Adsorption Phenomena: Definition, Mechanisms, and Adsorption Types: Short Review

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ABSTRACT
Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transfer of a molecule from a fluid bulk (liquid or gas) to a solid surface so, it is classified as a surface process. This layer is expressed by two kinds of interaction physical or chemical interactions. This process usually is reversible, and the reverse process is called desorption. In this review, the definition and types of the adsorption process will be defined. In addition to a brief explanation about the major adsorption isotherm models, adsorption kinetics, and adsorption thermodynamic

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1. INTRODUCTION
The mechanisms of adsorption process occurred by adhesion of material either gaseous, liquid, or solid called substrate on the surface of solid, or liquid, called sorbent or adsorbent [1].

There are different adsorption systems, liquid-gas or liquid-liquid. If a liquid material is an adsorbent, so the interfacial layer called film, micelle, or emulsion. The other system is solid-liquid or solid-gas; the adsorbent is a solid material, so the approved mechanism for adsorption process is interfacial layer model.
The interfacial layer describes the equilibrium exists between the adsorbent and bulk phase. The first region is the substrate bind to the sorbent surface and the second region is the surface layer of the sorbent. There are two principals to explain interfacial layer mechanism.

**Physical Adsorption:** also called physisorption, the bonding between substrate and adsorbent is a weak Van der Waals forces, no changes of chemical structure for both substrate and sorbent.

**Chemical Adsorption:** also called chemisorption, the chemical bonding formation between substrate and adsorbent, by rearrangement of electron density between the adsorbent and substrate, the nature of this bond is ionic bond or covalent bond.

Both models explain the adsorption mechanism; based on experimental physical criteria results the suitable adsorption model is determined for a system. The physical criteria used to compare two models are thermodynamic or adsorption isotherm studies and kinetics or equilibrium adsorption studies.

Thermodynamic or adsorption isotherm studies are represented by the degree of coverage (θ), \( θ = \frac{\text{Number of adsorption sites occupied on adsorbent}}{\text{Number of adsorption sites available on the adsorbent}} \).

Kinetics or equilibrium adsorption studies are used to explain the adsorption mechanism and adsorption characteristics.

Both thermodynamic and kinetic experimental results distinguish between physical adsorption and chemical adsorption. The results determine bonding type, binding specificity, temperature effect, enthalpy of the bonding process, concentration or pressure effect, saturation of the interfacial layer, and kinetics of the process [2]. Indeed, there is a difference between physical values for the two models as shown in (Table.1).

2. **KINETIC ADSORPTION**

Previous studies [3] describe the kinetic adsorption process in two steps. The first step assumes the transfer of the adsorbate from the bulk solution to the surface of the adsorbent. The second step diffuses of the adsorbate and arranges it inside the sorbent pores. The rate-limiting step of adsorption process elucidates the adsorption mechanism [4].

2.1. **Pseudo-first -Order Reaction Kinetic**

The adsorption rate constant assume to be first order reaction kinetic
\[ \frac{dq_t}{dt} = k_1(q_{e} - q_t) \] ......................................................(1).

Where \( k_1 \) is the adsorption rate constant for the first order adsorption, \( q_t \) is the amount of substrate adsorbed at time \( t \) (mg/g) and \( q_e \) is the amount of substrate adsorbed at saturation (mg/g).

The integration of Eq. (1) gives the following expression:

\[ \ln (q_e - q_t) = -k_1* t + C_1 \] ......................................................(2).

Where \( C_1 \) is the integration constant for the first order reaction kinetic. Integrating Equation (2) for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) where \( q_t \) reaches plateau, gives the following expression:

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \] ......................................................(3)

The value of \( k_1 \) and \( \ln q_e \) can be obtained from the slope and intercept respectively of the linear plot of \( \ln (q_e - q_t) \) versus \( t \). Comparing \( q_e \) values obtained from the intercepts of the plots with those obtained experimentally, prove the adsorption process is first-order kinetic reaction.

2.2. Pseudo-Second-Order Reaction Kinetic

If adsorption process obeys Pseudo-second-order reaction kinetic, it is manipulated by the following mathematical equations [3]:

\[ \frac{dq_t}{dt} = k_2(q_{e} - q_t)^2 \] ......................................................(4)

Where \( k_2 \) is the adsorption rate constant for the second order adsorption, \( q_t \) is the amount of substrate adsorbed (mg/g) at time \( t \) and \( q_e \) is the amount of substrate adsorbed at saturation (mg/g).

