Isothermal adsorption models: mini-focused observations

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Abstract

Adsorption is kinetically time-dependence controlled retention/ release mobility as a natural phenomenon in base and applicable in industry or in science. It is well-studied and modulated by known Langmuir, Temkin, Freundlich, and other models to describe how it occurred and explains kinetic- thermodynamic material behaviour.

Linear and/ or non- linear expressions may take place according to the theoretical base of these models to conclude the layer formation, uniformity besides reaction reversibility, and favourability from kinetic- thermodynamic principles.

Coefficient of determination (R^2) is a mean variation of data or a degree of proper or fitting as mostly used in kinetic and isotherm literatures. In adsorption investigations, experimental physical- chemical conditions and error sources are the main influenced factors, for example, at surface coverage (or inhibition efficiency) in corrosion treatments or adsorption capacity in pollution subject. Linearity variation will govern R^2 to predict adsorbate behaviour on adsorbent surface that is highly influenced by concentration, temperature, pH, type of measuring method, physical and chemical structures of the adsorbent and adsorbate, and error sources in each experiment.

Keywords: adsorption, isotherm model, Freundlich, Langmuir, Temkin, R^2.

1. Introduction - Brief Scope

Industrial activities and population seriously change, threat both environment and human life and health, and consume planet resources in spite of many regulations made by many countries. In this manner, ecosystem faces huge challenges in material deterioration issues that gained big research area through chemical, biological, physical, and engineering developments [1].

One of successful scientific phenomenon is surface adsorption of multi-components via simultaneous formation of chemical or physical interactions [2].

Currently, many scientific articles and practical applications by companies tend to use simple, viable, eco-friendly, re-generable materials to overcome pollution - corrosion problems [3, 4, 5]. Mineral (trace elements, radionuclides) or organic molecules (plant, animal, living microorganisms) as soluble or suspended particles in a fluid medium (water, acid, base, …) may interact with a material surface (solid, liquid, gas) in a mechanism having isothermal relationship known as sorption isotherm model. By reaching equilibrium state at constant status of all related physicochemical parameters especially temperature, this isotherm model is a mathematical prediction method. Adsorption is an example of precipitation or reducing of solute presence in its medium in a limited progressive state that finally reaches equilibrium [6, 7, 8].

This mini- review is aimed to give general look about adsorption as a kinetically time-dependence natural phenomenon in base and applicable in industry or in science. Also, a brief description about Langmuir, Temkin, Freundlich, and other models to explains kinetic-thermodynamic material behaviour through linear and/ or non- linear expressions, reaction reversibility, and favourability from kinetic- thermodynamic principles.

2. General look in adsorption and isotherm models

In fact, ideal adsorption needs an ideal equilibrium that its parameters, mechanism, and relationship can be calculated and/ or predicted. Quantitative adsorptive comparison is usually estimated from varied physical and chemical conditions to describe optimal design [9, 10].

To fix the research foundations to the fitted isotherm model, experimental data that are affected by error sources, chemical reaction, experiment design, and others are subjected to linear mathematical expression closely equal to unity Figure (1) [11]. Regression analysis provides intensive information about distribution in all system units under study and tests qualification of adsorption theories. So, regression correlation coefficient by its value specify how adsorption occurred and explains kinetic- thermodynamic material behaviour. Linear expression in isotherm models may present a damaged image of adsorption process and to solve this problem, researchers tend to apply non- linear or non-isotherm models [12, 13].
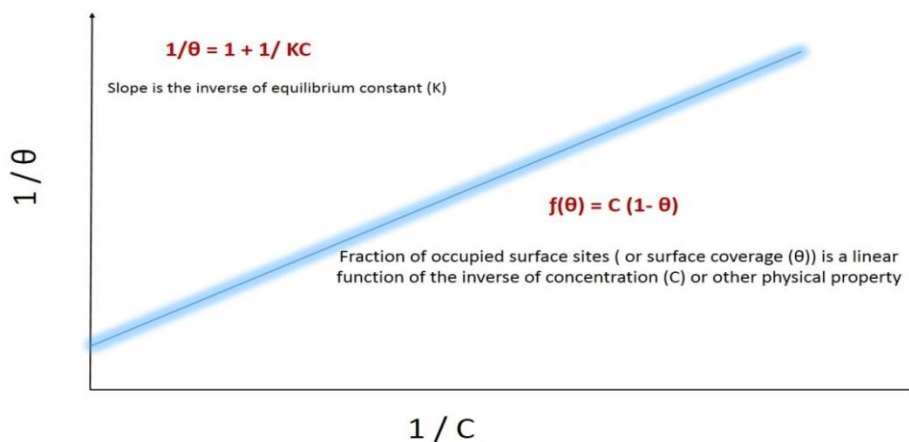
Fig. (1): Linear isotherm model equation

