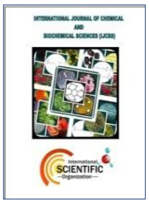

International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

Correct Interpretation of sorption mechanism by Isothermal, Kinetic and Thermodynamic models

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Abstract

A number of kinetic and isothermal models have been used by various researchers to interpret mechanisms involved behind sorption process. However, a careful review of literature shows that several times researchers have withdrawn wrong conclusions due to unawareness about postulates of models as well as regarding correct mathematical and statistical parameters. This review article presents the overall picture about the adsorption isotherms modeling, their fundamental characteristics and mathematical expressions. Furthermore, kinetic modeling and rate equations are also described in details with their mathematical expressions. There is need to develop suitable correlations for batch and continuous equilibrium data using theoretical or empirical equations that are key component in predictive modeling methods for the analysis and design of adsorption system. In conclusion, this single review will provide complete understanding of all models applicable to sorption data and will provide complete understanding to enable researcher to select correct model for explanation of the results of adsorption experiments.

Key words: Theoretical models, Adsorption, Wastewater Treatment

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1. Introduction

1.1 Adsorption Isotherm

Adsorption is a process in which solute particles are isolated from liquid phase with a solid adsorbent having specific affinity for a particular solute particle. Generally, adsorption processes are economically acceptable due to easy availability of sorbents, reduced cost and lower volume of the sludge for handling and disposal, recovery/extraction of metals from the absorbent and reuse of adsorbents for further treatments. Different natural, ecofriendly and synthetic adsorbents have been used for the removal of heavy metals (Cd^{2+}, Pb^{2+}, Ni^{2+}, As^{3+} and As^{5+}) by numerous researchers [1, 2]. The success of adsorption isotherm depends upon the amount of adsorbate per unit weight of the adsorbent and the concentration of adsorbate in the solution at a specific temperature and equilibrium conditions.

Empirical or theoretical equations play key role in predictive modeling procedures to understand and analyze the design of adsorption systems. There is need to develop a strong and appropriate correlations for the batch equilibrium data by using empirical or theoretical equations [2]. In general, adsorption isotherm is valuable curve explaining the release or movement phenomenon of substance from aqueous medium to a solid state at a specific pH and constant temperature. Adsorption equilibrium is developed when an adsorbate have a contact with the adsorbent for a plenty of time, with the concentration of adsorbate present in solution at a dynamic equilibrium interfering with its concentration. Thermodynamic assumptions and physicochemical parameters of adsorption equilibrium provide an internal picture of the adsorption mechanism, surface properties and the affinity of adsorbents.

Over the past few decades, variety of different isothermal models Freundlich [3], Langmuir [4], Redlich–Peterson [5], Dubinin–Radushkevich (Dubinin and Radushkevich 1947), Brunauer–Emmett–Teller [6], Toth (Toth,1971), Temkin [7], Sips [8], Khan [9], Koble–Corrigan [10, 11] and Hill [12] isotherm have been developed on the basis of three fundamental approaches. Kinetics is fundamental approach referred to time required to achieve adsorption equilibrium. Adsorption equilibrium is defined as "a state of dynamic equilibrium in which both adsorption and desorption rates are equal". Similarly, thermodynamics is the base of second approach, that provides a framework of deriving different forms of adsorption isotherm models and the third approach focuses on the generation of the characteristic curve. However, isothermal modeling plays pivotal role in generating characteristic curves of potential theories of adsorption isotherm models. An emerging trend in isotherm modeling is the derivation in one or more than approach, indicating differences in the interpretation of physical parameters of models [13].

It was found that results of different parameters obtained from linear analysis are easy to interpret, whereas modeling of isotherm data by linear analysis may cause discrepancies between experimental data and the predictions. Many researchers have examined the applicability of linear and non-linear isothermal models in illustrating different adsorption systems, e.g. adsorption of heavy metals, azo-dyes, and organic pollutants on to different adsorbents [14].

1.2 Adsorption Kinetics

Adsorption kinetic studies plays significant role by providing useful information about the reaction pathways and the mechanism of the reactions. Numerous kinetic models are being used to describe the mechanism of the adsorption process. Thus, it is important to evaluate the pollutant removal efficiency of the adsorbent from aqueous solution in order to design a more efficient treatment plant. Rate law is also a major factor in developing adsorption kinetics and is determined by experimentation. Zero (0), 1st, 2nd, 3rd order, pseudo 1st, pseudo 2nd order, Elovich [15], intra-particle diffusion [16] and the first order reversible kinetic equations were also used to explain the results obtained from experimental data [2].

1.3 Adsorption Thermodynamics

Thermodynamics describes the behavior of matter as a function of state variables. For example, adsorption temperature coefficient is directly proportional to the heat of immersion of the solid adsorbent in the gas. The most significant application of adsorption thermodynamics is the calculation of phase equilibrium between a solid adsorbent and a gaseous mixture. The base of thermodynamic calculation is adsorption isotherm that provides information about the gas absorbed on the nanopores as a function of external pressure. Adsorption isotherms are determined experimentally or calculated theoretically by using molecular simulations.

2. Isothermal Modeling of Adsorption

2.1 Langmuir Isotherm

2.1.1 Assumptions

Langmuir proposed his theory by making following assumptions in 1916 [4].

1) Langmuir isotherm defines adsorbate-adsorbent relationship in which the amount of adsorbate coverage is limited to a mono layer.
2) All sites are equal and each adsorbate molecule occupies only a single site on a homogeneous surface.
3) There is no interaction of adsorbate molecules on adjacent molecules.

2.1.2 Equation

The linear form of the Langmuir isotherm equation is given below:

$$\frac{C_e}{Q_e} = \frac{1}{Q^{\circ} K_l} + \frac{1}{Q^{\circ}} C_e \text{ .... (Eq 1)}$$

Where, Q_e is adsorption capacity at equilibrium, C_e is the concentration of adsorbate in liquid phase at equilibrium (mg/L). Q° and K_l are Langmuir constants related to the monolayer adsorption capacity of the adsorbent (mg/g) and defined as the maximum amount adsorbed on a layer. Langmuir constants related to the monolayer adsorption capacity of the adsorbent (mg/g) and it is the maximum amount adsorbed and the rate of adsorption (L/mg), respectively.

Essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (RL) where K_l is Langmuir constant and C° is liquid phase initial concentration of adsorbate (mg/L). This parameter is defined as [2].

$$R_L = \frac{1}{1+K_l C^{\circ}} \text{ .... (Eq 2)}$$

2.2 Freundlich Isotherm

2.2.1 Assumptions

1) Freundlich isotherm model provides the information about non-ideal and reversible adsorption.
2) This model is applied to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules.
3) The application of the Freundlich equation also suggests that sorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent.

