the presence of chloride ions were experimentally verified using activated POP in adsorption studies. Keeping all other factors constant, the determination of the percentage of metal ion or dye adsorbed from the particular initial concentration of the metal ion and dye solution with varying concentration of the added ion.

4.5.2.6. Temperature

The adsorption experiments were performed in between 30°, 40°, 50° and 60°C in a thermostat attached with a shaker. The temperature was maintained with an accuracy of ± 0.5°C.

4.5.3. Adsorption isotherms

In order to analyze the adsorption data, the Freundlich [Freundlich, 1906] and Langmuir [Adamson, 1960] adsorption isotherms are employed.
The adsorption isotherm was highly significant in the removal of metal ion and dye solution by the adsorption technique, as it provides an approximate estimation of the adsorption capacity of the adsorbent. The equilibrium data for the removal of metal ion and dye by adsorption on the adsorbent at different temperature have been used in Langmuir [Langmuir, 1916 and 1918; Slejko, 1985] and Freundlich isotherms [Freundlich, 1906].

**Langmuir isotherm:** \[
\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}
\]

**Freundlich isotherm:** \[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

Where, ‘\(C_e\)’ is the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); ‘\(Q_m\)’ and ‘\(b\)’ are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of ‘\(Q_m\)’ and ‘\(b\)’ have been obtained from the linear correlation of ‘\(C_e/Q_e\)’ against ‘\(C_e\)’. The Freundlich constants ‘\(K_f\)’ and ‘\(n\)’ are the measures of adsorption capacity and intensity of adsorption respectively, and these values have been calculated from the linear correlations of ‘\(\log Q_e\)’ against ‘\(\log C_e\)’.

The essential characteristics of the Langmuirs isotherm can be described by a separation factor, ‘\(R_L\)’ which was defined as [Weber and Chakraborty, 1974; Annadurai et al., 1997].

\[R_L = \frac{1}{1 + bC_0}\]

Where, ‘\(b\)’ is the Langmuir constant and ‘\(C_0\)’ is the initial concentration of the adsorbate in the adsorption studies. The value of ‘\(R_L\)’ infers the nature of adsorption isotherm and the feasibility of adsorption process as follows:
4.6. Adsorption kinetics

The kinetics of sorption describe the solute uptake rate, which in turn governs the residence time of sorption reaction [Bektas and Kara, 2004; Singh and Pant, 2006; Shakeri et al., 2012]. It is one of the important characteristics in defining the efficiency of sorption [Mansour et al., 2011].

The kinetic models such as, pseudo-second-order, Elovich and Intraparticle diffusion were used to fit the experimental data using linear regression analysis method [Ho and McKay, 2002; Vijayakumaran and Arivoli, 2012]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficient ($\gamma$), (the $\gamma$ values close or equal to 1). A relatively higher $\gamma$ value indicates that the tested model successfully describes the kinetics of adsorption of adsorbates [Okasha et al., 2012].

The batch kinetic [Hameed et al., 2009] experiments were essentially identical to those of adsorption equilibrium method. The aqueous samples were taken at different time intervals (10, 20, 30, 40, 50 and 60 minutes) and the concentrations of metal ions/dyes were similarly measured. All the kinetic experiments were carried out at a temperature of 30, 40, 50 and 60°C and at an initial concentration of 25, 50, 75, 100, 125 mg/L for metal ions and MB dye

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Adsorption Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
and 50, 100, 150, 200 & 250 mg/L for MG & RDB dyes. The amount of adsorption, $q_t$ (mg/g) at time $t$, was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W}$$

Where, $C_t$ (mg/L) is the liquid phase concentration of metal ions or dyes at different time interval.

### 4.6.1. Pseudo-second-order equation

The pseudo-second-order adsorption kinetic rate equation is stated by the following differential equation [Ho and McKay, 2000; Ho and McKay, 1998; Ho and McKay, 2002]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$

... (4.1)

Where, ‘$k_2$’ is the rate constant of pseudo-second-order adsorption (g/mg min).

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ the integrated form of equation (4.1) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$

... (4.2)

This is the integrated rate law for a pseudo-second-order reaction equation can be rearranged to obtain equation (4.3), which has a linear form:

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

... (4.3)

If the initial adsorption rate, $h$ (mg g$^{-1}$min$^{-1}$) is:

$$h = k_2 q_e^2$$

... (4.4)
then equations (4.3) become:

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} \quad \ldots (4.5)
\]

The plot of “\(t/q_t\)” against time “\(t\)” of the equation (4.5) should give a linear relationship from which ‘\(q_e\)’ and ‘\(k_2\)’ can be determined from the slope and intercept of the plot, respectively. The correlation coefficients (\(\gamma\)) were also calculated.

