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Modelling of Adsorption Kinetic Processes—Errors, Theory and Application

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Abstract

Adsorption has become a competitive method in the field of wastewater and air treatment. Adsorption kinetics is one of the main factors that must be understood before the applicability of any adsorbent. In every adsorption process, linear or non-linear analysis of the kinetics is applied. The goodness of fit index (coefficient of correlation or sum of squares) is applied to access the best model. The usage of linear or non-linear from of the adsorption kinetics has an impact on the distribution of error function. Almost in every adsorption study, linear forms have been used to conclude the best kinetic model that influence the adsorption mechanism—which might be an error. Therefore, this review highlights the mistakes in the usage of linear and non-linear models. The applicability of the adsorption kinetics in wastewater treatment is also illuminated.

Keywords: goodness of fit, error function, Boyd model, diffusion model, dyes, ion adsorption, emerging contaminants

1. Introduction

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 [1–3]. 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 determine 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.

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. Generally, analysis of PFO and PSO is done by plotting $ln(q_t - q_e)$ and t/q_t against time, respectively. As the system approaches equilibrium, $t/q_t \approx t/q_e$ produces a perfect fitting for PSO. However, at equilibrium, $ln(q_e - q_t)$ becomes enormously large reducing the fitting index. In addition, R^2 has been compared using different scales of various kinetics—which is statically wrong. Therefore, this work highlights the gaps in the linearization of adsorption kinetics, and the suitability of each kinetic model towards the removal of dyes, organics, metals, and anions from solution.

2. Adsorption kinetics

Adsorption is the process by which solute molecules attach to the surface of an adsorbent. The adsorption process is done in batch or column setup. Adsorption kinetics is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbents dose, temperature, flow rate and pH. During adsorption two main processes are involved; physical (physisorption) or chemical (chemisorption). Physical adsorption is as a result of weak forces of attraction (van der Waals), while chemisorption involves the formation of a strong bond between the solute and the adsorbent that involves the transfer of electrons.

2.1 Pseudo first order model (PFO)

Also known as Lagergren model, PFO describes the adsorption of solute onto adsorbent following the first order mechanism;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

where q_t is adsorbate adsorbed onto adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), and k_1 is rate constant per min. The integral of Eq. (1) from $t = 0$ to $t = t$ and $q_t = 0$ and $q_t = q_t$ yields a linear expression of PFO, Eq. (2).

$$\ln(q_e - q_t) = lnq_e - k_1t \qquad (2)$$

The value of k_1 is determined by plotting $\ln(q_e - q_t)$ vs. t. Albeit some studies have found k_1 to increase with initial solute concentration (C_0) or independent of C_0, the rate constant is always inversely proportional to the initial concentration of the solute. This is because a longer time is required for a large initial solute concentration. The controlling mechanism is affected by experimental conditions, thus the

validity of the model. PFO is varied under Henry regime adsorption, and under high sorbent dosage [4]. To account for experimental differences during the sorption of dyes on activated carbon, PFO is modified as follows [5];

$$\frac{dq_t}{dt} = k_1 \frac{q_e}{q_t}(q_e - q_t) \tag{3}$$

and the linear form

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The plot of $\frac{q_t}{q_e} + \ln(q_e - q_t)$ against t gives a better fit of dye adsorption compared to Lagergren PFO. Different models for adsorption of various solutes have been developed, but the applicability and consistence of their linear and non-linear form need to be tested.

2.2 Pseudo second order (PSO) model

PSO model assumes that the rate of adsorption of solute is proportional to the available sites on the adsorbent. And the reaction rate is dependent on the amount of solute on the surface of the adsorbent—the driving force $(q_e - q_t)$ is proportional to the number of active sites available on the adsorbent [4, 6]. Eq. (5) shows the curvilinear form of PSO.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

k_2 is PSO rate constant. Applying the integral limits for t (0, t) and q_t (0, q_t), the linearized form of PSO is;

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{6}$$

Eq. (6) has been rearranged in different forms, Eq. (7)–(10).