2.2.2 Equation

The empirical equation of Freundlich isotherm is given below:

$$q_e = K_f C_e^{1/n} \text{ ………… (Eq 3)}$$

Where Kf is Freundlich constant related to the bonding energy (mg/g) (L/g)1/n, n heterogeneity factor, Ce is adsorbate concentration in solution (mg/L) at equilibrium. Freundlich equilibrium constants could be determined from the linear plot of ln qe and ln Ce. The following equation provide

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \text{ ………… (Eq 4)}$$

Freundlich isotherm is widely applicable on heterogeneous systems particularly organic compounds or highly interactive species on molecular sieves and activated carbon. The slope (value of 1/n) ranges between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity. The value of the slope was calculated from the following equation:

$$q_t = \frac{C_o - C_e}{\mathrm{m}/\mathrm{v}} \text{ ………… (Eq 5)}$$

Where q_t represents sorption capacity at time t (mg/g), C_0 is the initial concentration of adsorbate in solution (mg/L), Ce is equilibrium concentration of adsorbate in solution (mg/L), m is the dry weight of adsorbent (g), V volume of aqueous solution (L) [17].

2.3 Dubinin Radushkevich Isotherm

2.3.1 Assumptions

1) The Dubinin–Radushkevich (DR) equation is broadly applied to exemplify the adsorption of sub-critical vapors in nano-porous solids such as activated carbons and zeolites.
2) The adsorption potential of this equation is depend upon the temperature.
3) Generally, it is utilized to understand the adsorption mechanism with Gaussian energy in a heterogeneous surface.
4) This methodology frequently applied to differentiate physical and chemical adsorption of metals ions with their mean free energy (Energy (E) per molecule of adsorbate) [18].

2.3.2 Equation

D-R model is represented by the following equation

$$\ln q_e = \mathrm{Ln} q_0 - \beta \varepsilon^2 \text{ ………… (Eq 6)}$$

β represents the activity coefficient of mean sorption energy and qe is adsorption capacity at equilibrium, ε Polanyi potential which is given by,

$$\varepsilon = \mathrm{RTLn}\ (1 + 1/\ \mathrm{Ce}) \text{ ………… (Eq 7)}$$

Where R (kJ/mol K) is a gas constant and T (K) is the temperature, C_e (mg/L) is the concentration of adsorbate in solution at equilibrium. The value of β (mol^2/J^2) is given by the slope of the plot of Ln q_e versus ε^2, and the ordinate intercept gives the adsorption capacity q_0 (mg/g) [19]. The mean adsorption energy E is given by

$$\mathrm{E} = \frac{1}{(-2\beta)^{1/2}} \text{ ………… (Eq 8)}$$

2.4 Temkin Isotherm

2.4.1 Assumptions

1) Temkin isotherm is the model that explains the adsorption of hydrogen on to platinum electrodes in acidic solution.
2) This isotherm occurs on the principal of adsorbate-adsorbate interactions in adsorption isotherm.
3) Heat of adsorption increased linearly with increasing surface coverage of the adsorbent and this adsorption is a characteristic of uniform distribution of binding energies up to a maximum binding energy.
4) This model also suggests that the adsorption is categorized by a uniform distribution of binding energies up to maximum binding energy (ΔG max) that result in the following equation.

2.4.1 Equation

$$Q = Q_T \ln (1 + K_T c) \text{ ………… (Eq 9)}$$

where K_T (M^{-1}) express equilibrium binding constant equivalent to the maximum binding energy (K_T= exp (-ΔGmax/RT)), c (M) (molar) represents the concentration of adsorbate in solution at equilibrium, Q (mol adsorbate/ml support) is the amount of adsorbate adsorbed to a surface, and Q_T (mol adsorbate/ml support) is the differential surface capacity of adsorbate adsorption per unit binding energy.

2.5 Flory-Huggins Isotherm

2.5.1 Assumptions

The Flory-Huggins (F-H) thermodynamic equation is frequently applied to interpret the equilibrium sorption mechanism in multi-component membrane systems.

1) The F-H equation is generally used to illustrate the liquid sorption isotherm of the pure liquid-polymer systems.

2) Independence of lattice constants on composition (artificial).
3) Polymer molecules are of same size.
4) Mean concentration of polymer segments in cells adjacent to cells unoccupied by the polymeric solute is equal to the overall average concentration.
5) No effect of mixing on volume change (while in some favorable interactions between solvent molecules and polymers may have negative impact on volume change).
6) There are no energetically preferred arrangements of polymer segments and solvent molecules in the solution.

2.5.1 Equation

$$\Delta G_{mix} = RT\ n_i \ln \varphi_i + n_M \ln \varphi_M + \chi_{iM}\ ni\ \varphi_M \text{ .... (Eq 10)}$$

Where ΔHmix represents the enthalpy change of mixing and ΔSmix represents the mixing entropy. The subscripts i and M represent the liquid component and membrane respectively. Φ is the volume fraction, R is the gas constant, T is the absolute temperature, ni is the number of moles of component i, and χiM are the F-H interaction parameters between the liquid and the membrane [20].

2.6 Hill Isotherm

2.6.1 Assumptions

1) Hill Isotherm explains the binding phenomenon of several species on to a homogeneous surface.
2) According to this model “adsorption is a process in which ligand binding ability at one site of the macromolecule, may affect the different binding sites of the same macromolecule [21].

2.6.2 Equation

$$qe = \frac{qHC_e^{nH}}{KD + C_e^{nH}} \text{ .... (Eq 11)}$$

Where, KD, nH, and qH are constants, qe is the amount of adsorbed solute per weight of adsorbent at equilibrium, Ce is the concentration of adsorbate at equilibrium.

2.7 Redlich Peterson Isotherm

2.7.1 Assumptions

1) This isotherm is a hybrid form of the Langmuir and Freundlich isotherms.
2) This model is applicable when concentration in numerator is linearly dependent and an exponential function in the denominator exists, but the adsorption mechanism is in hybrid state and does not fulfill the ideal condition of monolayer adsorption when high concentrations are presents in the liquid.
3) Redlich Peterson isotherm can easily be applied in both homogeneous and heterogeneous surfaces.
4) If high concentrations are present in liquid then Freundlich isotherm model is applicable due to the exponent β tends to zero factor and incase the condition of lower concentration in liquid is fulfill then Langmuir isotherm is applied as the β values are always close to one.

2.7.2 Equation

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \text{ .... (Eq 12)}$$

In this equation, K_R is the Redlich–Peterson isotherm constant (Lg^{-1}), a_R is also Redlich-Peterson constant having a constant unit (Lmg^{-1}), β is an exponent ranges between 0 and 1. Ce is the equilibrium liquid-phase concentration of the adsorbate (mgL^{-1}) and qe is the equilibrium adsorbate loading onto the adsorbent (mgg^{-1}) [13].

2.8 Sips Isotherm (Langmuir-Freundlich)

2.8.1 Assumptions

1) Sips isotherm is a combined form of Freundlich and Langmuir isotherms.
2) It describes an expression that demonstrates a finite limit of gas relatively at high pressure.
3) It is used to predict the adsorption systems on heterogeneous surface.
4) At lower concentrations of adsorbate, it illustrates the conditions of Freundlich isotherm, but at high concentrations fulfills the conditions of monolayer adsorption which is the characteristic of the Langmuir isotherm. Thus, sometimes it is also called as Langmuir-Freundlich isotherm.

