Original Research Article

EXPONENTIAL MODEL FOR ADSORPTION KINETICS

ABSTRACT

Adsorption is one of the most widely applied techniques for the removal of contaminants from the environment. The effectiveness of an adsorbent is dependent on its kinetics. There are lots of studies on adsorption kinetics, and several mathematical models have been developed to describe this process based on certain perceived underlying mechanism. However, most models which have been used to fit the kinetic data have shown a moderate level of correlation or no fit at all. This is mainly because of error in assuming the governing equation and erroneous assumptions when finding solutions to the governing equations. In this research an exponential model is proposed. It is believed that adsorption of an adsorbate onto an adsorbent follows essentially two stages. There is a rapid stage that tends towards a first phase pseudo-equilibrium ($Q_{r(0)}$)at a rate of $k_r$and transits at a time 'tr' and rate k_{tr} to a slow stage which tends towards a second phase pseudo-equilibrium ($Q_{s(0)}$) at a rate of k_a which marks the climax of the process. Mathematical equations were used to describe this process and solved analytically to obtain the new exponential model. The model was used to estimate kinetic data and compared with the first and second order equationswith an R^2 of 0.994, 0.999 and 0.998 respectively.The new adsorption parameters $Q_{r(0)}$, $Q_{s(0)}$, k_r, k_s, k_{tr} and t_r were also extracted from the calibrated model.

Key words: Models, Adsorption, Kinetics, Pseudo-equilibrium

1.0 INTRODUCTION

One technique widely applied for the removal of pollutants from a contaminated media is Adsorption. The common adsorbents include activatedcarbon, molecular sieves, polymeric adsorbents, andsome other low-cost materials. When adsorption isconcerned, thermodynamic and kinetic aspects shouldbe involved to know more details about its performanceand mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also ofgreat significance for the pilot application. From the kinetic analysis, the solute uptake rate,

which determinesthe residence time required for completion of adsorption reaction, may be established. Also, onecan know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorptionkinetics is the base to determine the performanceof fixed-bed or any other flow-through systems (Hui et al. 2009).
At present, adsorption reaction models havebeen widely developed or employed to describe thekinetic process of adsorption (Banat *et al*., 2003; Sun and Yang, 2003; Aksu and Kabasakal, 2004; Hamadi*et al*., 2004; Jain *et al*., 2004; Min *et al*., 2004; Shin *etal*., 2004; Namasivayam and Kavitha, 2005; Chen *etal*., 2008; Cheng *et al*., 2008; Hameed, 2008; Huang*et al*., 2008; Wan Ngah and Hanafiah, 2008; Rosa *et al*., 2008; Tan *et al*., 2008);Adsorption kinetics are required for selecting optimum operational conditions of water and wastewater treatment facilities for full-scale processes. Numerous adsorbents (carbon, clay, polymer, activates sludge, and zeolite) have been developed to remove solute form wastewater (Emik, 2014; Anirudhan and Rauf, 2013; Boyd et al. 1947). These adsorbents have large surface area and pore volume, thermal stability, with low acid/base reactivity. This makes them suitable to remove a wide range of organic and inorganic dissolved pollutants from wastewater and air.

The utmost parameter to consider while designing the adsorption system is adsorption kinetics; kinetics determines the rate at which the adsorption occurs. Kinetics are influenced by the surface complexity of the adsorbent, solute concentration and flow. Pseudo-First-order (PFO), Pseudo-Second-order (PSO), Elovich, and Intra-particle (IP) model are some of the kinetics that foretells the adsorbent-adsorbate interaction. The first two models have been widely applied in almost every sorption process. The suitability of any model depends on the error level—correlation coefficient (R^2) or Sum of Squared Errors (SSE). To study adsorption kinetics, the linear forms have been applied; a linear form of PSO has been favoured over PFO model for the last 2 decades (George, et al., 2018).

