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## Application of kinetic models in batch adsorption processes – A review

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### ABSTRACT

Population growth in recent times, coupled with large scale industrialization and urbanization activities have greatly contributed to production of very large quantities of pollutants which are injected into the biota at alarming rates. This situation has been causing great concern to environmentalists and health sectors worldwide. Adsorption is superior to all techniques applied in de-polluting the environment due to its environmental friendliness, low cost, easy to design, non-toxicity and other properties. Known precursors used in manufacturing adsorbents are costly. Researches in sourcing adsorbents from cheap materials are in progress. A very important way of predicting mechanisms of adsorption processes, is modeling experimental data obtained with adsorption isotherms to quantify adsorbent adsorption capacity. The time required for adsorption to run, especially in industries is so short that equilibrium is not reached. Hence, process-oriented kinetic models are applied in simulating experimental data. In this work, many kinetic models have been discussed presenting an overall review of the applications of the models as well as their strengths and weaknesses. The validity of any experimental result depends on the closeness of experimental and predicted parameters. This is achieved by use of determination of coefficient, and error functions.

**Keywords:** Batch adsorption, kinetic modeling, equilibrium, adsorption capacity, adsorption mechanism

## 1. INTRODUCTION

The use of adsorption isotherms to quantify the adsorption capacity of a given adsorbent for a given adsorbate is very important. However, equilibrium conditions are necessary for isotherm studies [1]. In practical terms, the time for which adsorption processes run, especially in industries is so short that equilibrium is not reached. Hence, information on adsorption processes based on time is obtained through process-oriented kinetic studies [2].

Rate of adsorption is affected by different parameters during adsorption. There are various resistances to mass transfer of adsorbate particles from the bulk phase to the adsorbent surface which influence adsorption mechanism. The resistance is external when it is encountered, as the adsorbate particles diffuse as a film onto the surface of the adsorbent; the resistance is internal if encountered as the adsorbate particles diffuse through the adsorbate filling the pores on the adsorbent as they move to the binding sites. Boyd et al (1947) [3] and Reinchenberg (1953) [4] developed a mathematical treatment applied to know if an adsorption process is particle diffusion or film diffusion. In an adsorption process, where solute particles are loaded onto a porous adsorbent, the solute particles undergo either particle or film diffusion, or are binded on the interior surface of the adsorbent. The third process which is too fast is not the rate-controlling step in the process [5].

The possibilities that arise from the first and second conditions are:

- The rate of adsorption is controlled by particle diffusion if external transport is higher than internal transport.
- Film diffusion is the rate-limiting step if external transport is lower than internal transport.
- If external and internal transports are almost equal, liquid film surrounded by adsorbent particles is formed as a result of solute particles not migrating to the adsorbate-adsorbent boundary at a considerable rate [6].

Several kinetic models have been developed for modeling experimental adsorption kinetics data. In this review, the models are discussed; their strengths and weaknesses revealed.

Various works that applied the models are given.

## 2. DISCUSSIONS

### 2. 1. Adsorption kinetic modeling

#### 2. 1. 1. Arrhenius Kinetic Models

The Arrhenius zero-, first- and second- order kinetic models [7, 8] are expressed as Eqns. 1-3:

#### 2. 1. 2. Zero- order model:

$$C_t = -k_0t + C_o \dots \dots \dots (1)$$

#### 2. 1. 3. First-order model:

$$-\ln\left(\frac{C_t}{C_o}\right) = k_1t \text{ or } \ln C_t = -k_1t + \ln C_o \dots \dots \dots (2)$$

**2. 1. 4. Second-order model:**

$$\frac{1}{C_t} = -k_2t + \frac{1}{C_o} \dots \dots \dots (3)$$

where  $C_t$ ,  $C_o$  (mg/L),  $k_o$  (mg/L min),  $k_1$  (1/min),  $k_2$  (L/mg min) and  $t$  (min) are adsorbate concentrations at time  $t$ , initial adsorbate concentration, zero-order rate, first-order rate, second-order rate constants and time for adsorption respectively;  $k_o$ ,  $k_1$  and  $k_2$  are slopes obtained from plots of  $C_t$  versus  $t$ ,  $\ln C_t$  versus  $t$  and  $1/C_t$  versus  $t$  respectively.

Riyanto and Prabalaras (2019) [7] applied these models in their study on the adsorption of Co (II) on activated carbon derived from water hyacinth leaves.

Their correlation coefficient  $R^2$  values were: for zero order 0.0117; first order 0.0177 and second order 0.0163; the values show that the models were not good fits for their experimental data.

The limitations of these models arise from the fact that they were designed and earlier used for solid/liquid systems only [8]. Again, the maximum or calculated adsorbent adsorption capacity,  $q_{e,cal}$  cannot be determined. Hence, adsorption mechanism is difficult to be determined.

**2. 2. Pseudo-nth order model**

The Pseudo-nth order kinetic model is expressed as Eq. 4:

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^n \dots \dots \dots (4)$$

where,  $n = 0$  for pseudo-zero-,  $n = 1$  for pseudo-first-, and  $n = 2$  for pseudo-second order kinetic models [9]

**2. 2. 1. Pseudo-zero order model**

The Pseudo-zero order model is expressed as Eq 5: [10]

$$\frac{dq_t}{dt} = k_o(q_e - q_t)^0 = k_o \dots \dots \dots (5)$$

Integration of Eq 5 under boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , the equation transforms to Eq. 6:

$$(q_e - q_t) = q_{e,cal} - k_o t \dots \dots \dots (6)$$

where,  $q_e$ ,  $q_t$ ,  $q_{e,cal}$ ,  $q_t$  (mg/g),  $k_o$  ( $\text{min}^{-1}$ ) and  $t$  (min) are equilibrium adsorption capacity, adsorption capacity at time  $t$ , adsorption rate constant and adsorption time respectively.

A plot of  $(q_e - q_t)$  against  $t$  gives a straight line with slope  $k_o$  and intercept  $q_{e,cal}$ .