2.8.2 Equation

The Sips isotherm expression for liquid phase is given below:

$$q_e = \frac{q_{ms}\,K_s C_e^{mS}}{1K_s + C_e^{ms}} \text{ .... (Eq 13)}$$

Here, q_e represents the adsorbed amount at equilibrium (mg g^{-1}), adsorbate concentration is expressed as C_e (mgL^{-1}) at equilibrium, Sips maximum adsorption capacity is expressed as q_{ms} (mg g^{-1}), K_S is the Sips equilibrium constant $(L\ mg^{-1})^m$ and Sips model exponent is represented as m_S [22].

2.9 Toth Isotherm

2.9.1 Assumptions

1) Though it was initially suggested for monolayer adsorption to improve Langmuir isotherm fittings and experimental data. It is also very helpful in providing valuable suggestions about heterogeneous adsorption systems satisfying both conditions of low and high concentrations of adsorbate in liquid system.

2) Both conditions of limits of the isotherm are satisfied in Toth's equation.
at p → 0 and p → ∞

Hence it is preferred over Sips isotherm equation [23].

2.9.2 Equation

$$\mathbf{q_e = \frac{q_{mT}\, C_e}{(\frac{1}{KT}+C_e^{mT})^{1/mT}}} \text{ .... } \textbf{(Eq 14)}$$

In this equation, adsorbed amount is represented by qe (mg g^{-1}) at equilibrium, adsorbate concentration at equilibrium is expressed by Ce (mgL^{-1}), Toth maximum adsorption capacity is denoted by q_mT (mg g^{-1}), KT is Toth equilibrium constant and mT is the Toth model exponent [22].

2.10 Koble Corrigan Isotherm

2.10.1 Assumptions

Basically, Koble–Corrigan isotherm is a three parameter equation that comprised of both Freundlich and Langmuir isotherm models that represent adsorption data at equilibrium stage. The values of isotherm constants A, B and n are calculated by drawing linear plot with a trial and error method [23].

2.10.2 Equation

Mathematical equation of Koble–Corrigan isotherm model can be presented as follows:

$$\mathbf{q_e = \frac{AC_e^n}{1+BC_e^n}} \text{ .... } \textbf{(Eq 15)}$$

In this expression, qe (mg/g)represents the concentration of adsorbate in adsorbent at equilibrium Koble-Corrigan isotherm constant is represented by A (Ln mg1-n/g),is B (L mg)n is also Koble-Corrigan isotherm constant, n is adsorption intensity, concentration is represented by Ce (mg/L) at equilibrium [13].

2.11 Khan Isotherm

2.11.1 Assumptions

It is a general model proposed for the pure solutions having ak and bk are used to represent model exponent and model constant respectively. Chi-square values or minimum ERRSQ (the sum of the squares of the errors) and values of high correlation coefficients can play pivotal role in determining maximum removal efficiency/ uptake values of the system [13].

2.11.2 Equation

Mathematical expression of Khan Isotherm model is given below:

$$\boldsymbol{q_e = \frac{q_s\, b_K C_e}{(1+b_K\, C_e\,)^{a_K}}} \text{ .... } \textbf{(Eq 16)}$$

Here, qe (mg/g)is the amount of adsorbate in adsorbent at equilibrium, qs (mg/g) is the theoretical isotherm saturation capacity, concentration is denoted by Ce (mg/L) at equilibrium, Khan isotherm model exponent is represented by aK khan isotherm model constant is represented by bK.

2.12 Radke–Prausnitz Isotherm

2.12.1 Assumptions

The correlation in Radke–Prausnitz isotherm model is commonly figured out by the high root-mean-square error (RMSE) and chi-square values. Radke–Prausnitz model exponent is characterized by βR and aR and rR are denoted as model constants [13].

2.12.2 Equation

Mathematical expression of Radke –Prausnitz Isotherm is given below:

$$\boldsymbol{q_e = \frac{a_{RP}\, r_R\, C_e^{\beta_R}}{a_{RP}+r_R C_e^{\beta_R-1}}} \text{ .... } \textbf{(Eq 17)}$$

In this expression, qe (mg/g) expressed the amount of adsorbate in adsorbent at equilibrium, arp and rR are denoted as Radke-Prausnitz isotherm model constants and βR is Radke-Prausnitz isotherm model exponent.

2.13 Brunauer–Emmett–Teller (BET) Isotherm

2.13.1 Assumptions

Brunauer–Emmett–Teller (BET) isotherm is a theoretical equation which is normally applicable in gas – solid adsorption equilibrium system. This theory aims to develop a multilayer adsorption system under the force of pressure from 0.05 to 0.30 that result in a monolayer coverage lying between 0.50 and 1.50.

1) This theory based on the concept of Langmuir theory that focused on adsorption of a molecule to a single or multilayer surface with the following postulates: (a) a molecule of a gas physically adsorbed to a solid surface infinitely; (b) no interaction occurs between each adsorption layer; (c) Langmuir theory is applicable to each layer and the process of adsorption only occurs on particular or well defines surface of the sample.
2) When the interaction occurs between the molecules each molecule provides/ act as a single adsorption site to a molecule of the upper layer.
3) Molecules from the upper layer will also in equilibrium state with the gas phase for example adsorption and desorption rates will be equal.
4) Desorption of a molecule from a solid surface is a kinetically limited process and there is also need to provide heat of desorption.

- These processes are homogeneous in nature e.g. a specific heat or energy is required for adsorption to a given or particular molecular layer.

- E_1 represents the energy of the 1st layer, i.e. heat of adsorption of adsorbate at the surface of the solid sample.

- Other layers are considered as similar and can be expressed as condensed species (liquid state). Thus, heat of adsorption EL is equal to the heat of liquefaction.

- Molecular layer numbers tends to infinity (equivalent to the sample being surrounded by a liquid phase), at saturation pressure.

2.13.2 Equation

Expression of BET isotherm model is given below:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)\left[1 + (C_{BET} - 1)({}^{C_e}/_{C_S})\right]} \text{ ………… (Eq 18)}$$

In this equation, q_e (mg/g) is amount of adsorbate in adsorbent at equilibrium, q_s (mg/g) is theoretical isotherm saturation capacity, C_{BET} (L/mg) is adsorption isotherm relating to the energy of surface interaction, C_e (mg/L) is concentration at equilibrium, and Cs (mg/L) is the concentration of adsorbate monolayer saturation.

2.14 Frenkel–Halsey–Hill (FHH) Isotherm Model

2.14.1 Assumptions

This adsorption isotherm defines the mechanism of multilayer water adsorption assuming that an adsorption potential gradient based on the distance of the adsorbed water layer from the surface of the particle [24].

