Chapter – IV

DATA PROCESSING TOOLS

Equilibrium studies

Adsorption of heavy metal/dye is considered to be a fast physical or chemical process and its rate is governed by the type of process. In another sense, it can also be defined as a collective term for a number of passive accumulation processes which in any particular case may include ion exchange, co-ordination, complexation, chelation, adsorption and micro-precipitation. Proper analysis and design of adsorption separation processes require relevant adsorption equilibria as one of the vital information.

In equilibrium, a certain relationship prevails between solute concentration in solution and adsorbed state (i.e., the amount of solute adsorbed per unit mass of adsorbent). Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred to as adsorption isotherm. Several adsorption isotherms originally used for gas phase adsorption are available and readily adopted to correlate adsorption equilibria in heavy metals / dyes adsorption. Some well-known ones are Freundlich, Langmuir, Redlich–Paterson and Sips equation. The most widely used among them are Freundlich and Langmuir equations. The application of Langmuir\textsuperscript{106} and Freundlich\textsuperscript{107} isotherms on adsorbent-assisted heavymetal/dye removal from water will be discussed in the subsequent paragraphs.
Langmuir isotherm

Widespread-used model for describing heavy metal/dye sorption to adsorbent is the Langmuir model. Langmuir equation relates to the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This isotherm is based on three assumptions, namely adsorption limited to monolayer coverage, all surface sites being alike and one site accommodating one adsorbed atom and the ability of a molecule to be adsorbed on a given site independent of its neighbouring sites occupancy. By applying these assumptions and a kinetic principle (rate of adsorption and desorption from the surface is equal), Langmuir equation is written in the following form

\[ Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad \ldots \ldots \quad 4.1 \]

This equation is often written in linear forms as

\[ \frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad \ldots \ldots \quad 4.2 \]

where \( Q_e \) is the amount of solute adsorbed per unit weight of adsorbent (mg/g), \( C_e \) the equilibrium concentration of solute in the bulk solution (mg/L), \( Q_m \) is adsorption efficiency and also called as the maximum monolayer adsorption capacity or saturation capacity (mg/g) and \( b \) is the adsorption energy, \( b \) is the reciprocal of the concentration at which half saturation of the adsorbent is reached. The linear equation is often preferred in favour of its simplicity and convenience. Within the Langmuir model, the saturation capacity \( Q_m \) is supposed to coincide with the saturation of a fixed number of identical surface sites and as such, it should logically be independent of temperature.\(^{[108]}\)
The essential characteristics of Langmuir isotherm can be described by a separation factor, $R_L$, which is defined by the following equation

$$R_L = 1 / (1 + bC_0) \ldots \ldots (4.3)$$

where $C_0$ is the initial concentration of the metal ion solution. The separation factor, $R_L$, indicates the shape of the isotherm and the nature of the adsorption process is given below:

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Nature of the process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L &gt; 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &gt; R_L &gt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L &gt; 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

**Freundlich isotherm**

Freundlich isotherm is an empirical equation. This equation is one among the most widely used isotherms for the description of adsorption equilibrium. Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents. This equation has the following form:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \ldots \ldots (4.4)$$

where $Q_e$ is the amount of adsorbate adsorbed (mg/g), $C_e$ is the equilibrium concentration of metal ion in solution (mg/L) and $K_f$ and $n$ are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. A favourable adsorption tends to have $n$ value between 1 and 10. Larger value of $n$ (smaller value of $1/n$) implies stronger interaction between adsorbent and heavy metal while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites.
As a robust equation, Freundlich isotherm has the ability to fit nearly into all experimental adsorption–desorption data and is especially excellent for fitting data from highly heterogeneous sorbent systems. Apart from the ability to represent well in most cases, a physical meaning of $1/n$ was not clear in several studied systems. A $1/n$ value of higher than unity ($n$ less than one) suggests the presence of a concave/curved upward isotherm in the case of non-linear form of graph drawn between quantity adsorbed at time ‘$t$’ ($Q_t$) and time ‘$t$’. This concave type isotherm is also called as solvent-affinity type isotherm.[108] In this case, strong adsorption of solvent as a result of strong intermolecular attraction within the adsorbent layers occurs. But in most cases, adsorption experimental data has the tendency to be in convex rather than in concave form.

Sorption of solute on any sorbent can occur either by physical bonding, ion exchange, complexation, chelation or through a combination of these interactions. In the first case of physical bonding, as the solute is loosely bound, it can easily be desorbed using distilled water. Given the fact that miscellaneous functional groups such as hydroxyl, carbonyl and carboxyl can be present within the structure of adsorbent, hence the mechanism of adsorption will not be restricted to physical bonding only. Different mechanisms as mentioned can be involved as the interaction between sorbent and solute molecules. The parameter ‘$n$’ value of Freundlich equation expresses these phenomena.