### 4.6.2. Elovich equation

The Elovich or Roginsky–Zeldovich model equation is generally expressed as [Low, 1960; Chien and Clayton, 1980; Sparks, 1986; Ho and McKay, 2002; Ozacar and Ayhan Sengil, 2005]:

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \ldots (4.6)
\]

Where; ‘\(q_t\)’ is the amount of adsorbate adsorbed by adsorbent at a time ‘\(t\)’, ‘\(\alpha\)’ is the initial adsorption rate (mg/g min), ‘\(\beta\)’ is the desorption constant (g/mg) during any one experiment.

To simplify the Elovich equation, Chien and Clayton [1980] assumed \(\alpha\beta\) t >> t and on applying the boundary conditions \(q_t = 0\) at \(t = 0\) and \(q_t = q_e\) at \(t = t\) equation (4.6) becomes

\[
q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \ldots (4.7)
\]

If metal ion or dye adsorption fits the Elovich model, a plot of \(q_t\) vs. \(\ln(t)\) should yield a linear relationship with a slope of \((1/\beta)\) and an intercept of
\[(1/\beta)\ln(\alpha\beta)\]. The Elovich model parameters \(\alpha\), \(\beta\) and correlation coefficient (\(\gamma\)) were calculated.

### 4.6.3. Intraparticle diffusion

The intraparticle diffusion process is often the rate limiting step in many adsorption processes [Weber Morris, 1963; Natarajan and Khalaf, 1986; Panday et al., 1984; Kannan and Vanangamudi, 1991; Mohammadi et al., 2014]. The sorption process was an overall conjunction of several mechanisms with a preponderant part played by intraparticle diffusion. Hence, the sorption performance of the adsorbent has been determined by the influence of the diffusion mechanism of adsorbate uptake [Karthikeyan et al., 2004]. Pore diffusion in the fluid phase within the particles represents the diffusion in the adsorbed state. When pore diffusion limits the adsorption process, the relationship between the initial adsorbate concentration and the rate reaction will not be linear. It seems that pore diffusion limits the overall adsorption rate by the adsorbent [Venkatraman et al., 2012].

As the metal ion or dye are vigorously agitated during the adsorption period, it was probably reasonable to assume that, mass transfer from the bulk solution to the external surface of the adsorbent does not at all limit the rate of the reaction. A functional relationship common to the majority of intraparticle diffusion treatments was that uptake varies almost proportionally with the half power of time was explained. The influence of intraparticle diffusion was estimated by evaluation of initial sorption rate. The intraparticle diffusion rate constant was given by the following equation:
\[ Q = K_{id} t^{0.5} + C \]

In the present study, the possibility of existence of intraparticle diffusion has been tested by plotting the graph between amount of metal ion or dye adsorbed and square root of time. The rate constant for intraparticle diffusion co-efficient, ‘\( K_{id} \)’ for metal ion or dye was determined from the linear portion of the respective plots.

4.7. Thermodynamic parameters

The thermodynamic parameters such as the standard change in free energy change (\( \Delta G^0 \)), enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) were calculated as follows:

The free energy of the sorption process considering the sorption equilibrium constant, \( K_0 \) is given by the equation:

\[ \Delta G^0 = -RT \ln K_0 \]

Where, \( \Delta G^0 \) is the free energy of adsorption (kJ/mol), \( T \) is the temperature in Kelvin and \( R \) is the universal gas constant (8.314 J/ Mol K). The adsorption distribution coefficient \( K_0 \) for the sorption reaction was determined from the slope of the plot of \( \ln(Q_e/C_e) \) against \( C_e \) at different temperature and extrapolating to zero \( C_e \) according to the method suggested by Khan and Singh [1987].

The adsorption distribution coefficient may be expressed in terms of enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) as a function of temperature,

\[ \ln K_0 = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]
Where, $\Delta H^0$ is the standard heat (or enthalpy) of adsorption (kJ/mol) and $\Delta S^0$ is standard entropy change. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of van’t Hoff plot of $\ln K_0$ against $1/T$ respectively.

4.8. Analytical measurements

Fourier Transform Infra Red (FTIR) spectra of the activated POP before and after adsorption of metal ions and dyes were recorded from a Shimadzu double beam spectrophotometer (made in Japan).

The surface morphology of the activated POP was examined with the use of Scanning electron microscopy (SEM), before and after adsorption of metal ions and dyes and the corresponding SEM micrographs were obtained at an accelerating voltage of 15 Kv (Hitachi SE 900) at 5000× magnification.

The X-ray diffraction patterns of the activated POP, before and after adsorption of metal ions and dyes were obtained from the X-ray Diffractometer, 40KV/30mA, Model D/Max ULTIMA III, Rigaku Corporation, Japan.

4.9. Data analysis

The experimental data were analyzed using origin (version 6) software. The linear fit of the model was discussed using correlation coefficient ($\gamma$) values.
References