The isotherm is derived by assuming the adsorbate as a uniform thin layer of liquid on a planar having homogenous and solid surface, considering the effect of replacement of the solid by the liquid. A molecule in the adsorbed layer will act differently in these two situations.

2.14.2 Equation

$$\ln\frac{C_e}{C_s} = -\frac{\alpha}{RT}\left(\frac{q_s}{q_e d}\right)^{\mathrm{r}} \text{ ………… (Eq 19)}$$

Where, Ce (mg/L) is the equilibrium concentration, Cs (mg/L) is the concentration of adsorbate on a monolayer saturation, d, α and r (m) are the sign of the interlayer spacing, isotherm constant (JmR/mole) and inverse power of distance from the surface (about 3), respectively.

2.15 MET Isotherm

2.15.1 Assumptions

MacMillan–Teller (MET) isotherm is an adsorption model interpreted from the inclusion of surface tension effects in the BET isotherm [13].

2.15.2 Equation

$$q_e = q_s\left(\frac{K}{\ln\frac{C_s}{C_e}}\right)^{1/3} \text{ ………… (Eq 20)}$$

Where, q_e(mg/g) is amount of adsorbate in adsorbent at equilibrium, q_s (mg/g) is theoretical isotherm saturation capacity, K is MacMillan-Teller isotherm constant, Cs (mg/L) is adsorbate monolayer saturation concentration, Ce (mg/L) is concentration at equilibrium.

3. Kinetic Modeling of Adsorption

3.1 Chemical Kinetics

Chemical kinetics, commonly recognized as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics play vital role in determining the effect of different experimental conditions on the speed of chemical reaction, yield information about the reaction mechanism, transition states as well as in developing mathematical models that describes the physical and chemical characteristics of a chemical reaction. In 1864, "Cato Guldberg" and "Peter Waage" were considered as the pioneer of chemical kinetics by proposing a theory "the law of mass action". According to this law "the speed of chemical reaction is directly proportional to the quantity of the reactants". Chemical kinetics has an important role in the determination of reaction rates that are also very helpful in developing rate constants and rate laws. Normally, rate laws are exists for zero (0) (rate of reaction is not depend on concentration), 1st and 2nd order reactions. Elementary reactions follow the law of mass action. The rate laws of stepwise reactions may also be determined by joining rate laws of different elementary steps that involve more complex steps during the reaction process. The rate-determining steps in a chemical reaction also determine reaction kinetics in a continuous reaction. In continuous 1st order reaction, steady states also determine the rate law and the activation energy of the reaction system also experimentally calculated by solving the Eyring and Arrhenius equations. Physical states of the reactants, concentrations of the reactants, temperature required for the reaction and the type of catalysts either taking part or not in the reaction all are regarded as key factors influencing the reaction rate.

3.2 Rate Equation

The rate equation or rate law of a chemical reaction is defined as "an equation that interconnects the rate of reaction with pressure or concentration of reactants with suitable constants (rate coefficients and partial reaction orders)". Normally, the expression of rate law is expressed as power law:

$$\mathbf{r = k[A]^x[B]^y} \text{ ………… (Eq 21)}$$

Where [A] and [B] represents the concentration of the species A and B, respectively and usually expressed in moles per liter (molarity, M).

Partial reaction order exponents are represented in the above equation and can be calculated experimentally. The values of x and y exponents are not equal to the values of stoichiometric coefficients. Rate constant or rate coefficient of the reaction is represented by k and the value of "k" is depend upon the ionic strength, temperature, light irradiation and the surface area of an adsorbent these factors.

The equation rate of a reaction having multi-step mechanism can frequently derived theoretically by using quasi-steady state assumptions from the underlying elementary reactions, and compared with the experimental rate equation as a test of the assumed mechanism. The equations may also involve a fractional order, and may depend on the concentration of an intermediate species.

The rate equation is a differential equation, and can be integrated to obtain an integrated rate equation that interconnects the concentrations of reactants or products with time.

3.3 Order of Reaction

The order of a reaction regarding a particular substance like catalyst, reactant or product is defined as the exponent or index in which the concentration term in the rate equation is increased. The typical form of a rate equation is in the following form

$$\mathbf{r = k\,[A]^x[B]^y} \;\ldots\ldots\ldots\ldots\; \textbf{(Eq 22)}$$

Where [A] and [B] ... are the concentrations and the reaction orders (or partial reaction orders) for x and y substance are represented by A and B respectively. The overall sum of reaction order is the sum x + y + ...

For example, chemical reaction between mercury (II) chloride and oxalate ion is given below

$$\mathbf{2HgCl_{2(aq)} + C_2O^{-2}_{4(aq)} \rightarrow 2Cl^{-}_{(aq)} + 2CO_{2(g)} + Hg_2Cl_{2(S)}} \;\ldots\ldots\ldots\ldots\; \textbf{(Eq 23)}$$

Rate equation for the reaction is as follows:

$$\mathbf{r = k[HgCl_2]^1\,[C_2O_4^{-2}]^2} \;\ldots\ldots\ldots\ldots\; \textbf{(Eq 24)}$$

In this equation, reaction order for HgCl2 reactant is 1 and for oxalate ion is 2 and the overall order of a reaction is 1+2=3. The reaction orders in this equation 1 and 2 differ from the stoichiometric coefficients i.e. 2 and 1. Reaction orders are calculated experimentally and may help in producing knowledge about the reaction mechanism and determining rate steps involved in a reaction.

Elementary or single-step reactions also have reaction orders that are equal to the stoichiometric coefficients of individual reactant. The sum of stoichiometric coefficients of reactants in a reaction is always equal to the molecularity of the elementary reaction Complex or multi-step reactions may or may not have reaction orders equal to their stoichiometric coefficients. Generally, orders of reaction are positive integers, but they may also be negative, zero or fractional for each reactant taking part in a reaction.

3.4 Factors affecting Reaction Rate

3.4.1 Nature of Reactants

Nature/type and strength of bond between molecules of the reactants significantly accelerate the rate of transformation into products. Normally, reaction rate varies, depending upon the type of elements or substances participating in a reaction. In acid-base reactions, the formation of salts or ion exchange occurs rapidly. When the formation of covalent bond occurs between the molecules or in the formation of macro molecules the reactions takes place very slowly.

3.4.2 Physical State of Reactants

Physical states (liquid, solid or gas) of reactant is also a key factor that alters the rate of reaction of reactants in chemical reaction. When reactants are in same states i.e. in aqueous solution, thermal motion of the liquid molecules brings them to close that result in contact, but, when the reactants are in distinct phases, the reaction is limited to the interface between the reactants. Chemical reactions only occur at their particular areas of intact, for example, in liquids and gases at the surface of fluid. More fine particles of liquid or solid reactants have larger areas/unit volume that result in more contact of reactants with the surface, thus speed up of chemical reaction. In organic chemistry, water reactions are exempt from the rule that homogeneous reactions occurs at faster rate than heterogeneous reactions.