If eq (4) is integrated, the following expression is obtained:

\[ \frac{1}{q_e - q_t} = k_2 * t + C_2 \] ......................................................(5).

Where \( k_2 \) is the second order reaction constant (g mg\(^{-1}\) min\(^{-1}\)), \( q_e \) and \( q_t \) are the amount of metal ions adsorbed per unit weight at equilibrium and time \( t \), respectively. Integrating equation (5) for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) gives eq (6):

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \] ......................................................(6).
The values of $q_e$ and $k_2$ are calculated by plotting of $t / q_t$ vs. $t$. gives a straight line, experimental $q_e$ values comparing by the calculated value.

3. ADSORPTION ISOTHERM

The adsorption isotherms describe the pathway of the interaction of a substrate from the bulk solution to the surface of adsorbate. It represents a relation between the amount of substrate adsorbed per unit mass of adsorbent and the substrate concentration or pressure in the bulk solution at a fixed temperature [3].

The role of temperature is to determine a modal that describe how adsorption process between sorbent and adsorbate and describe the effect of temperature on adsorption process if favorable or not. Adsorption isotherms were classified into four main groups: L (Langmuir type), H (high affinity), S (cooperative) and C (constant partition) (Figure 1).

The classification depends on the lower part of the curve when the adsorbate solution is very dilute [5].

S-type isotherm: indicates cooperative adsorption which works when adsorbate-adsorbate interaction is stronger than adsorbate-adsorbent interaction. Consequently, clustering of adsorbate molecules is favored at the surface because they interact strongly with each other than with the surface (Figure 1), [5].

L-type isotherm: indicates high affinity of the adsorbate for the adsorbent, which suggests chemisorption. This kind of isotherms occurs when adsorbate-solution interaction is weaker than adsorbate-adsorbent interaction (Figure 1), [5].

H-type isotherm: it is an extended case of L-type which suggests extremely high affinity of adsorbate for adsorbent, so in dilute solution, the adsorbate is almost completely adsorbed (Figure 1), [5].

C-type isotherm: indicates a constant proportional affinity of the adsorbate molecules for the adsorbent and is always noticed only at low range of adsorbate concentration (Figure 1), [5].

3.1 Langmuir Adsorption Isotherm

Langmuir isotherm is the simplest isotherm model obtained in 1916, which was originally derived from studying of the adsorption of gases by solids. It describes the single adhesion layer on the homogenous surface [6], where the attraction between molecules
adsorbed on the adsorbate and non-adsorbed analyte in the bulk solution decreases as they are getting away from the adsorbate surface.

There is a limitation of Langmuir equation because it assumes that adsorption is monolayer with no attraction between molecules on the surface of adsorbate. Therefore, this model is for low concentration or low pressure for the gas system.

Langmuir isotherm is defined according to the following mathematical equations:

\[ q_e = \frac{q_m \cdot K \cdot C_e}{1 + K \cdot C_e} \]  

where \( q_e \) is the equilibrium amount of solute adsorbed per unit mass of adsorbent (mg/g), \( C_e \) is the equilibrium concentration of solute (mg/L), \( q_m \) is the adsorption capacity of the monolayer (mg/g), and \( K_L \) is the Langmuir constant related to the energy and affinity of binding sites of adsorption (L/mg). eq (9) can be written in the following linear form (I):

\[ K_d = \frac{C_e}{q_e} \]

Other linear forms of Langmuir results from taking the inverse of equation (9), to get linear form (II)

\[ \frac{1}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{1}{K_L \cdot q_m} \]  

or by multiplying equation (11) by \( C_e \), to get linear form (III)

\[ \frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{1}{q_m} \cdot \frac{C_e}{C_o} \]

The values of \( q_m \) and \( K_L \) can be evaluated from the slope and the intercept of the plot of the linear forms of Langmuir equation. One of the basic features of the Langmuir isotherm model can be expressed in a dimensionless constant called equilibrium parameter \( R_L \) which is defined as [7]:

\[ R_L = \frac{1}{1 + K_L \cdot C_o} \]

Where the value of \( R_L \) indicates that the behavior of the isotherm is described as unfavorable adsorption (\( R_L > 1 \)), linear adsorption (\( R_L = 1 \)), no adsorption (\( R_L = 0 \)), and favorable adsorption (\( 0 < R_L < 1 \)), where \( C_o \) is the highest initial concentration.