Application of the Pseudo-zero order model is rare. The rate constant is independent of adsorbate concentration [10].

Sampranpiboon and Feng (2016) [10] applied this model in kinetic modeling of chromium (VI) adsorption on activated carbon derived from oil palm kernel. Their R<sup>2</sup> values were 0.74 – 0.91 at 30-50 °C. The model fitted experimental data moderately.

**2. 2. 2. Pseudo-first order model**

The Pseudo-first order kinetic model is widely used for adsorbing adsorbate solutions onto solid adsorbent, based on adsorption capacity at various intervals of time [11, 12]. This model [13, 14] also known as Lagergren model is expressed [9, 15] as Eq.7:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots (7)$$

Integration under boundary conditions t = 0 to t = t and q<sub>t</sub> = 0 to q<sub>t</sub> = q<sub>e</sub>, the non-linear form of Eq. 7 is Eq. 8:

$$q_e = q_{e,cal.}(1 - e^{-k_1t}) \dots \dots \dots (8)$$

The linear log expression of Eq. 8 is Eq 9:

$$\log(q_e - q_t) = \log q_{e,cal.} - \frac{k_1}{2.303}t \dots \dots \dots (9)$$

Non-linear curve fitting of Eq. 8 or a plot of log (q<sub>e</sub>-q<sub>t</sub>) versus t to give a straight line helps determine the values of K<sub>1</sub> and q<sub>e,cal.</sub> K<sub>1</sub>(min<sup>-1</sup>) is the adsorption rate constant.

Application of this model, which is wide, to experimental equilibrium adsorption capacity must be specified and should be higher than the adsorption capacity at time t. If the experimental equilibrium adsorption capacity is unknown, it depicts that the adsorption is too slow to be measured [13]. The limitation of this model is that it is based on adsorption capacity and it is within the first few minutes it shows linearity [8].

Studies have shown that the Pseudo-first order rate constant k<sub>1</sub> is indirectly proportional to the initial adsorbate concentration whether it increases with or independent of the initial concentration. This is due to the fact that longer time is needed for large adsorbate concentration [16]. Diffusion of adsorbate particles is not explained. Hence, diffusion mechanisms should be investigated before making conclusions about Pseudo-first order modeling.

If true Pseudo-first order kinetics is followed in an adsorption process, the intercept of the log (q<sub>e</sub>-q<sub>t</sub>) versus t plot should equal the log of q<sub>e</sub> determined experimentally or adjusted to experimental value. True equilibrium is hard to reach when adsorption is slow. Hence, it is very difficult to determine q<sub>e</sub> accurately. At times the Lagergren Pseudo-first order equation does not fit well for the entire adsorption time. The Lagergren Pseudo-first order model under such condition is relevant within the initial 20-30 min of the adsorption process. There is the necessity to extrapolate experimental data to an infinite time to obtain q<sub>e</sub>. In such a case, q<sub>e</sub> becomes an adjustable parameter that can be obtained by trial and error. In certain cases the Pseudo-first order equation [17, 18] is expressed as Eq.10:

$$\frac{1}{q_t} = \frac{(k_1/q_1)}{t} + \frac{1}{Q_1} \dots \dots \dots (10)$$

where,  $Q_1$  (mg/g) is the equilibrium adsorption capacity and  $k_1$  ( $\text{min}^{-1}$ ) is the adsorption rate constant.

If a plot of  $1/q_t$  versus  $1/t$  gives a perfect straight line, it shows that the adsorption is in accordance with Eq. 10.

There is another variation of Pseudo-first order equation when adsorbent dosage is high and under Henry regime adsorption [19]. In order to explain variation in data obtained during adsorption of dyes on activated carbon, this model is modified [20] as Eq. 11:

$$\frac{dq_t}{dt} = k_1 \frac{q_e}{q_t} (q_e - q_t) \dots \dots \dots (11)$$

The linear expression of Eq. 11 is Eq. 12:

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln q_{e,cal.} - k_1 t \dots \dots \dots (12)$$

If a plot of  $(q_t/q_e) + \ln(q_e - q_t)$  against  $t$  gives a straight line then the model simulates data from adsorption of dyes well in comparison with the Lagergren PFO [16].

Yildiz, (2017) [13] applied the Pseudo-first order model in his kinetic and isotherm analysis of the adsorption of Cu(II) on almond shell. He obtained  $R^2 \geq 0.9$ .

Kuete et al (2020) [21] also applied the model in their study of the batch adsorption of thymol blue on powdered activated carbons from *Garcinia cola*. Their  $R^2$  values were 0.92 and 0.76 respectively.

**2. 2. 3. Pseudo-second order model**

The Pseudo-second order (PSO) kinetic model is widely used for analyzing single-component adsorption kinetics at the adsorbent-adsorbate interface [22]. The PSO rate law [23, 24] is expressed as Eq. 13:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots \dots \dots (13)$$

Under boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_e$ , the integrated form of Eq. 13 becomes Eq. 14:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_{e,cal.}} + k_2 t \dots \dots \dots (14)$$

Rearrangement of Eq. 14, gives four non-linear and three linearized [25] expressions.