Adsorption capacity is the most important characteristic of an adsorbent. It is defined as the amount of adsorbate taken up by adsorbent per unit mass of adsorbent. This variable is governed by a series of properties,
such as pore and particle size distribution, specific surface area, cation exchange capacity, pH, surface functional groups, and also temperature.

**Kinetic studies**

Adsorption equilibria studies are important in determining the efficiency of adsorption. Added despite of this, it is also necessary to identify the adsorption mechanism type in a given system. With the purpose of investigating the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to test the experimental data. In addition, information on the kinetics of metal/dye uptake is required to select the optimum condition for full-scale batch metal removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface.

Generally, several steps are involved during the sorption process by porous sorbent particles: (i) Bulk diffusion; (ii) External mass transfer (boundary layer or film diffusion) between the external surface of the sorbent particle and the surrounding fluid phase; (iii) Intraparticle transport within the particle and (iv) Reaction kinetics at phase boundaries.

In practice, kinetic studies were carried out in batch reactions using various initial sorbate concentrations. Sorption kinetic models have been proposed to clarify the mechanism of sorption from aqueous solution on to an adsorbent. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris sorption kinetic model, Natarajan and Khalaf first-order reversible reaction model, etc.
Natarajan and Khalaf equation

It is applicable to heterogeneous reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solutions and the activated carbon is expressed as follows:

\[ \begin{array}{c}
A \\
\downarrow k_2 \\
B
\end{array} \]

\[ k_1 \quad k_2 \]

where \( k_1 \) is the forward rate constant and \( k_2 \) is the backward rate constant. ‘A’ represents adsorbate remaining in the aqueous solution and ‘B’ represents adsorbate adsorbed on the surface of activated carbon.

The equilibrium constant \( (K_0) \) is the ratio of the concentration of adsorbate in adsorbent and in aqueous solution \( (K_0 = k_1 / k_2) \).

Natarajan Khalaf equation is.

\[
\log \frac{C_0}{C_t} = \frac{k_{ad}}{2.303} t \quad \text{…… (4.5)}
\]

Where \( C_0 \) and \( C_t \) are the concentrations of the adsorbate (in mg/L) at time zero and at time \( t \), respectively. \( k_{ad} \) is the first order rate constant \( \text{(min}^{-1}) \) for adsorption.

The rate constants \( (K_{ad}) \) for the adsorption can be calculated from the slope of the linear plots of \( \log \frac{C_0}{C_t} \) versus \( t \) for different concentrations and for different temperatures. The determination of forward rate constants and backward rate constants using this \( k_{ad} \) and \( K_0 \) values is described as below:

\[
K_{ad} = k_1 + k_2 \quad \text{……… (4.6)}
\]

\[
k_1 + k_2 = k_1 + \left( \frac{k_1}{K_0} \right) \quad \text{……… (4.7)}
\]

\[
k_1 + \left( \frac{k_1}{K_0} \right) = k_1 \left[ 1 + 1 / K_0 \right] \quad \text{……… (4.8)}
\]
Intra particle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of $Q_t$ versus $t^{0.5}$ represents multi linearity, which characterizes two or more steps involved in the sorption process. According to Weber and Morris,[110] an intra particle diffusion co-efficient $K_p$ is defined by the equation:

$$K_p = \frac{Q}{t^{0.5}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.9)$$

Thus the $K_p$ (mg/g min$^{0.5}$) value can be obtained from the slope of the plot of $Q_t$ (mg/g) versus $t^{0.5}$

Thermodynamic parameters

To evaluate the feasibility of the adsorption process, thermodynamic parameters such as change in free energy $\Delta G^\circ$ (kJ/mol), enthalpy $\Delta H^\circ$(kJ/mol) and entropy $\Delta S^\circ$ (J/K/mol) can be determined using the following equations.\(^97\)

$$K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.0)$$

$$\Delta G^\circ = -RT \ln K_0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.1)$$

$$\log K_0 = \frac{\Delta S^\circ}{(2.303RT)} - \frac{\Delta H^\circ}{(2.303R)}T \quad \ldots \ldots \ldots (5.2)$$

where $K_0$ is the equilibrium constant, $C_{\text{solid}}$ is the solid phase concentration at equilibrium (mg/L), $C_{\text{liquid}}$ is the liquid phase concentration at equilibrium (mg/L), $T$ is the temperature in Kelvin and $R$ is the gas constant. The Vant Hoff plots are drawn between $\log K_0$ versus $1/T$. $\Delta H^\circ$ and $\Delta S^\circ$ values can be evaluated from the slope and intercept of the plot respectively. Positive value of $\Delta H^\circ$ indicates endothermicity and negative value indicates the
exothermicity of the adsorption process. Positive value of $\Delta S^\circ$ indicates that the adsorption accompanies increased randomness while the negative value infers adsorption accompanies with reduction in the randomness. Spontaneity of the adsorption can be understood from the sign of $\Delta G^\circ$ value. Negative sign indicates the spontaneous process while the positive sign indicates the non-spontaneity of the process.