3.4.3 Concentration of Reactants

Reactions are occurs due to the collision of reactant molecules involved in a chemical reaction. The frequency of colliding ions or molecules is influenced by concentrations of reactants. The more packed the molecules of the reactants are, the more rapidly the molecules collide and react with each other. Hence, an increase in the amount of reactants will result in rise in the reaction rate and vice versa. For example, combustion process takes place more rapidly in normal amount of oxygen (21%) as compared to in pure oxygen.

3.4.4 Temperature of Reactants

Typically, temperature has a key influence on the rate of a chemical reaction. Molecules of reactants at higher temperature gain more thermal energy. Although, collision frequency of the vibrating molecule is increased at higher temperatures, but this alone contributes only a very small proportion of the energy to increase the rate of reaction. Moreover, an interesting fact that the amount of reacting molecule with sufficient amount of energy to react (energy greater than activation energy: $E>E_a$) is considerably higher and is illustrated by Maxwell–Boltzmann distribution energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where temperature coefficient (α) is often between 1.5 and 2.5.

3.4.5 Catalysts

A catalyst is a chemical species which have capability to start a chemical or biochemical reaction and also have a potential to alter the rate of chemical reaction without being a part of resultants in a chemical reaction. The catalyst accelerates the rate of a reaction by providing a different reaction mechanism by lowering the activation energies of the reactants. In autocatalysis, a reaction product is itself a catalyst for that reaction which leads to positive feedback. Catalysts speed up the forward and backward rate of reactions and do not affect the position of the equilibria in a chemical reaction.

3.4.6 Pressure

Pressure play vital role in defining the rate equation for gaseous reactions. Generally, it is observed that an increase in pressure will result in rise the number of collisions between reactants, thus increasing the rate of reaction. This is because of the fact that the state of a gas is directly proportional to the partial pressure inserted to a gas. Furthermore, the rate coefficient of a system may be changed due to pressure in a straightforward mass-action system. The products of different high-temperature gas-phase and rate coefficients of reaction change, when an inert gas is added in a solution mixture and this process is commonly known as fall-off and chemical activation. This happens when endothermic or exothermic reactions occur at faster rate than heat transfer, causing the reacting molecules to have non-thermal energy distributions (non-Boltzmann distribution). When the pressure of a system is increased the heat transfer rate between the reacting molecules also increases and the rest of the system nullifies this effect [25].

3.5 Zero Order Reactions

A reaction in which the rate is dependent upon the concentration of the reactants is known as zero (0) order reaction. Increasing the concentration of reacting molecule does not speed up the rate of reaction (i.e. the amount of substance taking part in chemical reaction is directly proportional to time). Zero order reactions are usually initiated when a particular material or substance is required to start up a chemical reaction like catalyst or surface saturated by the reactants. The rate law for a zero order reaction is

$$\mathbf{r = k}$$

Where r is the reaction rate and k is the reaction rate coefficient with units of concentration or time.

3.5.1 Assumptions of Zero Order Reactions

Zero order reactions:

1) Occurs in a closed system.
2) No net build-up of intermediates.
3) No other reactions occur in a chemical reaction.

3.5.2 Equation

Keeping in view of above mentioned assumptions, it can be shown by solving a mass balance equation for the system:

$$r = -\frac{d[A]}{dt} = k \text{ ………… (Eq 25)}$$

If this differential equation is integrated it gives an equation often called as "integrated zero order rate law".

$$[A]_t = -kt + [A]_0 \text{ ………… (Eq 26)}$$

Where $[A]_t$ represents the concentration of the chemical of interest at a particular time, and $[A]_0$ represents the initial concentration.

A reaction is said to be zero order reaction when the graph of concentration data is plotted or drawn versus time and a straight line is obtained in as a result. A plot of $[A]_t$ vs. time t gives a straight line with a slope of -k.

The half-life of A_a reaction describes the time required for a half of the reactant to be depleted. For a zero order reaction the half-life is given by

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k} \text{ ………… (Eq 27)}$$

3.6 First Order Reactions

A first order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be in zero order. The rate law for a reaction that is first order with respect to a reactant A is given below

$$\frac{-d[A]}{dt} = r = k[A] \text{ ………… (Eq 28)}$$

k is the first order rate constant, which has units of 1/s

The integrated first order rate law is

$$\ln[A] = -kt + \ln[A]_0 \text{ ………… (Eq 29)}$$

A plot of lnA vs. time t gives a straight line with a slope of -k. The half-life of a first order reaction is depend upon the initial concentration and is given by

$$t_{1/2} = \frac{\ln 2}{k} \text{ ……….. (Eq 30)}$$

3.7 Pseudo-First-Order Rate Equation

It is very difficult to measure a second order reaction rate with presence of two reactants A and B. The concentration of two reactants needed to be followed simultaneously that is more difficult to calculate the concentration of reactants as a difference. A solution to the problem is given by pseudo-first order rate equation.

The concentration of one reactant remains unchanged when supplied in excess amount. The concentration can be absorbed within the rate constant, obtaining a pseudo first order reaction constant, because it depends on the concentration of only one reactant.

For example if the concentration of [B] remains constant during a chemical reaction, then:

$$\boldsymbol{r = k[A][B] = k'[A]} \text{ .... } \textbf{(Eq 31)}$$

Where, $k'=k[B]_0$ (k' or k_{obs} with units s^{-1}) The Pseudo-first order reaction is also used to calculate the concentration of reactants ([B]>>[A] for above said example) so that the reaction may proceed. When only a small quantity of the reactant is used it is assumed that the concentration of reactant must be constant. The value of k' for many reactions having higher but different concentrations of [B], a graph of k' versus [B] gives K (generally rate constant for second order) as a slope.

Liquid-solid state adsorption phenomenon of malonic acid and oxalic acid on charcoal surface was firstly described by Lagergren in 1898 to describe the first order rate equation [26]. This adsorption describe the adsorption rate on the basis of adsorption capacity of a system taking part in a chemical process and can be represent as

$$\boldsymbol{\frac{dqt}{dt} = kp_1(q_e - q_1)} \text{ .... } \textbf{(Eq 32)}$$

Where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium at a specific time (t) respectively. k_1 (1 min^{-1}) is the pseudo-first-order rate constant for the kinetic model. Integrating equation with the boundary conditions of $q_t=0$ to $q_t=q_e$ and t =0 to t = t, yields

$$\boldsymbol{\ln\left(\frac{qe}{qe-qt}\right) = k_{p1}t} \text{ .... } \textbf{(Eq 33)}$$

This can be rearranged to:

$$\boldsymbol{\log(qe - qt) = \log qe - \frac{k_{p1}}{2.303}t} \text{ .... } \textbf{(Eq 34)}$$

Where, qe and qt represents the adsorption capacity (mgg-1) and at time t at equilibrium respectively , k1 (min-1) is the rate constant of pseudo first order adsorption [27].To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order. In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in different fields, such as the adsorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fiber [28].