**Table 1.** Non-linear expressions of PSO kinetic models

S/N	Type	Expression	Reference
1.	Sobkowsk and Czerwinski	$q_t = \frac{q_e k_2 t}{k_2 t + 1} \dots \dots \dots (15)$	[26]

2.	Blanchard	$q_t = \frac{k_2 t q_e + \alpha q_e}{k_2 t + \alpha} \dots \dots (16)$ <p>When <math>\alpha = 1/q_e</math>, the equation reduces to</p> $q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \dots \dots (17)$	[27]
3.	Ritchie	$q_t = \frac{q_e k_2 t}{k_2 + 1} \dots \dots \dots (18)$	[28]
4.	Ho	$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \dots \dots \dots (19)$	[24]

**Table 2.** Linear forms of PSO model.

S/N	Type	Expression	Plot	Ref.
1.	Sobkowsk and Czerwinski	$\frac{\theta}{1 - \theta}$ $= k_2 t \dots \dots (20)$	( $\theta/1-\theta$ ) vs t	[26]
2.	Blanchard	$\frac{1}{(q_e - q_t)} - \frac{1}{q_e}$ $= k_2 t \dots (21)$	1/( $q_e-q_t$ ) vs t	[27]
3.	Ritchie	$\frac{q_e}{(q_e - q_t)}$ $= k_2 t + 1 \dots (22)$	$q_e/(q_e-q_t)$ vs t	[28]
4.	Ho and McKay	$\frac{t}{q_t}$ $= \frac{1}{k_2 q_e^2}$ $+ \frac{1}{q_e} \dots (23)$	t/ $q_t$ vs t	[24]

where,  $\theta$  is adsorbent surface coverage.

Ho Pseudo-second order kinetic model is popular in application especially in analyzing chemisorptions data [29]. This model is based on the presumption that chemisorptions is the rate-determining step and predicts the adsorption behavior throughout the adsorption process. The rate of adsorption depends on adsorption capacity and not on adsorbate concentration. A major advantage of the PSO over Lagergren Pseudo-first order model is the direct calculation of  $q_e$  from the non-linear model equation, Eq. 19.

Hence, there is theoretically no need of evaluating equilibrium adsorption capacity from experiment [17, 18]. This makes it possible to calculate  $k_2$  and the initial rate of adsorption,  $h_0$ , [30] following Eq. 24:

$$h_0 = k_2 q_e^2 \dots \dots \dots (24)$$

PSO has been used successfully in removing through adsorption, dyes, herbicides, metal ions, oils, and organic substances [31, 32].

Vasanth Kumar (2006) [25] applied the four linear and non-linear Pseudo-second order models in his work on the adsorption of Safranin on carbon. For the linear regression method,  $r^2$  values were: 0.793-0.939 for Ritchie; 0.793-0.889 for Sobkowsk and Czerwinski; 0.793-0.939 for the Blanchard model. For the non-linear regression approach,  $R^2$  values were: 0.924-0.996 for Ritchie; the Ho model showed  $r^2 > 0.999$  for linear regression and  $R^2$  0.987 -0.996 for non-linear regression methods.

Inyinbor et al. (2016) [33] applied the Ho PSO model in analyzing experimental data from liquid phase adsorption of Rhodamine B dye onto *Raphia hookerie* fruit epicarp. They obtained  $r^2 > 0.98$  for all initial concentrations.

Mekonnen et al. (2020) [34] applied the PSO model to analyze experimental results from their work on adsorption of phosphate ions from aqueous solutions onto leftover coal at pH 2.3 and adsorbate initial concentration 5 mg/L. They had  $q_e$  198 mg/kg and  $R^2$  0.99. The limitation of the Ho Pseudo-second order kinetic model is that it is based on adsorption capacity. Hence, a specific but different rate constant is got for any system variable change [8].

**2. 2. 4. Elovich kinetic model**

In order to understand the nature of chemisorptive adsorption, the Elovich kinetic model is used. The model which was developed by Zeldowitsh [16] was earlier used in gaseous adsorption on solids [35]. Today it is also applied in the treatment of waste waters. The Elovich model is useful in predicting mass and surface diffusion, as well as the activation and deactivation energy of an adsorption process. The model presumes that decrease in adsorbate adsorption rate decreases exponentially as the uptake into the adsorbent increases [16]. The Elovich kinetic model is expressed as Eq 25:

$$\frac{dq_t}{dt} = \alpha \exp - \beta q_t \dots \dots \dots (25)$$

where,  $\alpha$  (mg/g.min) and  $\beta$  are the initial rate of adsorption and desorption constants respectively. Integration of Eq. 25 within the boundary conditions:  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives Eq. 26 [21].

$$q_t = \frac{1}{\beta} (1 + \alpha\beta t) \dots \dots \dots (26)$$

The linearized form of Eq. 26 is Eq 27:

$$q_t = \frac{1}{\beta} \ln \left( t + \frac{1}{\alpha\beta} \right) - \frac{1}{\beta} \ln(\alpha\beta) \dots \dots \dots (27)$$

As the adsorption process approaches equilibrium,  $t \gg 1/\alpha\beta$  [16] and Eq 27 reduces to Eq. 28.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots \dots \dots (28)$$

A plot of  $q_t$  versus  $\ln t$ , if applying the linearized equation, gives a straight line with slope  $1/\beta$  and intercept  $1/\beta \ln(\alpha\beta)$ .  $1/\beta > 1$  reflects number of sites available for adsorption [36].

Heterogeneity of the adsorbent surface is very important in the application of this model [16]. The Elovich model cannot predict the calculated maximum adsorption capacity. Again, it is relevant in modeling chemisorptions [8]. Dada et al (2017) [36] used the Elovich model to simulate experimental data from their work on liquid-phase adsorption of  $Pb^{2+}$  onto wood activated carbon supported zerovalent iron nanocomposite. They had  $R^2$  0.953 which shows the model to be a good fit and the process was chemisorption.

The Elovich model describes the second-order kinetics assuming that the solid surface has heterogeneous energy but does not propose any mechanism for adsorption [37]. Borhan et al. (2019) [38] applied the Elovich model in simulating experimental data from their work on adsorption of  $CO_2$  on activated carbon derived from rubber-seed shell. They got  $\beta$  (g/mg) 0.022,  $\alpha$  (mg/g min) 2.92,  $q_e$  (cm<sup>3</sup>/g) 43.509, and  $R^2$  0.819 at 25°C, 1.25 bar

**2. 2. 5. Diffusion-Chemisorption kinetic model**

The Diffusion-chemisorption model was first formulated by Sutherland in 2004 [39] for the analysis of experimental data from the adsorption of heavy metals on heterogeneous surfaces. It is expressed as Eq. 29:

$$\frac{dq_t}{dt} = \frac{nk_{DC}t^{n-1}}{q_e^2} (q_e - q_t)^2 \dots \dots \dots (29)$$

where,  $k_{DC}$  (mg/g.t<sup>0.5</sup>) is the mass transfer rate of solute to the adsorbent site from the bulk fluid phase and  $n$  an integer.