It is thought that instead of assuming order of the reaction as 1 or 2, the direct calculation of rate constant and order of the adsorption reaction is a more appropriate method (Özer, 2007). Thus, *nth*-order kinetic model can be used. The model is expressed as Equation (1) (Cheung, 2001):

$$Q_t = Q_e\left\{1 - \left[\frac{1}{\beta_n + k_n(n-1)t}\right]^{1/(n-1)}\right\} \qquad (1)$$

where $Q_e$is the amount of solute adsorbed on the surface of the adsorbent at equilibrium, (mg/g); $Q_t$is the amount of solute at any contact time, (mg/g); $k_n$is the rate constant and its unit depends on the order of the reaction, (1/min) (mg/g)1–n, $\beta_n$is related to impurities pre-adsorbed on the surface (β_n= 1/(1 − θ_0)n−1), $\theta_0$is surface coverage at pre-adsorbed stage (θ_0= Q_0/Q_e), dimensionless.

Chiron, et al., (2003) proposed a double exponential model that describes the adsorption process with respect to both chemical and mathematical points of view,correlating the two-step mechanism as rapidly and slowly adsorbed fractions (Wilczak and Keinath, 1993). The model is expressed by Equation (2):

$$Q_t = Q_e - \left(\frac{D_1}{m_{ads}}\right) e^{-K_{D1}t} - \left(\frac{D_2}{m_{ads}}\right) e^{-K_{D2}t} \tag{2}$$

Where $D_1$and $D_2$are the amount of rapidly and slowly adsorbed fraction of solute (mg/l), respectively, and $K_{D1}$and $K_{D2}$are rapid and slow rate constants (min^{-1}). It should be noted that the sum of $D_1/m_{ads}$and D_2/m_{ads}has the same physical meaning as the calculated value of Q_e, and $K_{D1}$is greater than K_{D2}.

To further understand the chemisorption nature of adsorption, Elovich model developed by Zeldowitsch (1934) is applied. This model helps to predict the mass and surface diffusion, activation and deactivation energy of a system. Although the model was initially applied in gaseous systems, its applicability in wastewater processes has been redeemed meaningful. The model assumes that the rate of adsorption of solute decreases exponentially as the amount of adsorbed solute increase. This is shown as Equation 3

$$\frac{dq}{dt} = ae^{-\alpha q} \tag{3}$$

where ‘q’ represents the amount of gas adsorbed at time ‘t’, ‘a’ the desorption constant, and ‘α’ the initial adsorption rate (Ho and McKay, 1998a). Integrating and applying the limits for t (0, t) and q_t(0, q_t), the Elovich model can be linearized:

$$q = \left(\frac{2.3}{\alpha}\right) log(t + t_0) - \left(\frac{2.3}{\alpha}\right) log t_0 \tag{4}$$

To examine the rate limiting step during adsorption, intra-particle difussion model has been widely applied. The adsorption of solute in a solution involves mass transfer of adsorbate (film diffusion), surface diffusion, and pore diffusion. Film diffusion is an independent step, whereas surface and pore diffusion may occur simultaneously. Crank (1956) gave an exact solution for the “infinite bath” case where the sphere is initially free of solute and the concentration of the solute at the surface remains constant (George, et al., 2018). External film resistance can be neglected according to the constant surface concentration (Cooney, 1999). Then, Crank’s solution is written as Equation (5).

$$\frac{q}{q_s} = 1 + \frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{R}\, exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \tag{5}$$

where R is the total particle radius. Ds is intraparticle diffusion coefficient, r radial position, and q the adsorption quantity of solute in the solid varying with radial position at time t. Dumwald-Wagner proposed another intraparticle diffusion model as (Wang et al., 2004)

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp(-n^2 K t) \tag{6}$$

Where K (min^{-1}) is the rate constant of adsorption.

(Tran, et al., 2017). If the system is characterised by poor mixing, small solute size, and low concentration, film diffusion becomes the rate controlling step; otherwise, IP diffusion controls the process.