By applying the adsorption model, the mobility of material in a specific environment towards adsorption surface at the experimental condition like temperature, concentration, time, pH, and others is described by a curve. From this curve or graphical description, equilibrium state is a balance or ratio between adsorbate and adsorbent at particular physical-chemical conditions [14]. In general, practical adsorption isotherm curve is controlled by adsorbate concentration in medium (C_m) and on the adsorbent surface after adsorption process (C_s) at specific physical-chemical conditions or their ration (C_m/C_s) that are mainly used in pollution studies and known as partition or distribution coefficient [15]. This curve has various forms such as:

-   Linear curve with zero start when the ratio (C_m/C_s) is constant at any point of process progress and used at low concentration of adsorbate and suitable adsorbent quantity to minimize error presence.
-   Concave curve is obtained when (C_m/C_s) is reduced with rising of adsorbate concentration.
-   Sigmoidal curve is another adsorption curve that depends upon adsorbate polarity.

Various designed systems in adsorption science were modelated to predict surface interaction with material according to kinetic, potential, or thermodynamic status such as Langmuir, Temkin, Freundlich, Flory-Huggins, and other more. These designed systems demonstrate the final state of adsorption according to some known principles Table (1).

In physisorption, a molecule binds to the surface then diffuse with formation of a weak non-covalent interaction (van der Waals). Here, this diffusion or mobility is highly happened with and after formation of monolayer macromolecule or organic frameworks under particular practical conditions. This is potentially useful reversible process in gas phase, framework,

solvent, dense packing, or porous surface linked to temperature – concentration variation, entropy, enthalpy, and equilibrium. From chemical, kinetic, predominant, and structural point of view, chemisorption is a term of strong bonding with forbidden site exchange (delocalization) [8, 16].

Table (1) General comparison between adsorption states

Character	Physical adsorption (Physisorption)	Chemical Adsorption (Chemisorption)
Reversibility	Occur	Not occur
Adsorbate-adsorbent bonding	Weak (van der Waals)	strong
Equilibrium state	Close	Far
Possibility of re-adsorption after desorption	Possible	Not possible because of strong bonding between adsorbate and the surface (adsorbent)
Diffusion possibility	Possible especially at low surface coverage	Not possible

To be more knowledgeable about these models, several brief statements will be introduced of their aspects as below.

2.1 Langmuir isotherm model

Langmuir model: is an empirical description of adsorption with two parameters assuming that adsorption occurred in thickness with one localized molecule does not affected by neighbour molecules giving one homogenized layer. In this model, each molecule has zero interaction affinity by other molecules reflecting constant enthalpy and activation energy. It is viable and supple model for low concentration of adsorbate with computerized models depending on single molecule adsorption, binding energy, and multi-occurred mechanisms (adsorption, desorption, and / or dissociation) [6, 7, 8, 17].

In this position, surface coverage (θ) becomes identical character of practical relative ratio between adsorption and desorption when both dynamic processes reaching equilibrium state. So, surface coverage symbolizes sum of all occupied sites by adsorbate. These occupied sites are not all available sites on adsorbent surface. In fact, they are only a part of them, and for this scientific reason, researchers present their isotherm model in adsorbate quantity per adsorbent weight. So, this model expresses reversible kinetic process between adsorbate and adsorbent.