3.8 Second-Order Rate Equation

A second order reaction depends on the concentrations of one second order reactant, or two first order reactants.

Reaction rate for a second order reaction is given by

$$\boldsymbol{-\frac{d[A]}{dt} = k[A]^2} \text{ .... } \textbf{(Eq 35)}$$

Or

$$\boldsymbol{-\frac{d[A]}{dt} = k[A][B]} \text{ .... } \textbf{(Eq 36)}$$

Or

$$\boldsymbol{-\frac{d[A]}{dt} = 2k[A]^2} \text{ .... } \textbf{(Eq 37)}$$

The integrated second order rate laws are respectively

$$\boldsymbol{\frac{1}{[A]} = \frac{1}{[A]_0} + kt} \text{ .... } \textbf{(Eq 38)}$$

Or

$$\boldsymbol{\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0}e^{([A]_0-[B]_0)kt}} \text{ .... } \textbf{(Eq 39)}$$

$[A]_0$ and $[B]_0$ must be different to obtain that integrated equation.

The half-life equation for a second order reaction dependent on one second order reactant is as follows

$$\boldsymbol{t_{\frac{1}{2}} = \frac{1}{k[A]_0}} \text{ .... } \textbf{(Eq 40)}$$

For such a reaction, the half-life progressively doubles as the concentration of the reactant falls to its half initial value.

By taking the log of both sides, the above expression is expressed as

$$\boldsymbol{\ln r = \ln k + 2\ln[A]} \text{ .... } \textbf{(Eq 41)}$$

3.9 Pseudo-Second-Order Rate Equation

In 1995, Ho illustrated kinetic adsorption process for divalent metal ions on peat [29-31]. The chemical bonding among divalent metal ions and availability of polar functional groups (ketones, aldehydes, phenolics and acids are responsible for cation exchange capacity of peat. Peat-metal reaction may be presented in the following equation which is the most dominant phenomenon in the adsorption process of Cu^{2+} ions onto peat surface.

$$\boldsymbol{2P^- + Cu^{+2} \rightarrow CuP_2} \ldots\ldots\ldots\ldots(\boldsymbol{Eq}\ \mathbf{42})$$

and

$$\boldsymbol{2HP + Cu^{+2} \rightarrow CuP_2 + 2H^+} \ldots\ldots\ldots\ldots(\boldsymbol{Eq}\ \mathbf{43})$$

Where: P and HP are active sites on the peat surface.

The base of the above two equations were mainly the adsorption mechanism may considered as second order and the rate determining step may be due to chemical adsorption involving adhesion forces through the exchange or sharing of electrons between divalent metal ions and peat.

Furthermore, the adsorption follows the Langmuir equation and the rate of adsorption represented by these equations is depend upon the amount of metal ions adsorbed on the surface of peat at time (t) at equilibrium [32]. Hence, the rate expression may be expressed as

$$\frac{d(P)_t}{dt} = k_{p2}[(P)_0 - (P)_t]^2 \text{ .... (Eq 43)}$$

Where qe (mg g^{-1}) and qt are the sorption capacity at equilibrium at time t, respectively and k (g mg^{-1} min^{-1}) represents the rate constant of pseudo-second order sorption. The driving force, (qe−qt), is proportional to the available fraction of active sites. Then, it yields

$$\frac{dq_t}{dt} = k_{p2}(q_0 - q_t)^2 \text{ .... (Eq 44)}$$

Integrating equation with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t=t yields

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_0} + k_{p2}t \text{ .... (Eq 45)}$$

3.10 Third Order Reaction

Third order reaction is said to be a third order if the rate of reaction is determined by the variation of the concentration of three species taking part in a reaction. In simple form, there is need at least three molecules to start a chemical reaction.

Normally, in chemical reactions, the kinetic behavior of the reaction is calculated by taking the constants of the steps having lower rate constant, known as rate limiting step or rate determining step. Some trimolecular reactions shows 3rd order kinetics with the following expression

$$v = k_{abc} \ldots\ldots\ldots (Eq\ 46)$$

Where: k is a constant of third order reaction. Three dimensional collision between the molecules is not a necessary condition for a third order reaction Alternatively, , it was assumed that two-step mechanism is involved but the first step is occurring reversibly at a faster rate thus, the concentration of X is given by x = K_{ab}, where, K is the equilibrium constant for binding of A to B, the association constant of X. The rate of reaction is then the rate of the slow second step:

$$v = k'x_c = k'k_{abc} \text{ .... (Eq 47)}$$

Where: k' is the rate constant of second-order for second step in a chemical reaction. Hence the observed third-order rate constant is actually the product of a second-order rate constant and equilibrium constant.

A number of reactions are found to have third order kinetics. An example is the oxidation of NO, for which the overall reaction equation and rate law are given below.

$$2NO + O_2 \rightarrow 2NO_2 \text{ .... (Eq 48)}$$

$$\frac{d[NO_2]}{dt} = k[NO]^2[O_2] \text{ .... (Eq 49)}$$

One possibility for the mechanism of this reaction would be a three-body collision (i.e. a true tri molecular reaction). However, such collisions are extremely rare. The rate of this reaction is found to decrease with increasing temperature, thus, indicating that complex mechanisms are occurring. Alternative mechanism which leads to the same rate law is a two-step process involving a pre-equilibrium.

$$NO + NO \overset{k1}{\leftrightarrow} (NO)_2 \text{ .... (Eq 50)}$$

$$(NO)_2 + O_2 \overset{k2}{\rightarrow} 2NO_2 \text{ .... (Eq 51)}$$

The overall rate is

$$v = \frac{1}{2}\frac{d[NO_2]}{dt} = k_2[(NO)_2][O_2] \text{ .... (Eq 52)}$$

However, from the pre-equilibrium, we have

$$k = \frac{[(NO)_2}{[NO]^2}$$

So

$$[(NO)_2] = k[NO]^2 \text{ .... (Eq 53)}$$

and the overall rate is

$$v = k_2K[NO]^2[O_2] \text{ .... (Eq 54)}$$

i.e third order as required.

3.11 Fractional Order

In fractional order reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism. For example, the pyrolysis of ethanal (CH_3-CHO) into carbon monoxide and methane proceeds with an order of 1.5 with respect to ethanal: r = k[CH_3-CHO]$^{3/2}$. The breakdown of phosgene ($COCl_2$) to chlorine and carbon monoxide has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine: r = k[$COCl_2$] [Cl_2]$^{1/2}$.

The order of a chain reaction can be rationalized by using the steady state calculations for the concentration of reactive intermediates such as free radicals. For the pyrolysis of ethanal, the Rice-Herzfeld mechanism is

Initiation

$$CH_3CHO \rightarrow {}^{\bullet}CH_3 + {}^{\bullet}CHO \text{ .... (Eq 55)}$$

Propagation

$${}^{\bullet}CH_3 + CH_3CHO \rightarrow CH3CO^{\bullet} + CH_4 \text{ .... (Eq 56)}$$

$$CH_3CO^{\bullet} \rightarrow {}^{\bullet}CH_3 + CO \text{ .... (Eq 57)}$$

Termination

$$2\ {}^{\bullet}CH_3 \rightarrow C_2H_6 \text{ .... (Eq 58)}$$

Where • denotes a free radical. To simplify the theory, the reactions of the ${}^{\bullet}CHO$ to form a second ${}^{\bullet}CH_3$ are ignored.

