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. An exponential equation is proposed. It is believed that there are two stages of adsorption, the rapid first stage and the slow second stage. The rapid first stage tends towards a first phase pseudo-equilibrium and transits to the slow stage which tends towards a second phase pseudo-equilibrium. The model was used to estimate kinetic data with an R^2 of 0.993.

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 activated carbon, molecular sieves, polymeric adsorbents, and some other low-cost materials. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems (Hui et al. 2009).

At present, adsorption reaction models have been widely developed or employed to describe the kinetic 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 *et al*., 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. Although water covers 70% of the world's surface, the availability of fresh water for animal consumption is becoming scarce. This is attributed to the improved standards that have resulted in rapid usage of pollutant infused substances such as pesticides, heavy metals, anions, pharmaceuticals, phenolic, personal care products, dyes, and hydrocarbons. Different methods have been developed to remove such substances from the wastewater, these include; biological, precipitation, membrane technology, electrochemical, and adsorption. Currently, the latter has received a considerable attention because it is cost and energy effective, easy to design and operate. 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).

The linearization of a function involves assumptions—any change in the assumption means a change in the error parameter. This leads to biasness in the data producing vast outcomes which violate the variance and normality assumption of the standard least squares. For example, the linearization of PSO has resulted in more than five different forms of PSO model. Using the non-linear form of the function means distributing the error on the entire curve.

2.1 ADSORPTION REACTION MODELS

2.1.1 nth-Order Kinetics

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, β_n is related to impurities pre-adsorbed on the surface (β_n = 1/(1 − θ_0)n−1), θ_0 is surface coverage at pre-adsorbed stage (θ_0 = Q_0/Q_e), dimensionless.

2.1.2 Double Exponential Model

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

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

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}.

2.1.3 Elovich model

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

$$\frac{dq}{dt} = ae^{-\alpha q} \qquad (3)$$

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:

$$q = \left(\frac{2.3}{\alpha}\right) log(t + t_0) - \left(\frac{2.3}{\alpha}\right) logt_0 \qquad (4)$$

2.1.4 Intra-particle diffusion (IP) model

IP model has been widely applied to examine the rate limiting step during adsorption. 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).

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

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)

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

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

There are four main mechanisms that describe the transfer of solute from a solution to the adsorbent. The first is called mass transfer (bulk movement) of solute particles as soon as the adsorbent is dropped into the solution. This process is too fast, thus it is not considered during the design of kinetic systems. The second mechanism is called film diffusion; it involves the slow movement of solutes from the boundary layer to the adsorbent's surface. When the solute reach the surface of the adsorbent, they move to the pores of the adsorbent—third mechanism. The final mechanism involves rapid adsorptive attachment of the solute on the active sites of the pores; being a rapid process, it is not considered during engineering design of kinetics (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.

3.1 PROPOSED EXPONENTIAL MODEL FOR ADSORPTION KINETICS

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}. This phenomenon is represented mathematically as Equations (7) and (8)

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

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

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

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

where q_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

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

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

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

Equation (18) can be rearranged to the form

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

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

3.2 MODELLING ADSORPTION RATE

Udeh and Amah (2022), investigated the adsorption potential of $ZnCl_2$ activated unripe musa paradisiaca peels for adsorption of phenol from aqueous solution. With the aid of Excel solver, the result of the adsorption rate was modelled using Equation (20) and shown as Figure 1. The adsorption parameters from the modelled data was extracted and shown as Table 1.

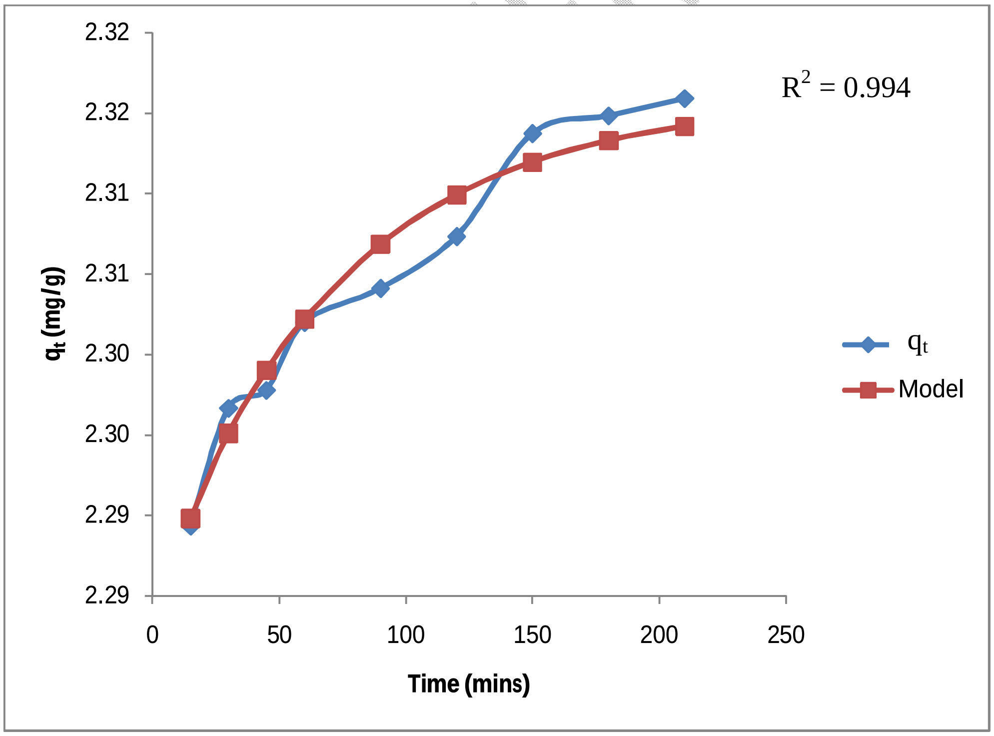

Figure 1: Modelled adsorption rate of phenol onto activated unripe musa paradisiaca peels

Table 1: 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 coefficient of determination 'R^2' is 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 value closely. The rate of rapid adsorption is observed to be greater than the rate of slow and transition phases, as observed in Table 1. The time of transition 't_r' is observed to begin 1.702 mins from the start of the adsorption process. 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.

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 are much greater than the rapid phase.

4.1 CONCLUSION

The exponential model developed (Equation 20) is observed to predict the reaction kinetics of experimental data with a coefficient of determination of 0.993. This is significant because it takes into account two stages of the adsorption process. 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 capacities, 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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