Curve linearity in this model illustrates adsorption favourability while non- linearity outlines irreversibility or non-favourability Figure (2) [18].
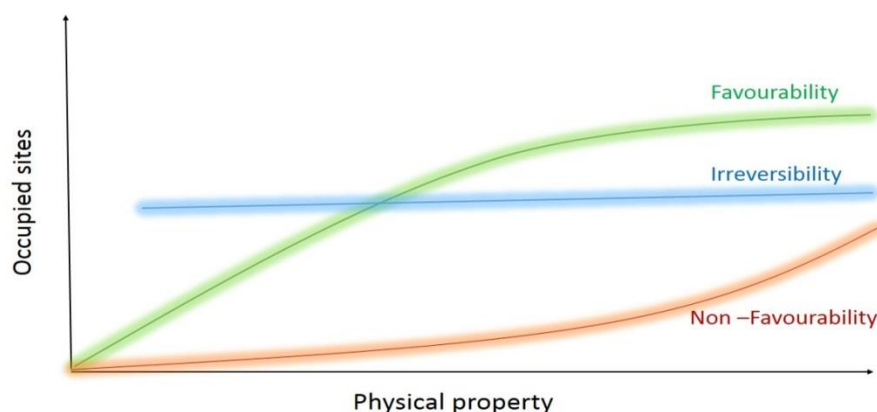

Fig. (2): Adsorption favourability

2.2 Temkin isotherm model

The model that deduces linearity decreasing of adsorption heat with coverage (or inhibition efficiency in corrosion science) is **Temkin model** which demands, as mainly considerations, internal interactions control surface coverage (θ) that have an exert influence on heat or enthalpy linearity. So, Temkin model is highly neglected concentration at minimal or high value and does not suppose logarithm of heat because it assumes uniformity in adsorbate distribution on the surface.

2.3 Flory – Huggins and Dubinin – Radushkevich isotherm models

Flory and Huggins in their model suggested that adsorption is a spontaneous process that can be predicted by free Gibbs energy and equilibrium constant [8, 18, 19].

Another empirical temperature – dependent model is **Dubinin – Radushkevich isotherm** that describes how heterogeneous adsorption surface is formed relying upon energy distribution that specify the physical or chemical interaction between each adsorbate molecule and the surface. Its representative equation is semi- empirical temperature dependent description of a surface having pores that physically hold adsorbate molecule with Van der Waals forces. For example, it is usually used in ions pollution or corrosion studies [20].

2.4 Freundlich and Hill isotherm models

Freundlich model inverses of Langmuir model in its principles of adsorption layer formation and uniformity beside reaction reversibility. Here, adsorption intensity designates how energy of

active sites distributes molecules on the surface towards forming heterogenetic layers. So, this multilayer adsorption model describes how various adsorbate to adsorbent ratio is gained with changing of concentration leading to surface heterogeneity. In this model even in competitive state between different adsorbates, concave curve may represent an adsorption situation with an appropriate correlate coefficient [15, 18, 21].

Multisystem action of adsorbate (like ion or organic molecule) into homogeneous adsorbent as a macromolecule reflecting non-competition binding phenomenon is known as Hill isothermal model [22].

3. <u>Coefficient of determinations (R^2) as isotherm model fitting character</u>

By applying any isothermal model to specify adsorption mechanism, number of formed layers, and other important features in this process, linear regression or the coefficient of determination (R^2) is estimated as determent fitting character. Linear analysis characterizes adsorption performance in details according to the experimental data and usefulness of the applied model. R^2 is mean variation of data and in many models is a degree of proper or fitting as it is mostly used in kinetic and isotherm literatures [8, 15, 18].

In pollution-adsorption issue, many published papers examined in adsorption capacity as a main target of removal of pollutant(s) from its environment with various adsorbents. Several researchers observed that consistency and accuracy of the applied isotherm were influenced by linearity estimation as a major factor of adsorption prediction. Also, equilibrium relationship faces unfeasible behaviour with practical scattered points creating error in prediction and validation of the applied isotherm model [5, 23, 24].