In the steady state, formation and destruction rates of methyl radicals are equal, thus, the concentration of methyl radicals satisfy

$$\frac{d[\cdot CH_3]}{dt} = k_i[CH_3CHO] - k_t[{}^{\bullet}CH_3]^2 = 0 \text{ .... (Eq 59)}$$

$$[{}^{\bullet}CH_3] \propto [CH_3CHO]^{1/2} \text{ .... (Eq 60)}$$

The reaction rate equals to the rate of the propagation step which produces the main reaction products CH_4 and CO in agreement with the experimental order of 3/2.

$$v = \frac{d[CH_4]}{dt} = k_p[{}^{\bullet}CH_3][CH_3CHO] \propto [CH_3CHO]^{3/2}$$
$$\text{............ (Eq 61)}$$

3.12 Mixed Order

Different complex rate laws have been used for studying mixed order reactions; they are applicable to the laws for more than one order at different concentrations of the chemical species involved in a chemical reaction. For example, a rate law of the form $r = k_1[A]+k_2[A]^2$ represents concurrent first order and second order reactions (or more often concurrent pseudo-first order and second order) reactions, and can be defined as mixed first and second order. For sufficiently large values of [A] such reactions will considered as second order kinetics, but for smaller [A] the kinetics will assumed as first order (or pseudo-first order). As the reaction progresses, the reaction can change from second order to first order as reactant is consumed.

Another type of mixed-order rate law has a denominator of two or more terms, often because the identity of the rate-determining step depends on the values of concentrations. An example is the oxidation of an alcohol to a ketone by hexacyanoferrate (III) ion $[Fe(CN)_6^{-3}]$ with ruthenate (VI) ion (RuO_4^{-2}) as catalyst.

For this reaction, the rate of disappearance of hexacyanoferrate (III) is

$$r = \frac{[Fe(CN)_6]^{-2}}{k_\alpha + k_\beta[Fe(CN)_6{}^{-2}} \text{ .... (Eq 62)}$$

This is zero-order with respect to hexacyanoferrate (III) at the onset of the reaction (when its concentration is high and the ruthenium catalyst is quickly regenerated), but changes to first-order when its concentration decreases and the regeneration of catalyst becomes rate-determining step.

Notable mechanisms with mixed-order rate laws with two-term denominators include:

1) Michaelis-Menten kinetics for enzyme-catalysis: first-order in substrate (second-order overall) at low substrate concentrations, zero order in substrate (first-order overall) at higher substrate concentrations
2) Lindemann mechanism for unimolecular reactions: second-order at low pressures, first-order at high pressures.

3.13 Negative Order

Rate of a chemical reaction may have a negative partial order with respect to a substance. For example the conversion of ozone (O_3) to oxygen follows the rate equation in an excess of oxygen. This corresponds to second order in ozone and order (-1) with respect to oxygen.

$$r = k\frac{[O_3]^2}{[O_2]} \text{ .... (Eq 63)}$$

When a partial order is negative, the overall order is usually considered as undefined. In the above example for instance, the reaction is not described as first order even though the sum of the partial orders is 2 + (-1) = 1, because the rate equation is more complex than that of a simple first-order reaction.

3.14 Elovich's Equation

A kinetic equation of chemisorption was established by Zeldowitsch in 1934 [33]. It was used to define and calculate the adsorption rate of carbon monoxide on manganese dioxide which decreases exponentially with increasing the concentration of adsorbed gas commonly called as Elovich equation. The expression for Elovich equation is as follows [34].

$$\frac{dq}{dt} = ae^{-\alpha q} \text{ .... (Eq 64)}$$

Where q represents the amount of gas adsorbed at time t, a is the desorption constant, and the initial adsorption rate is expressed as α [35]. The linear expression of the above equation is given as

$$q = \frac{2.3}{\alpha}\log(t + t_0) - \left(\frac{2.3}{\alpha}\right)\log t_0 \text{ .... (Eq 65)}$$

With

$$t_0 = \frac{1}{\alpha a} \text{ .... (Eq 66)}$$

The plot of q versus log (t+t0) provides a straight line with an opposite value of t0. Elovich equation is applied to determine the kinetics of chemisorption of gases onto heterogeneous solidswith the assumption of aαt>>1 [36]. Equation was integrated by using the boundary conditions of q=0 at t=0 and q=q at t=t to yield

$$q = \alpha \ln(a\alpha) + \alpha \ln t \text{ .... (Eq 67)}$$

Elovich's equation has been widely applied to estimate the amount of a gas adsorbed to a solid surface [28]. Recently, it has also been widely applied in wastewater treatment process for the adsorption of toxic pollutants on a solid surface in aqueous solutions, for example, removal of Cd(II), Cu(II) and Cr(VI) by using bone char [37], rhizopus arrhizus and chitin, chitosan respectively in aqueous solutions [28] removal from effluents using bone char [37] and Cr(VI) and Cu(II) adsorption by chitin, chitosan, and Rhizopus arrhizus [28].

4. Thermodynamic Modeling of Adsorption

4.1 Thermodynamics

The term thermodynamics derived from the Greek word and is a combination of therme (heat) and dynamic (power). It is a science of energy that deals with the molecular motion with respect to time. Thermodynamics is also known as "macroscopic science" which provides information about the average changes taking place among larger numbers of molecules Thermodynamics first emerged as a science after the construction and operation of steam engines by Thomas Savery and Thomas Newcomen in 1697 and 1712 respectively. Later on, Rankine, Carnot, Kelvin, Clausius, Gibbs and many others have developed thermodynamic principles for by describing the laws of conversion and conservation of energy in a system. The theoretical equations of classical thermodynamics are a set of natural laws providing information about the behavior of macroscopic systems. These laws lead to a large number of equations, entirely based entirely on logics, and attached to well-defined constraints in a reaction. Natural conditions and natural phenomenon are far from adiabatic, reversible, equilibrium, isothermal or ideal laws, thus, the engineers exercise these pragmatic approaches in applying the principles of thermodynamics to real systems. Some other new attempt has been made to present thermodynamic principles and there is need to understand and apply these principles of thermodynamics in modeling, designing, and describing some natural and complex phenomena. All disciplines of science and engineering have followed the applications of thermodynamics. Thermodynamics principles may also presents methods and "generalized correlations" for the calculation of physical and chemical properties of a substance, when there is no experimental data exists. Such estimations are often necessary in simulation and designing of various processes.