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{t}{q_e} \tag{7}$$

$$\frac{1}{q_t} = \left[\frac{1}{k_2 q_e^2}\right]\frac{1}{t} + \frac{1}{q_e} \tag{8}$$

$$q_t = q_e - \left[\frac{1}{k_2 q_e}\right]\frac{q_t}{t} \tag{9}$$

$$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t \tag{10}$$

The approach used to linearize the curvilinear function of PSO determines the distribution of the error function of the same kinetic model. Among the linearized equations of PSO, Eq. (7) yields better fitting results compared to other forms. Therefore, the PSO constants can be determined from a graph of t/q_t vs. t. Even though the PSO model may be affected by pH, dose amount, particle size, and temperature—the model assesses the impact of observable rate parameters.

PSO can be used to determine the initial solute uptake and adsorption capacity of an adsorbent. Within the last 2 decades, PSO fits the experiment better and it has been concluded that the adsorption mechanism is chemisorption in nature, involving the transfer of electrons between the adsorbate and adsorbent—this conclusion is wrong. Adsorption mechanism cannot be based on simple fitting of PSO model.

When the solute concentration is low, Eq. (7) explains the adsorption mechanism more than any other kinetic model; however, at high initial concentration, PFO model is favoured [7]. This is because at low C_0 the value of $\ln(q_e - q_t)$ increases exponentially increasing the error function—which is the reverse for high C_0. Although the applicable of linear forms has improved, they may be misleading in developing kinetic systems. For example, the R^2 of the linear PSO model during the adsorption of methylene green 5 onto activated was above 0.99; however, using non-linear form, the fit index was below 0.70 [6]. Both PSO and PFO do not explain the diffusion of solute into the adsorbent; therefore, before any conclusions are made about adsorption mechanism, diffusion models should be investigated.

2.3 Elovich model

To further understand the chemisorption nature of adsorption, Elovich model (developed by Zeldowitsch) 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.

$$\frac{dq_t}{dt} = \alpha \exp^{-\beta q_t} \tag{11}$$

As $q_t \approx 0, \frac{dq_t}{dt} \approx \alpha$ which is the initial adsorption rate (mg/g.min), and β is desorption constant. Integrating and applying the limits for t $(0, t)$ and q_t $(0, q_t)$, the Elovich model can be linearized as;

$$q_t = \frac{1}{\beta} \ln\left[t + \frac{1}{\alpha\beta}\right] - \frac{1}{\beta} \ln(\alpha\beta) \tag{12}$$

As the system approaches equilibrium $t \gg \frac{1}{\alpha\beta}$, thus Eq. (12) becomes;

$$q_t = \frac{1}{\beta} \ln[\alpha\beta] + \frac{1}{\beta} \ln t \tag{13}$$

The graph of q_t *vs* t helps to determine the nature of adsorption on the heterogeneous surface of the adsorbent, whether chemisorption or not. A number of solutes have been reported to follow Elovich kinetics model [8, 9].

2.4 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. IP is studied by examining Weber and Morris (1963) model, Eq. (14).

$$q_t = K_p \sqrt{t} + C \tag{14}$$

K_p is a rate constant mg/g.min$^{0.5}$, and C is boundary layer thickness. The values of C determines the boundary layer effect—higher values, the greater the effect. The plot of q_t *vs* $\sqrt{t}$, gives a linear function. If the line passes through the origin, IP diffusion controls the adsorption process. However, on many occasions, the plot does not pass through the origin and it gives multiple linear sections; these sections corresponds to different mechanisms that control the adsorption process. 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 [6]. 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.

Misrepresentation of diffusion model: Couple of papers have assessed IP model using a straight of Eq. (14); however, in reality, pore diffusion is a slow process making Eq. (14) to follow a curvilinear trend. When the segment analysis is applied, the values of K_p and C differ enormously. The segments can be got by visual or application of regression on different points.