In adsorption studies, researchers tend to validate their isotherm model(s) under study mostly by the coefficient of determination (R^2) with / without combined with others. As it is known in adsorption investigations, experimental physical- chemical conditions and error sources are the main influence factors in the resulting data such as surface coverage (or inhibition efficiency) in corrosion subject or adsorption capacity in pollution subject. So, any variant of linearity increasing or decreasing will govern R^2 and other characters under considerations [5, 18, 23 - 26].

For more understanding of choosing isotherm model to be fitted to the experiment under study, some recent studies is tabulated (Table 2) [27- 30].

Table (2) R^2 – isotherm model fitting in several corrosion studies.

Inhibitor	Specimen	Medium	Method	Concentration	Temperature, K	R^2 according to isotherm model		Ref.
Allium cepa extract	Austenitic stainless steel	Sea water	Weight loss	(0.1-0.6) g/L	298	Langmuir	0.9544	27
						Temkin	0.8763	
						Freundlich	0.9158	
						El-Awady	0.8586	
						Adejo Ekwuchi	0.8086	
sweet prayer leaf extract	Mild steel	NaOH, 1M	Weight loss	(0.2-1.0)g/L	293	Langmuir	0.98	28
						Temkin	0.9445	
						Freundlich	0.871	
					303	Langmuir	0.9815	
						Temkin	0.5756	
						Freundlich	0.9116	
					313	Langmuir	0.9651	
						Temkin	0.3414	
						Freundlich	0.9625	
					323	Langmuir	0.904	
						Temkin	0.1701	
						Freundlich	0.9382	
					333	Langmuir	0.7446	
						Temkin	0	
						Freundlich	0.5767	
Methanol leaf extract of Maihot esculentum	Mild steel	HCl, 2M	Weight loss	(0.1-0.5) g/dm³	301	Langmuir	0.9948	29
						Temkin	0.9589	
						Freundlich	0.9876	
						Adejo Ekwuchi	0.8908	
					305	Langmuir	0.9949	
						Temkin	0.9967	
						Freundlich	0.9986	
						Adejo Ekwuchi	0.9582	
					309	Langmuir	0.9393	
						Temkin	0.9909	
						Freundlich	0.9839	
						Adejo Ekwuchi	0.954	

Inhibitor	Specimen	Medium	Method	Concentration	Temperature, K	R^2 according to isotherm model		Ref.
					313	Langmuir	0.9815	
						Temkin	0.9956	
						Freundlich	0.9967	
						Adejo Ekwuchi	0.9507	
Prothioconazole (Fungicide)	Copper		Potentiodynamic polarization	$(5 \times 10^{-6} - 10^{-4})$ M	288	Frumkin	0.97528	30
						Bockris-Swinkels	0.98707	
						Kastening-Holleck	0.98027	
						Flory-huggingf	0.98781	
						Dhar-Flory-Huggins	0.98781	
						Langmuir	0.99862	
					298	Bockris–Swinkels	0.9704	
						Flory–Huggins	0.96932	
						Dhar–Flory–Huggins	0.96932	
						Langmuir	0.99976	
					308	Bockris–Swinkels	0.97118	
						Flory–Huggins	0.97133	
						Dhar–Flory–Huggins	0.97133	
					318	Frumkin	0.99769	
						Bockris–Swinkels	0.98957	
						Damaskin–Parsons	0.99769	
						Kastening–Holleck	0.99807	
						Flory–Huggins	0.98881	
						Dhar–Flory–Huggins	0.98881	
						Langmuir	0.98733	