Separation of variables in Eq. 29 gives Eq 30:

$$\frac{q_e^2 dq_t}{(q_e - q_t)^2} = nk_{DC} dt. t^{n-1} \dots \dots \dots (30)$$

Integration of Eq. 30 at boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives Eq. 31:

$$\frac{q_e^2}{q_e - q_t} = k_{DC}t^n + q_e \dots \dots \dots (31)$$

Sutherland, 2004 [39] determined the value  $n$ , empirically by non-linear regression analysis of twenty data sets applying the Lavenberg-Marquardt algorithm.

He obtained  $n \approx 0.5$ . Rearrangement of Eq. 31 and substitution of  $n$  gives Eq. 32:



$$q_t = \frac{1}{\frac{1}{q_{e,cal.}} + \frac{1}{k_{DC}t^{0.5}}} \dots \dots \dots (32)$$

Eq. 32 can be rearranged to Eq. 33:

$$\frac{t^{0.5}}{q_t} = \frac{t^{0.5}}{q_{e,cal.}} + \frac{1}{k_{DC}} \dots \dots \dots (33)$$

A plot of  $t^{0.5}/q_t$  against  $t^{0.5}$  gives a straight line with slope  $1/q_{e,cal}$  and intercept  $1/k_{DC}$ . Experimental kinetic curve initial slope is empirically found to be a function of  $k_{DC}$  and  $q_e$ . This relationship is got by presuming a linear regression at  $t \gg 0$ . The initial adsorption rate which is obtained through an empirical relationship is expressed as Eq. 34:

$$k_i = \frac{k_{DC}^2}{q_e} \dots \dots \dots (34)$$

where,  $k_i$  (mg/g.t) is the initial rate of adsorption. Sutherland and Venkobachar (2010) [39] applied this model in their work on biosorption using forest macro-fungus, *Fomes fasciatus*. They obtained  $r^2 > 0.9$ .

Zhu et al. (2014) [40] used this model to simulate experimental data from their work on the adsorption of strontium on novel zwitterionic hybrid membranes. One of the membrane samples gave  $k_{DC}$  2218.524 mg/g h<sup>0.5</sup>;  $q_{e,cal}$  23.976 mg/g;  $q_{e,exp}$  23.9 mg/g and  $R^2_{adj}$ .

**2. 2. 6. Fractional power kinetic model**

This model [24, 33] is a form of Freundlich isotherm model that has been modified. It is expressed as Eq. 35:

$$q_t = at^b \dots \dots \dots (35)$$

where, a and b are constants;  $b < 1$ .

The linearized form of Eq 35 is Eq. 36:

$$\ln q_t = \ln a + b \ln t \dots \dots \dots (36)$$

ab which is a constant when  $t = 1$ , is the specific adsorption rate per time.

Inyinbor et al (2016) [33] used this model to analyze experimental data from the adsorption of Rhodamine B dye on *Raphia hookerie* fruit epicarp. They obtained  $R^2$  0.885 – 0.961 for various initial adsorbate concentrations.

Ho and McKay (2000) [24] applied the fractional power model in their study on the adsorption of copper (II) on peat. They had  $r^2$  0.981

**2. 2. 7. Modified Freundlich kinetic model**

The modified Freundlich kinetic model was developed by Kuo and Lotse (1973) [42]. It is expressed as Eq. 37:

$$q_t = k_{mf} C_o t^{1/m_{mf}} \dots \dots \dots (37)$$

where,  $k_{mf}$  (L/g min) and  $M_{mf}$  are the apparent rate constant and model constant respectively. The linearized logarithmic form [10] of Eq. 37 is Eq. 38:

$$\ln q_t = \ln(k_{mf} C_o) + \frac{1}{m_{mf}} \ln t \dots \dots \dots (38)$$

The limitations of this model are the apparent nature of the rate constant and the fact that the maximum adsorption capacity of the adsorbent cannot be predicted.

Sampranpiboon and Feng (2016) [10] applied this model in their study of chromium (VI) adsorption on carbonized oil palm kernel. They obtained  $R^2 > 0.93$  for all initial concentrations and temperatures used.

Varank et al (2012) [42] also used this model in simulating experimental data from their work on the removal of 4-nitrophenol from aqueous solution, using zeolite and bentonite. They obtained  $r^2 > 0.9$ .

**2. 2. 8. Avrami kinetic model**

The Avrami kinetic model was developed by Melvin Avrami [43] as a theory on phase change kinetic. It is used to find out specific changes that occur in kinetic parameters when there are changes in initial concentration, temperature and time during adsorption [44-46]. The model is expressed as Eq. 39:

$$q_t = q_e [1 - \exp(k_{Av} t)^{n_{Av}}] \dots \dots \dots (39)$$

The linearized logarithmic form [47] of Eq 39 is Eq. 40:

$$\ln \left[ \ln \left( \frac{q_e}{q_e - q_t} \right) \right] = n_{Av} \ln k_{Av} + n_{av} \ln t \dots \dots \dots (40)$$

A plot of  $\ln [\ln (q_e/(q_e - q_t))]$  against  $\ln t$  gives a straight line with slope  $n_{AV}$  and intercept  $n_{AV} \ln k_{AV}$

where,  $k_{AV}$  ( $\text{min}^{-1}$ ) and  $n_{AV}$  are the Avrami kinetic constant and the fractional adsorption order [47-49] respectively.

Selcuk et al (2017) [47] used this model to simulate experimental data from their work on the adsorption of methylene blue from aqueous solution on Paliurus spina-christi (Mill) fruits and seeds. They got  $R^2$  0.943-0.991 at 25 °C.