Thermodynamic is an ideal and model system that represents a real system describing the theoretical thermodynamics approach. A simple system is a single state system with no internal boundaries, and is not subject to external force fields or inertial forces. The boundary of the volume separates the system from its surroundings. A system may be taken through a complete cycle of states, in which its final state is the same as its original state. In a closed system, a material content is fixed and an internal mass changes only due to a chemical reaction. Closed systems exchange energy only in the form of heat or work with their surroundings. Material and energy contents are variable in an open system, and the systems freely exchange mass and energy with their surroundings. Isolated systems cannot exchange their matter and energy. A system surrounded by an insulating boundary is called a thermally insulated system. The features of a system are based on the behavior of molecules that related to microscopic state, which is the key concern of statistical in thermodynamics. In contrast, classical thermodynamics formulates the macroscopic states, which describe the average behavior of large groups of molecules having macroscopic properties e.g. pressure and temperature. The macroscopic state of a system can be fully specified by a small number of parameters, such as the temperature, volume and number of moles.

4.2 Thermodynamic Properties

Thermodynamic macroscopic attributes of a system are derived from the long time average of the observable microscopic coordinates of motion by statistically. For example, the pressure is an average measure over about 1024 molecule-wall collisions per second per square centimeter of a surface for a gas at standard conditions. Thermodynamic is a property of state function and it depends only on the properties of the initial and final conditions of the system. The infinitesimal change of a state function is an exact differential. Properties like mass m and volume V are defined by the system as a whole. Such properties are additive, and called as extensive properties. Separation of the total change for a species into the external and internal parts may be categorized to any extensive property. All extensive properties are homogeneous functions of the first order in the mass of the system. For example, doubling the mass of a system at constant composition doubles the internal energy. The pressure P and temperature T defines the values at each point of the system and are therefore called intensive properties. Some features of a system can be expressed as derivatives of extensive properties, such as temperature.

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} \text{ .... (Eq 68)}$$

Where U is the energy and S is the entropy.

4.3 Energy

Energy is a conserved and extensive property of every system in any state, and hence its value depends only on the state. Energy is transferred in the forms of heat or work through the boundary of a system. In a complete cycle of steady state process, internal energy change is zero and hence the work done on the system is converted to heat (work=heat) by the system. The mechanical work of expansion or compression proceeds with the observable motion of the coordinates of the particles of matter. Chemical work, on the other hand, proceeds with changes in internal energy due to changes in the chemical composition (mass action).

4.4 Gibbs Free Energy

In thermodynamics, the Gibbs free energy (Gibbs energy or Gibbs function; also known as free enthalpy) refers to a thermodynamic potential that measures the "efficacy" or process-initiating work obtained from a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy (kJ/mol) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (one that can exchange heat and work with its surroundings, but not matter)the maximum form of energy can be achieved only in a completely reversible process. When a system undergo in a change from a well-defined initial state to a well-defined final state, a change in the expression of Gibbs free energy (ΔP) equals to the amount of work that has been substituted by a system with its surroundings, minus the work of the pressure forces, during a reversible transformation of the system from the initial state to the final state [38].

4.4.1 Equation

$$\mathbf{G(p,T) = U + pV - TS} \text{ ………… (Eq 69)}$$

Which is same as:

$$\mathbf{G(p,T) = H - TS} \text{ ………… (Eq 70)}$$

Where:

U is the internal energy (joule), P is pressure (Pascal), V is volume (m^3), T is the temperature (kelvin), S is the entropy of a system (joule per kelvin), H is the enthalpy (joule) [39].

4.5 Helmholtz Free Energy

In thermodynamics, the Helmholtz free energy is a thermodynamic potential that measures the “useful” form of a work obtained from a closed thermodynamic system at a constant temperature. The negative difference in the Helmholtz energy is equal to the maximum amount of work that the system can perform in a thermodynamic process at constant temperature. If the volume of a system is changed, the part of this work done will be performed as boundary work. The Helmholtz energy is commonly used for systems held at constant volume. Since in this scenario, no work is done on the environment, the drop in the Helmholtz energy is equal to the maximum amount of useful work that can be extracted from the system. For a system at constant temperature and volume, the Helmholtz energy will be the minimum at equilibrium.

4.5.1 Equation

$$\mathbf{A = U - TS} \text{ ………… (Eq 71)}$$

Where, A is the Helmholtz free energy (joules, CGS: ergs), U is the internal energy of the system (joules, CGS: ergs), T is the absolute temperature (kelvins), S is the entropy (joules per kelvin, CGS: ergs per kelvin).

The Helmholtz energy is the Legendre transform of the internal energy, U, in which temperature replaces entropy as the independent variable [40].

4.6 Entropy

In thermodynamics, entropy (usual symbol S) is the measure of the number of specific ways in which a thermodynamic system may be arranged, commonly understood as a measure of disorder. According to the second law of thermodynamics the entropy of an isolated system will never decrease and a system will spontaneously proceed towards its thermodynamic equilibrium configuring with maximum entropy. Since entropy is a state function, the change in the entropy of a system is the same for any process that goes from a given initial state to a given final state, whether the process is reversible or irreversible. However, irreversible processes increase the combined entropy of the system and its surrounding environment.

4.6.1 Equation

$$\mathbf{\Delta S = \int \frac{dQ_{rev}}{T}} \text{ ………… (Eq 72)}$$

Where: T is the absolute temperature of the system, dividing an incremental reversible transfer rate of heat into that system (dQ). (If heat is transferred out the sign would be reversed giving a decrease in entropy of the system). Entropy is an extensive property and has a dimension of energy divided by temperature, which is a unit of joules per kelvin ($J\ K^{-1}$) in the International System of Units (or $kg\ m^2\ s^{-2}\ K^{-1}$ in terms of base units). The entropy of a pure substance is generally given as an intensive property - either entropy per unit mass ($J\ K^{-1}\ kg^{-1}$) or entropy per unit amount of substance ($J\ K^{-1}\ mol^{-1}$).

5. Conclusion

Adsorption has been recognized as an effective technology in which solute particles are detached or separated from a liquid through surface interaction with a solid adsorbent capable of special affinity to a particular solute particle. Adsorbents used in adsorption mechanism have different benefits and preferred due to their less expensive operational cost, easy availability of the sorbent material, reduced the volume of sludge generated from industries and the reuse of the adsorbent after the adsorption process.

Adsorption isotherms are associates with the amount of adsorbate adsorbed or accumulate per unit weight of the adsorbent and the concentration of adsorbate in the solution at a given temperature and equilibrium conditions. So far, extensive research efforts have been devoted in building a sound understanding of adsorption isotherm, kinetics and thermodynamics models that will helpful in understanding the real time applications of low cost adsorption materials for the treatment of contaminated wastewater. In comparison to adsorption isotherm and kinetics, there is a lack between theoretical and experimental values of sorption data and disability of the model to interpret the results.

Over 95% of the experiments have applied linear models to explain their results related to adsorption data and hence it is a promising method [13].Thus, there is need to develop both isotherm and kinetic models in different adsorption systems in a real field experiment.

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