From these examples in Table (2), Adebayo et al. studied a corrosion inhibition and tested R^2 after applying three different equations [28] as below:

$$C/\theta = 1/K + C \qquad (1)$$

$$\log \theta = \log K + n \log C \qquad (2)$$

$$\theta = (-\ln K / 2a) - \ln C / 2a \qquad (3)$$

where C: inhibitor concentration (g/L), a: molecular interaction parameter, K: equilibrium constant. Slope, intercept, K, n, a, and R^2 were calculated after plotting C/θ against C (equation (1)), log θ against log C (equation (2)), θ against ln C (equation (3)). From mathematical points, surface coverage (θ) has inverse, logarithm, and non –equal natural logarithm relationships with concentration (C) as represented in equations (1), (2), and (3) respectively. These difference influenced the obtained factors from plotting these equations especially C/θ against C (equation (1)). The most important factor in choosing the isotherm fitting to the study is R^2 which mainly affected by surface coverage (θ). Also, this θ is affected by practical conditions (concentration, temperature, pH, type of measuring method, and physical and chemical structures of the adsorbent and adsorbate) and error sources in each experiment Figure (3). As shown in Figure (3). R^2- Temkin isotherm model relationship was highly affected by temperature increasing. Also, Langmuir was the most suitable isotherm model for the corrosion inhibition study even with its lower R^2 value at high temperature effect.
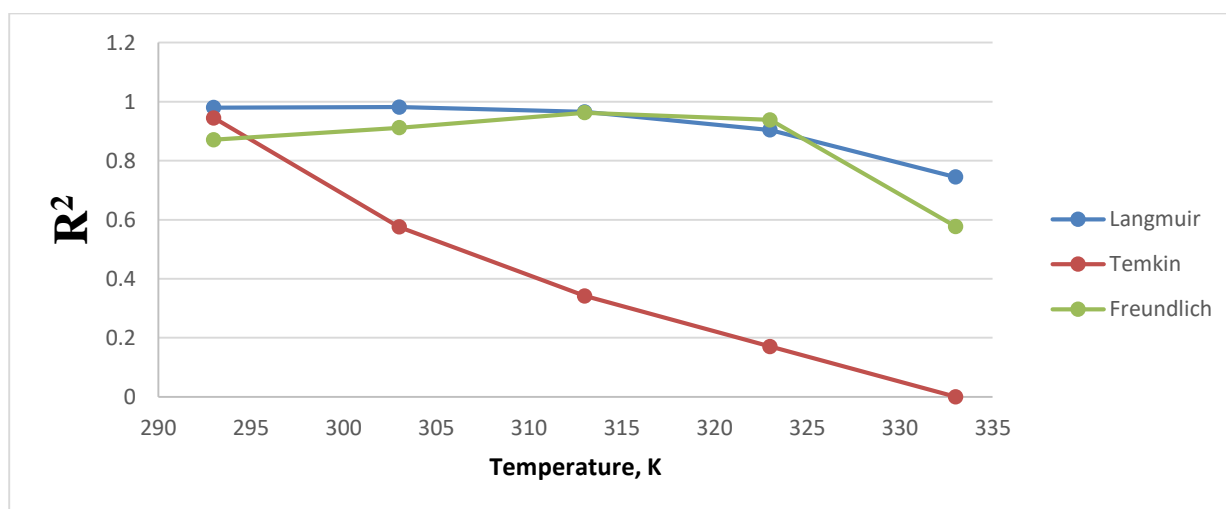

Fig. (3): R^2 variation with temperatures and tested isotherm models

4. <u>Conclusions</u>

Adsorption likes any process that occurs in nature, lab, and industry is well-studied phenomenon. It was modulated by many scientists: Langmuir, Temkin, Freundlich, and others to describe how it occurred and explains kinetic- thermodynamic material behaviour. Linear and/ or non- linear expressions in isotherm models took place in published research or reviewed articles or books. These expressions specify the theoretical base of the models and conclude the layer formation, uniformity beside reaction reversibility, and favourability from kinetic-thermodynamic standardizations.

Coefficient of determination (R^2) is a mean variation of data or a degree of proper or fitting as mostly used in kinetic and isotherm literatures. In adsorption investigations, experimental physical- chemical conditions and error sources are the main influence factors at surface coverage (or inhibition efficiency) in corrosion subject or adsorption capacity in pollution subject. So, any variant of linearity increasing or decreasing will govern R^2 and other characters under considerations. R^2 or model choosing to predict adsorbate behaviour on the adsorbent surface is highly influenced by concentration, temperature, pH, type of measuring method, physical and chemical structures of the adsorbent and adsorbate, and error sources in each experiment.

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