Balarak et al (2018) [44] also used the Avrami model in their study on the adsorption of tetracycline on Lemna minor. They got  $R^2 > 0.997$ .

**2. 2. 9. General Order kinetic model**

The General Order kinetic model works on the basis of the number of binding sites present for adsorption on the adsorbent surface [44]. It is expressed as Eq. 41:

$$q_t = q_e - \frac{q_e}{[k_N (q_e)^{n-1} t (n-1) + 1]^{1/n-1}} \dots \dots \dots (41)$$

where,  $n \neq 1$  is the adsorption order and  $k_N [\text{min}^{-1}(\text{g} \cdot \text{mg}^{-1})^{n-1}]$  is the adsorption rate constant;  $q_{e,\text{cal}}$ ,  $k_N$  and  $n$  can be obtained through non-linear curve fitting.

Balarak et al (2018) [44] applied this model in their work on adsorption of tetracycline on *Lemna minor*.  $R^2 > 0.92$  for all initial concentrations were obtained showing that General Order kinetic model was a good fit to their experimental data.

Liu et al. (2019) [50] applied  $\text{Fe}_3\text{O}_4$  nanoparticles functionalized activated carbon as an adsorbent to remove rhodamine B and methyl orange from aqueous solution. The General Order kinetic model simulated experimental data from rhodamine B adsorption very well with  $q_e$  182.48 mg/g.

Machado et al. (2016) [51] applied single and multi-walled carbon nanotubes (SWCNT and MWCNT) to adsorb dye from aqueous solution at optimum pH 2, temperature 298-318 K and fixed adsorption time of 65 and 100 min for SWCNT and MWCNT respectively;  $q_e$  values were 312.5 and 135.2 mg/g for SWCNT and MWCNT respectively. The General Order kinetic model best fitted experimental data.

### 2. 3. Batch adsorption mechanism

There are four major mechanisms involved in the movement of adsorbate particles from the bulk phase to the adsorbent surface. Mass transfer which is the mass movement of the adsorbate particles from the bulk phase to the adsorbent surface, immediately the adsorbent is contacted with the adsorbate, is the first mechanism. This phenomenon is too fast, hence, it is not useful in designing kinetic systems. The second mechanism termed film diffusion involves gradual movement of the adsorbate particles from the adsorbate-adsorbent boundary to the surface of the adsorbent. The third mechanism is the movement of the solute particles to the pores on the adsorbent when the solute particles reach the adsorbent surface. The fourth mechanism involves very fast binding on sites on the pores. This fourth mechanism which is rapid is not valuable in kinetics designing by Engineers [16]. Many models have been developed to determine the mechanism which is the rate-controlling step in an adsorption process.

#### 2. 3. 1. Intra-particle diffusion kinetic model

This model, also termed pore diffusion model was developed by Boyd et al 1947 [3]. The mechanism considered here is the transportation of the solute particles to the adsorbent surface and diffusion into the internal pores of the adsorbent. This process is slow. The intra-particle diffusion model is expressed [52, 53] as Eq. 42:

$$q_t = k_{id}t^{0.5} + C \dots \dots \dots (42)$$

where,  $k_{id} (\text{mg/g} \cdot \text{min}^{0.5})$  is the rate constant and  $C$ , the constant that indicates the boundary layer thickness. The value of  $C$  is directly proportional to the boundary layer effect.  $C$  represents the degree of adsorbent uptake (mg/g) [54]. If a plot of  $q_t$  (mg/g) against  $t^{0.5}$  ( $\text{min}^{0.5}$ ) is a straight line which passes through the origin, it means that intra-particle diffusion is the rate-controlling step [39]. If there is intercept  $C$ , it shows that liquid diffusion is active in the diffusion process [47, 55]. The weakness of this model is that practically, intra-particle diffusion is a slow process that makes the  $q_t$  versus  $t^{0.5}$  plot a curvilinear trend. If the analysis is applied to segments that are generated,  $k_{id}$  and  $C$  values differ greatly. The various segments can be obtained by visual

or applying regression at various points [16]. Sutherland and Venkobachar (2010) [39] applied the diffusion-chemisorption kinetic model to simulate bosorption using macro-fungus. They obtained  $R^2$  0.808 – 0.988 for all initial concentrations and adsorbent particle sizes.

Isiuku and Onyema (2017) [53] also applied the model in analyzing data from the work on adsorption of mentanil yellow from aqueous solution on activated carbon from gmelina bark.

**2. 3. 2. Liquid Film Diffusion kinetic model**

This model, also known as surface diffusion or external mass transfer model deals with diffusion mechanism involving the transportation of solute particles from the bulk adsorbate phase to the adsorbent external surface. The Liquid Film Diffusion model is expressed [56] as Eq. 43:

$$\ln(1 - F) = -k_{ld}t \dots \dots \dots (43)$$

where,  $F = q_t/q_e$  is fractional attainment to equilibrium,  $k_{ld}$  ( $\text{min}^{-1}$ ) is the rate coefficient for particle-diffusion governed process which corresponds to the adsorbent particle size. A plot of  $-\ln(1-F)$  against  $t$  yields a straight line with slope  $k_{ld}$ . A straight line with zero intercept shows that the rate-limiting step is liquid diffusion. Poor mixing, low adsorbate concentration and small solute size enhance liquid film diffusion [16].

Oyelude et al (2017) [57] used the liquid film diffusion model to simulate experimental data from their work on the adsorption of eosin yellow on tea leaf litter powder from aqueous solution. They obtained  $r^2$  0.97 – 0.981.

**2. 3. 3. Spaghn-Schlunder kinetic Model**

This model is used to confirm whether liquid film diffusion (or external mass transfer) is the rate-controlling step [58]. It is expressed as Eq. 44:

$$V \frac{dC_t}{dt} = -k_s A (C_t - C_o) \dots \dots \dots (44)$$

Integration of Eq. 44 under boundary conditions  $t(0,t)$  and  $C_t(0, t)$ , and linearization gives Eq. 45:

$$-\ln\left(\frac{C_t}{C_o}\right) = k_s \left(\frac{A}{V}\right) t \dots \dots \dots (45)$$

where,  $k_s$ ,  $A$  ( $\text{m}^2$ ) and  $V$  (mL) are the rate constant, external adsorption area and total adsorbate volume.