In this research, the adsorption of an adsorbate onto an adsorbent is assumed to take place in two stages. The first stage is an initial rapid stage during which the adsorbate rapidly fills the adsorption sites because of availability of such sites. This process continues until a first stage pseudo-equilibrium is reached. The rapid adsorption rate constant is denoted as K_r. However, as contact time increases, the available site diminishes and most of the energy is used up filling these sites so the adsorption speed gradually reduces. The rapid adsorption gradually transits into slow adsorption until a second stage pseudo-equilibrium is reached. This is the second adsorption stage. The slow adsorption stage proceeds with a rate constant K_s. It is assumed that there is a transition phase during which the rapid adsorption becomes slow adsorption. The rate at which the rapid adsorption transits to slow adsorption is denoted as K_{tr}.

2.0 MATERIAL AND METHODS

2.1 Proposed Exponential Model

The two stage phenomenon earlier described is represented mathematically as Equations (7) and (8)

$$\frac{dQ_s}{dt} = k_{tr}Q_r - k_s(Q_s) \tag{7}$$

$$\frac{dQ_r}{dt} = -k_r(Q_r) \tag{8}$$

Where Q_s and Q_r are the slow and rapid stages of the adsorption respectively. K_s, K_r and K_{tr} are slow, rapid and transition rate constants respectively.

Integrating Equations(7) and (8) gives:

$$Q_r = Q_{r(0)}e^{-k_r t} \tag{9}$$

$$Q_s e^{k_s t} = \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{-k_r t + k_s t} + G \tag{10}$$

Where G is the constant of integration

At t = t_r(Start of transition)

$$Q_s = Q_{s(0)} \tag{11}$$

$$G = Q_{s(0)}e^{k_s t_r} - \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{(k_s - k_r)t} \tag{12}$$

Then

$$Q_{s(t)} = \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{-k_r t} + \left[Q_{s(0)}e^{k_s t_r} - \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{(k_s - k_r)t}\right] e^{-k_s t} \tag{13}$$

where$Q_{s(t)}$ is the available adsorbent capacity for the slow phase at any time t (mg/g), $Q_{s(0)}$ is the max adsorbent capacity available for slow phase at any time t (mg/g) and $Q_{r(0)}$ is the maximum adsorbent capacity available for the rapid phase at any time t (mg/g).

Since

$$q_t = Q_{max} - Q \tag{14}$$

whereq_t is the amount adsorbed at any time t (mg/g),Q_{max} and Q is the is the available adsorbent capacity at maximum time and any time t (mg/g), respectively.

$$Q_{(0)} = Q_{max} \tag{15}$$

$$q_{s(t)} = Q_{s(0)} - \left\{\frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{-k_r t} + \left[Q_{s(0)} e^{k_s t_r} - \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{(k_s - k_r)t}\right] e^{-k_s t}\right\} \tag{16}$$

$$q_{r(t)} = Q_{r(0)} - Q_{r(0)} e^{-k_r t}$$

Therefore

$$q_t = q_{s(t)} + q_{r(t)} \tag{17}$$

$$q_t = Q_{s(0)} - \left\{\frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{-k_r t} + \left[Q_{s(0)} e^{k_s t_r} - \frac{k_{tr}Q_{r(0)}}{k_s - k_r} e^{(k_s - k_r)t}\right] e^{-k_s t}\right\} + Q_{r(0)} - Q_{r(0)} e^{-k_r t} \tag{18}$$

$$Q_{max} = Q_{s(0)} + Q_{r(0)} \tag{19}$$

Equation (18) can be rearranged to the form

$$q_t = Q_{max} - \left\{\frac{k_{tr}Q_{er}}{k_s - k_r}\left(e^{-k_r t} - e^{k_s(t_r - t) - k_r t_r}\right) + Q_{s(0)} e^{k_s(t_r - t)} + Q_{r(0)} e^{-k_r t}\right\} \tag{20}$$

Thus Equation (20) can be regarded as the exponential model for adsorption kinetics.