### 3.2. Freundlich Adsorption Isotherm

Freundlich isotherm is a special case of Langmuir, used for modeling the multi-layer adsorbed on heterogeneous surfaces; it can be explained by the following equations [8].

\[ q_e = K_p \cdot C_e^\beta = K_p \cdot C_e^{\frac{1}{n}} \]  

…….……………………………... (13).
Where $q_e$ is the equilibrium amount adsorbed per unit mass of adsorbent (mg/g), $C_e$ is the equilibrium concentration of the adsorbate in solution (mg/L); $K_F$ is the Freundlich isotherm constant, and $n$ is the adsorption intensity.

The logarithmic linear form of the Freundlich equation is given as:
\[
\log q_e = \log(K_F) + \frac{1}{n}(\log C_e) \tag{14}
\]

3.3. **Dubinin–Radushkevich (D–R) Isotherm**

Langmuir and Freundlich isotherms are considered simple models, to explain the physical and chemical characteristics of adsorption, by layer-by-layer surface coverage. Another model used is Dubinin–Radushkevich (D–R) isotherm, commonly used to describe the sorption isotherms of single substrate systems. The D–R isotherm similar to Langmuir isotherm but it rejects the homogeneous surface or constant adsorption potential. It postulates the mechanism of adsorption done by pore-filling of sorbent rather than layer-by-layer sorbent surface coverage.

The liner D–R isotherm is expressed as:
\[
\ln q_e = \ln q_{\text{max}} - \beta \varepsilon^2 \tag{15}
\]

Where $q_e$ is the substrate amount (mg/g) that is removed per unit adsorbate mass, $q_{\text{max}}$ is the D–R adsorption capacity (mg/g), $\beta$ is a constant related with adsorption energy (mol$^2$ kJ$^2$), and $\varepsilon$ is the Polanyi potential. According to Eq. (15), the Polanyi potential ($\varepsilon$) can be given as:
\[
\varepsilon = R \frac{1}{T} \ln(1+1/C_e) \tag{16}
\]

Where $R$ is the gas constant (kJ K$^{-1}$ mol$^{-1}$) and $T$ is the temperature (K).

The main energy of adsorption ($E$) is calculated by using the following formula:
\[
E = (2\beta)^{-0.5} \tag{17}
\]

Where $E$ gives information about the physical and chemical features of adsorption, it is defined as the free energy change required for transferring one mole of ions from solution to solid surface [3].

4. **ADSORPTION THERMODYNAMICS**

Thermodynamic parameters such as free energy ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were estimated using the following equations:
\[
\Delta G^o = -RT \ln K_d \tag{18}
\]
\[ \ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \] \hspace{1cm} (19)

Where \( R \) is the gas constant \((8.3145 \text{ J.mol}^{-1}\text{K}^{-1})\), \( T \) is the temperature in Kelvin and \( K_d \) is the thermodynamic distribution coefficient, as in equation (20):

\[ K_d = \frac{q_e}{C_e} \] \hspace{1cm} (20)

The values of \( \Delta H^o \) and \( \Delta S^o \) are calculated from the slope and intercept of the linear variation of \( \ln K_d \) with reciprocal temperature. The \( \ln K_d \) was calculated from the intercept of \( \ln \left( \frac{q_e}{C_e} \right) \) vs \( q_e \) [9].

**Table 1:** Differences between physical and chemical adsorption.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specificity</td>
<td>Non-specific.</td>
<td>Highly-specific</td>
</tr>
<tr>
<td>Nature of adsorption</td>
<td>Depend on nature of adsorbent.</td>
<td>Depend on nature of adsorbent.</td>
</tr>
<tr>
<td>Reversibility</td>
<td>Reversible process.</td>
<td>Mainly irreversible</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Low (20-40 kJ/mol).</td>
<td>Higher than physical adsorption (40-300 kJ/mol).</td>
</tr>
<tr>
<td>Activation energy</td>
<td>Does not require high activation energy.</td>
<td>Require high activation energy.</td>
</tr>
<tr>
<td>Layer of adsorption of interfacial region (saturation)</td>
<td>Multi layers.</td>
<td>Mono layer.</td>
</tr>
</tbody>
</table>
Bonding

Week Van der Waals, London forces, and dipole-dipole attraction. This attraction has longer range than chemical type, and there is no chemical composition change for substrate.

Strong ionic bond, or covalent bond formed between substrate and adsorbent, there is a chemical composition change. This attraction has shorter range than the physical type.

Figure 1: Classification of adsorption isotherm, [5].
5. REFERENCES