If a plot of  $-\ln(C_t/C_s)$  against  $t$  gives a straight line with zero intercept, liquid film diffusion as the rate-limiting step is suggested not minding the values of  $k_s$ ,  $A$  or  $V$  [59].

An (2020) [58]; Dada et al (2017) [36] and Gupta et al (2011) [59] successfully applied this model in their works to confirm liquid film diffusion as rate-limiting step. Dada et al 2017 [36] had  $r^2$  0.967.

Qi et al (2012) [60] applied the Spaghn-Schlunder model in their work on the use of Victorian lignite as an alternative industrial adsorbent for water pollution control. They had  $r^2$  0.84 – 0.95.

**2. 3. 4. External Diffusion model**

The liquid film (external mass transfer) model is used for adsorption mechanism analysis when the transport of adsorbate particles from the liquid phase to the adsorbent solid phase boundary is paramount [61]. The assumption in the use of this model is that the adsorbate concentration at the surface of the adsorbent tends to zero or intra-particle resistance is infinitesimal [62, 63]. Hence, pore diffusion can be ignored at the early part of the adsorption [62-64]. Fick's laws are applied in the derivation of the external diffusion model, which expresses the concentration of the adsorbate in the bulk phase as a function of concentration difference of the adsorbate in the solution and at the adsorbent surface [65].

Solute concentration change with respect to time is expressed as Eq. 46:

$$\frac{d\left(\frac{C_t}{C_o}\right)}{dt} = -k_f A \dots \dots \dots (46)$$

where,  $k_f$  and  $A$  ( $m^{-1}$ ) are the external mass transfer coefficient and surface area of adsorbent per unit volume of adsorbent particle free slurry.  $A$  is expressed as Eq. 47:

$$A = \frac{6M}{Vd_p\rho(1 - \epsilon_p)} \dots \dots \dots (47)$$

where,  $V(L)$ ,  $M(g)$ ,  $\epsilon_p$ ,  $\rho$  ( $g/cm^3$ ) and  $d_p$  ( $cm$ ) are the volume of the solution, adsorbent mass, bed porosity, bulk density, and particle diameter of the adsorbent respectively [66, 67].  $k_f$  can be determined as the slope of a plot of a dimensionless curve of  $C_t/C_o$  versus time  $t$ .

**2. 3. 5. Particle Diffusion model**

Most adsorbents are porous in nature. Hence, intra-particle diffusion can limit the rate of adsorption when they are used [61, 68-70]. Adsorption capacity at any time  $t$  and at equilibrium, are related by the Eq 48:

$$\ln\left[\frac{1}{1 - F^2(t)}\right] = \frac{\pi^2}{a^2} D_e t \dots \dots \dots (48)$$

$$F(t) = \frac{q_t}{q_e} \dots \dots \dots (49)$$

where,  $a$  ( $m$ ) is the adsorbent particle radius and  $D_e$  the diffusion coefficient. A plot of  $-\ln [1 - F^2(t)]$  against  $t$  gives a straight line with slope  $\pi^2 D_e/a^2$  from which  $D_e$  is calculated [61].

**2. 3. 6. Bangham kinetic model**

The Bangham model [42, 47] is used to confirm whether the rate-limiting step of an adsorption process is intra-particle diffusion.

The model is expressed as Eq. 50:

$$\log \left[ \log \left( \frac{C_o}{C_o - q_t m} \right) \right] = \log \left( \frac{k_B m}{2.303V} \right) + \alpha \log t \dots \dots (50)$$

where, m (g/L) is the adsorbent dosage, V (mL) is adsorbate volume,  $\alpha$  (<1) and  $k_B$  [mL/(g/L)] are constants.

If a plot of  $\log [\log (C_o/(C_o-q_t m))]$  against  $\log t$  gives a straight line with zero intercept, intra-particle diffusion is the rate-limiting step but if non-linear or linear with significant intercept values are got, intra-particle diffusion is not the rate-limiting step; both liquid film diffusion and intra-particle diffusion are involved [47].

Inyinbor et al (2016) [33] applied the Bangham model in their work on adsorption of Rhodamine B dye on *Raphia hookerie* fruit epicarp. Their  $R^2$  values were greater than 0.9 for all initial concentrations used.

Selcuk et al (2017) [47] also applied the model in their study on adsorption of methylene blue from aqueous solution on *Paliurus spina Christi* fruits and seeds. Their  $R^2$  values were 0.848-0.901 for all initial concentrations at 25 °C.

Edet and Ifelebuegu (2020) [37] used the Bangham model to analyze experimental data from their work on the adsorption of phosphates from model wastewater using recycled brick waste. They obtained  $R^2 > 0.95$  for all temperatures.

### 2. 3. 7. Boyd kinetic model

Boyd model can be used to establish the rate-limiting step in an adsorption process. It is expressed as Eq. 51:

$$F = 1 - \left( \frac{6}{\pi^2} \right) \exp(-B_t) \dots \dots \dots (51)$$

where,  $B_t$  is the function of F, the fraction of adsorbed adsorbate at various times t.

$B_t$  is the Boyd time constant at time t, and is expressed [40, 53] as Eqs. 52 and 53:

$$B_t = -0.4977 - \ln(1 - F) \dots \dots \dots (52)$$

For  $F > 0.85$  or

$$B_t = \left[ \sqrt{\pi} - \sqrt{\pi - \left( \frac{\pi^2 F}{3} \right)} \right]^2 \dots \dots \dots (53)$$

For  $F \leq 0.85$ .