2.2 Experimental Setup

Udeh and Amah (2022), investigated the adsorption potential of $ZnCl_2$ activated unripe musaparadisiaca peels for adsorption of phenol from aqueous solution. Unripe musaparadisiaca peels were cut into smaller pieces and thoroughly washed with distilled water to remove impurities and then sun-dried until it was very dry. The samples were chemically activated with zinc chloride ($ZnCl_2$) at impregnation ratio of 1:2 and then carbonized in a muffle furnace at 400^{o}C for 2hrs and then ground into powder after cooling in a desiccator. This was labelled as UPPAC

At varying time intervals of 15 to 210 mins,the adsorption kinetics was conducted using initial phenol concentration of 22mg/l at pH of 2. Fixed dosage (5g) of the adsorbent was added to 50ml of phenol in different 100ml containers and they were shaken at 200rpm using the temperature-controlled incubator shaker. The samples were withdrawn at specific interval of time (t) and then filtered using Whatman paper.The filtrates were analyzed for phenol residual concentration (C_t) using HACH method. The adsorption capacity (q_t) of the adsorbent at specific time intervals was calculated from Equation (21).

$$q_t = \frac{(c_o - c_t)}{w} \times V \tag{21}$$

whereC_o is the initial adsorbate conc. (mg/l), $C_t$is the final adsorbate conc. (mg/l), V is the volume of solution used (L) and W is the weight of adsorbent used (g).

3.0 RESULTS AND DISCUSSION

Table 1 presents the phenol adsorption rate unto the adsorbent at the various time intervals.With the aid of Excel solver, the result of the adsorption rate was modelled and shown as Figure 1using Pseudo first order equationshown as Equation (22), second order equation shown as Equation (23) and the new model (Equation 20).

$$\log(q_e - q_t) = \log(q_e) - \frac{K_{p1}}{2.303}t \qquad (22)$$

$$\frac{t}{q_t} = \frac{1}{k_{p2}\,q_e{}^2} + \frac{1}{q_e}t \qquad (23)$$

whereq$_e$ is the adsorption capacity at equilibrium (mg/g), q$_t$ is the adsorption capacity at time t (mg/g), k$_{p1}$, is the rate constant of first order adsorption (mg/mins), k$_{\mathbf{p2}}$ is the rate constant of pseudo second order adsorption (mg/min).

Table 1: Adsorption rate of phenol unto UPPAC

t (mins)	**q$_t$ (mg/g)**
15	2.29
30	2.30
45	2.30
60	2.30
90	2.30
120	2.31
150	2.31
180	2.31
210	2.32

Source: Udeh and Amah (2022)