A plot of  $B_t$  against time t, is used to confirm if the rate of an adsorption process is controlled by liquid film diffusion or not. A straight line with intercept or non linear plot for a particular initial adsorbate concentration confirms liquid film diffusion as the rate-limiting step [53].

The slope of the straight line  $B_t$  termed the time constant is applied in determining the effective diffusion coefficient,  $D_e$ , for any initial concentration value. It is expressed [6, 53] as Eq. 54:

$$B = \frac{\pi^2 D_e}{r_o^2} \dots \dots \dots (54)$$

where,  $r_o$  (mm) is the geometric mean radius of the adsorbent particle. The geometric mean diameter  $d_o$  from which  $r_o$  is obtained is expressed [71] as Eq. 55:

$$d_o = (d_1 d_2)^{0.5} \dots \dots \dots (55)$$

where,  $d_1$ (mm) is the diameter of the lower sieve on which the adsorbent particles are retained and  $d_2$ (mm) the diameter of the upper sieve the adsorbent particles pass through [71, 72].

The effect of temperature on diffusion during adsorption [6] can be evaluated applying rate coefficient according to Eq.56:

$$D_e = D_o \exp \left[ - \left( \frac{E_a}{RT} \right) \right] \dots \dots \dots (56)$$

where,  $D_o$ ,  $E_a$  (J/mol),  $R$  (J/mol/k) and  $T$ (K) are pre-exponential constant, activation energy, gas constant and absolute temperature respectively.

The linear expression of Eq. 56 is Eq. 57:

$$\ln D_e = \ln D_o - \frac{E_a}{RT} \dots \dots \dots (57)$$

A plot of  $\ln D_e$  against  $1/T$ , gives a straight line with slope  $E_a/R$  and intercept  $\ln D_o$ . The pre-exponential factor  $D_o$  [6] is expressed as Eq. 58:

$$D_o = \left( \frac{2.72 d^2 k T}{h} \right) \exp \left( \frac{\Delta S^o}{R} \right) \dots \dots \dots (58)$$

where,  $d$ ,  $k$ ,  $h$  and  $\Delta S^o$  are the average distance between two successive binding sites on the adsorbent, Boltzmann constant, Planck's constant and standard entropy change respectively.

The linearized logarithmic form of Eq. 58 is Eq. 59:

$$\ln D_o = \ln \left( \frac{2.72 d^2 k T}{h} \right) + \frac{\Delta S^o}{R} \dots \dots \dots (59)$$

A plot of  $\ln D_o$  against  $\ln T$  gives a straight line with slope  $\ln(2.72 d^2 k/h)$  and intercept  $\Delta S^o/R$ .

If  $\Delta S^o$  value is negative, it shows that the adsorbent's internal structure did not undergo any noticeable change during the adsorption [6]. A major weakness of the Boyd model is that it assumes that the adsorbent boundary surrounding layer has a profound influence on the adsorbate diffusion [16]. Dada et al (2017) [36] applied the Boyd model in their work on liquid-phase adsorption of  $Pb^{2+}$  onto wood activated carbon supported zerovalent iron nanocomposite. They obtained  $R^2 > 0.93$ . Isiuku et al (2021) [73] used the Boyd model to study the mechanism

of the adsorption of phosphate ions from the aqueous phase on biochar derived from rubber pod. They found out that liquid film diffusion played a major role as  $R^2 > 0.86$ .

Dada et al (2016) [56] in their work on the adsorption of Cu(II) onto bamboo supported manganese (BS-Mn) nanocomposite, applied the Boyd model and obtained  $R^2 > 0.88$ .

### 2. 3. 8. Mass Diffusivity

Diffusion coefficient values majorly depend on adsorbent surface characteristics. The coefficient of diffusion for intra-particle transport of adsorbate particles within adsorbent pores is expressed as Eq. 60:

$$D_m = \frac{0.03a^2}{t^{0.5}} \dots \dots \dots (60)$$

where,  $D_m$ ,  $a$  (mm) and  $t^{1/2}$  are mass diffusivity, adsorbent particle radius and half-adsorption time respectively. [74].

Half-adsorption time  $t^{1/2}$  is the time taken for up-take of 50% of adsorbent adsorption capacity at equilibrium [75]. This time is applied in determining the rate of adsorption according to Eq. 61:

$$t^{0.5} = \frac{1}{k_2 q_e} \dots \dots \dots (61)$$

where,  $k_2$  is the second order rate constant. It is presumed in the application of this model that the solid adsorbent particles are spherical with average radius between the radii of the upper and lower size fractions [74, 76].

### 2. 3. 9. Biot number

The Biot number  $B_i$  is a dimensionless entity used to study mass transfer behavior of adsorbate particles. The Biot number is the ratio between the rate of transport across the bulk phase and the rate of intra-particle mass transfer [77]. Derivation of the Biot number which is concentration dependent shows the impact of concentration on the adsorption process [78]. It is expressed as Eq. 62:

$$B_i = \frac{k_f d}{D_e} \dots \dots \dots (62)$$

where,  $k_f$  is the film mass transfer coefficient,  $d$  (mm) is the adsorbent particle diameter and  $D_e$  is the effective diffusion coefficient for a given initial concentration which can be derived from Boyd's plots.

If  $B_i > 100$ , intra-particle diffusion is the rate-limiting step and if  $B_i < 100$ , the rate-controlling step is liquid film diffusion [79].

### 2. 3. 10. Transport number

Transport number is a means of determining the type of diffusion that occurs during diffusion [80, 81]. It is expressed as Eq. 63:



$$\frac{q_e}{q_e} = k_m t^n \dots\dots\dots (63)$$

where,  $k_m$  is the adsorbent – adsorbate coefficient of interaction and  $n$  is the transport number. The value of  $n$  can be obtained by plotting  $\log (q_t/q_e)$  against  $\log t$ . The slope of the straight line gives the value of  $n$  while the intercept gives the value of  $\log k_m$ .

If  $n = 1$ , it shows that the mechanism of the adsorption is non-fickian. If  $n = 0.5$ , it shows fickian (surface) mechanism of adsorption. Non-fickian or abnormal mechanism of adsorption occurs when the adsorbent is a porous solid that changes structure or swells in the course of adsorption [82-84].

**2. 4. Regression analysis**

Regression or curve fitting is a method applied to describe experimental data to standardize the interpretation of such data into a form that is generally recognized. Experimental data are expressed as mathematical equations:  $y = f(x)$ , where  $x$  is the independent variable controlled by the researcher, and  $y$ , the dependent variable which is measured;  $f$  is the function comprising parameters that describe the data [85]. Linear regression oversimplifies practical results by assuming a linear relationship among the variables. The transformation into linear equation and analysis yields inaccurate analysis which can change the relationship in  $x$  and  $y$  values or gives a distorted experimental error. Hence, it is preferable to use nonlinear regression in the analysis [85, 86]. The regression coefficient (also called correlation coefficient or the coefficient of determination) for linear regression is symbolized as  $r^2$  and  $R^2$  for nonlinear regression.

**2. 4. 1. Interpretation of regression coefficient**

There is a positive relationship between two variables when the values of one of the variables increase as the values of the other increase. On the other hand, when the values of one of the variables increase as those of the other decrease, there is a negative relationship [87, 88]. The ranges of correlation values and their interpretations are shown in Table 3 [88-90]

**Table 3.** Correlation value ranges and their interpretations

S/N	Value Range	Interpretation
1.	0.9 – 1 or -0.9 – (-1)	Very high positive or negative correlation
2.	0.7 – 0.89 or -0.7 – (-0.89)	High positive or negative correlation
3.	0.5 – 0.69 or -0.5 – (-0.69)	Moderate positive or negative correlation
4.	0.3 – 0.49 or -0.3 – (-0.49)	Low positive or negative correlation
5.	0 – 0.29 or 0 – (-0.29 (-0.29)	Negligible positive or negative correlation
6.	0	No relationship

**2. 4. 2. Error analysis**

Error analysis is a method of mathematically evaluating the relationship between experimental and predicted data [91]. To show the closeness of experimental and calculated data, Coefficient of determination  $R^2$  is used, but it is not always enough [92]. Some of the commonly used error functions are displayed in Table 4. To carry out accurate analyses, many error functions are used together with  $R^2$ . For a perfect model, error functions are low and  $R^2$  values are high. The closer  $R^2$  is to unity, the better the model [19].

Coefficient of determination  $R^2$  is expressed [54] as Eq. 64:

$$R^2 = 1 - \left[ \frac{\sum_{i=1}^N (q_{e,exp} - q_{e,cal.})}{\sum_{i=1}^N (q_{e,exp})^2 - \frac{(\sum_{i=1}^N q_{e,exp})^2}{N}} \right] \dots \dots \dots (64)$$

**Table 4.** Error Functions

S/N	Error function	Abbrev.	Formula	Ref.
1.	Chi-square	$\chi^2$	$\sum_{i=1}^N (q_{e,exp} - q_{e,cal})/q_{e,cal}$	[54, 93]
2.	Adjusted R-squared	$R^2_{adj}$	$1 - \left[ 1 - R^2 \left( \frac{N-1}{N-P-1} \right) \right]$ N=number of data points; P=number of parameters	[94]
3.	Reduced Chi-squared	$\chi^2_{red}$	$\sum_{i=1}^N \frac{(q_{e,exp} - q_{e,cal})^2}{N-P}$	[95]
4.	Residual sum of squares	RSS	$\sum_{i=1}^N (q_{e,exp} - q_{e,cal})^2$	[45]
5.	Sum of squares	SSE	$\sum_{i=1}^N (q_{e,exp} - q_{e,cal})^2$	[54]
6.	Normalized standard deviation	$\Delta q(\%)$	$100 \sqrt{\sum_{i=1}^N [(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2 / N - 1}$	[54]
7.	Average relative error	ARE	$\frac{1}{N} \sum_{i=1}^N \left  \frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}} \right $	[54]
8.	Residual Root Mean Square Error	RMSE	$\sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{e,exp} - q_{e,cal})^2}$	[21]

9.	Sum of absolute error	EABS	$\sum_{i=1}^N  (q_{e,exp} - q_{e,cal}) $	[21]
10.	Marquardt's percent standard deviation	MPSD	$100 \sqrt{\frac{1}{N-P} \sum_{i=1}^N \left( \frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}} \right)^2}$	[99]
11.	Root mean square error	RMSe	$\sqrt{\sum_{i=1}^N [(q_{e,cal} - q_{e,exp})/q_{e,exp}]^2 / N}$	[9]
12.	Standard deviation	Sd	$\sqrt{\sum_{i=1}^N [(q_{e,exp} - q_{e,cal})/q_{e,cal}]^2 / N}$	[96]
13.	The hybrid fractional error function	HYBRID	$\frac{100}{N-P} \sum_{i=1}^N \left[ \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]$	[21]
14.	Relative Percent Error	RPE %	$\left  \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right  \times 100$	[97, 98]
15.	Durbin-Watson test	DWT	$\sum_{i=2}^N \frac{(q_{e,exp} - q_{e,cal}^{-1})^2}{\sum_{i=1}^N q_{e,exp}^2}$ (for a good fit, DWT >> 1)	[99, 100]
16.	Normalized Deviation	ND	$\frac{100}{N} \sum \left  \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right $	[101]

### 3. CONCLUSIONS

Batch isotherm modeling demands equilibrium conditions which need long time to actualize. This problem is handled by applying kinetic modeling in order to obtain various theoretical adsorption parameters. The validity of any experimental adsorption data and the right kinetic model for simulation depend on the closeness of the experimentally and theoretically determined parameters. This validity is determined by applying error functions and correlation coefficients. In many cases, non-linear regression gives better fits. However, it is needful to identify and clarify the usefulness of both types of regression analysis in different adsorption processes. More researches need to be carried out to address the weaknesses of some of the models.

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