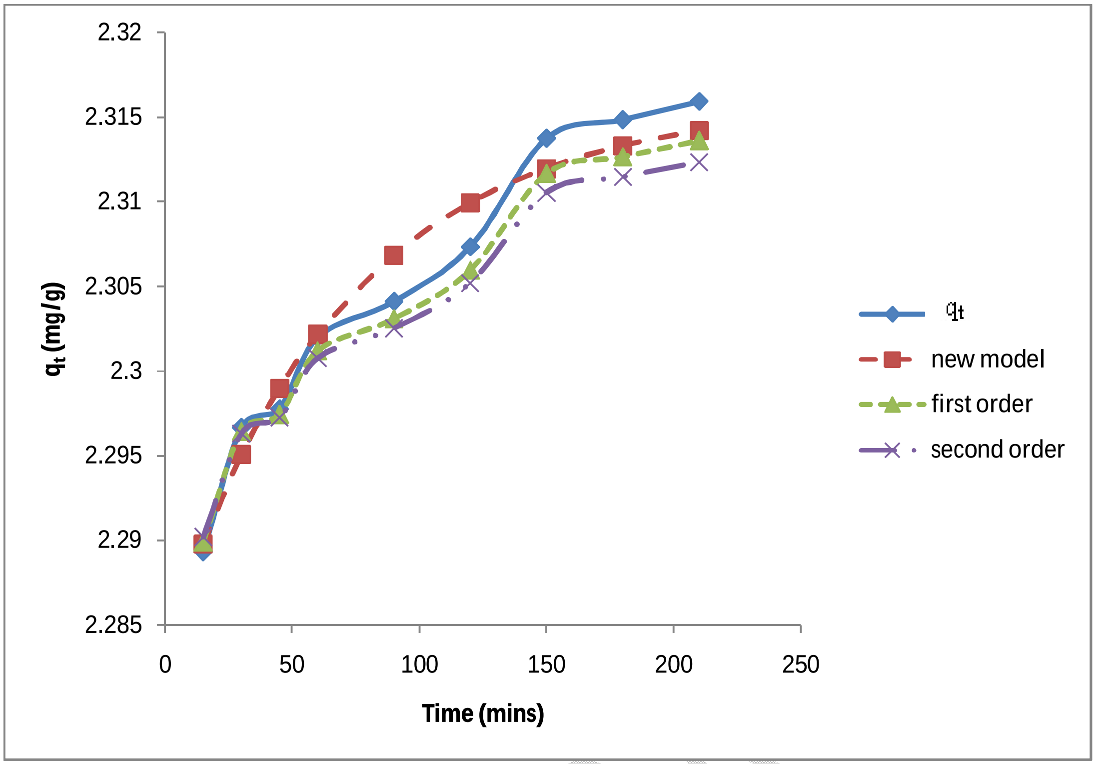

Figure 1: Modelled adsorption rate of phenol onto activated unripe musaparadisiaca peels

The adsorption parametersof Equation (20) from the modelled data were extracted and shown as Table 2.

Table 2: Adsorption parameters.

k_{tr} (t^{-1})	**k_s (t^{-1})**	**k_r(t^{-1})**	**t_r(mins)**	**$Q_{s(0)}$ (mg/g)**	**$Q_{r(0)}$ (mg/g)**
0.623	0.0139	0.636	1.702	2.300	0.0158

As observed in Figure 1, the experimental result is seen to follow the assumption of a two phase process. The first and second order models follow the curve closely with a coefficient of determination ‘R^2’ calculated to be 0.999 and 0.998, respectively. The new exponential model is observed to be a smooth parabolic curve, with a steep initial phase (rapid phase) and it becomes less steep as it progresses indicating the slow adsorption phase. The coefficient of determination ‘R^2’ was determined to be 0.994. This is significantly different from zero at 5 % level of significance for a two tailed test, an indication that the model estimates the experimental data closely. The rate of rapid adsorption is observed to be greater than the rate of slow and transition phases, as observed in Table 2. The time of transition ‘t_r’ is observed to begin 1.702 mins from the start of the adsorption process. The slow phase pseudo-equilibrium $Q_{s(0)}$is further observed to be greater than the rapid phase pseudo-equilibrium $Q_{r(0)}$, which is expected because at the onset of the adsorption process, the available sites are rapidly being filled but not completely. As time progresses, energy in filling those sites diminishes and so the process occurs much more slowly. Hence the available sites for slow adsorption aremuch greater than the rapid phase.

It is the opinion of the authors that at the beginning of the transition phase, the rapid adsorption dominates the slow phase adsorption. However as the transition phase progresses, the rapid adsorption slows down and is dominated by the slow phase which becomes the general description of the adsorption process. However, the processes occurring within the transition phase requires further investigation. It is also opined that for the duration of the adsorption process to be optimized, the rapid phase will have to be optimized too. This will push the transition time farther into the entire adsorption process, thereby reducing the time for the slow phase adsorption. This might be accomplished by optimized carbonization, chemical activation, increased adsorption area and so on.

4.1 CONCLUSION

The exponential model developed (Equation 20) is observed to compare favourably with the first and second order models in predicting the reaction kinetics of experimental data. The coefficient of determination ‘R^2’ of the first order, second order and the new models were determined to be 0.999, 0.998 and 0.994, respectively. The newmodel clearly reveals the suggested two phases in the adsorption process, as can be observed in the smooth parabolic curve it produces.The model also reveals new adsorption parameters such as the rapid, slow and transition rate constants, the transition start time and the rapid and slow phase adsorption capacities. From the relationship between the rapid and slow phase adsorption, it can be deduced that for any adsorption process to take place within a shorter period of time, the rapid phase must be optimized, pushing the start of transition farther up the adsorption process.However, further studies should be done to investigate the transition stage and a possible lag phase due to the presence of impurities or other deterrents at the adsorption sites.

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