2.4.1 Boyd model

To understand if film diffusion is the rate controlling step, Boyd developed a single-resistance model that can be used to assess this effect. Boyd assumes that the boundary layer surrounding the adsorbent has a greater effect on the diffusion of solute [3]. To determine this effect, Eq. (15) is applied.

$$F = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(-n^2 B_t\right) \tag{15}$$

F is the fraction of solute adsorbed at time t (q_t) to solute adsorbed at infinite time (q_∞) ($t_\infty > 24h$ for better results). B_t is a mathematical function of F.

$$F = \frac{q_t}{q_\infty} \tag{16}$$

It is hard to estimate appropriate values of B_t with Eq. (15); B_t can be calculated using the integrated Fourier transform of Eqs. (17) and (18).

$$0 \leq F \leq 0.85: B_t = 2\pi - \frac{\pi^2 F}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{1/2} \tag{17}$$

$$0.86 \leq F \leq 1: B_t = -0.4977 - \ln(1 - F) \tag{18}$$

The graph of B_t *vs* t helps to predict the rate limiting step. If the graph approximates y = mx + 0.0 line, the rate limiting step is intra-particle diffusion, otherwise film diffusion model governs the process. Treatment of water was estimated to

follow IP model [10, 11]. However, in many studies film diffusion is the limiting step during the initial stages of the process followed by IP diffusion when particles reach the surface of the adsorbent [1, 12, 13]. There is barely any non-linear form of IP model. A couple of published papers have mispresented Boyd model. The values of B_t are obtained using Eq. (18) over the entire time scale [11, 12], this is wrong.

3. Goodness of fit

To determine the kinetic model that best describes the interaction between the adsorbent and solute, the goodness of fit is used. The coefficient of correlation (R^2), sum-of-squared errors (SSE), average relative error, Spearman's correlation coefficient, non-linear chi-square test, hybrid fractional error function, Marquardt's percent standard deviation, and standard deviation of relative errors are some of the error functions that have been employed to study model fit. **Table 1** summaries the error function [4, 14–17].

3.1 Sum of squared errors

This is one of the most used error function in determining the model. The main challenge of using SSE is that at higher concentration the squares of error increase. This gives a good fit which is not the case always [15].

3.2 Coefficient of correlation

Almost given in every adsorption study, R^2 shows the degree of variability of dependent variable which is explained by all independent variables. It ranges from 0 to 1, with values close to zero showing a perfect fit.

3.3 Marquardt's percent standard deviation

Although not commonly used in adsorption kinetics analysis, this error function is a modification of geometric mean distribution. It is based on the number of degrees of freedom of a system [16].

Error function	Expression
Coefficient of correlation (R^2)	$\dfrac{\sum_{i=1}^{n}\left[q_{cal}-\overline{q_{exp}}\right]^2}{\sum_{i=1}^{n}\left[q_{cal}-\overline{q_{exp}}\right]^2+\sum_{i=1}^{n}\left[q_{cal}-q_{exp}\right]^2}$
Marquardt's percent standard deviation (MPSD)	$100\left[\sqrt{\dfrac{1}{n-p}\sum_{i=1}^{n}\left(\dfrac{q_{exp}-q_{cal}}{q_{exp}}\right)^2_i}\right]$
Sum-of-squared errors (SSE)	$\sum_{i=1}^{n}\left[q_{cal}-q_{exp}\right]^2_i$
Hybrid fractional error function	$\dfrac{100}{n-p}\sum_{i=1}^{p}\left[\dfrac{q_{exp}-q_{cal}}{q_{exp}}\right]_i$

q_{cal}: *calculated amount of adsorbate adsorbed onto adsorbent, q_{exp}: experimental amount of adsorbate adsorbed, n: data points, p: number of parameters in each model.*

Table 1.
Common error functions.

3.4 Hybrid fractional error function

Developed by Porter [17], the model was aimed to improve the applicability of SSE at a lower concentration. The error function is divided by the measured value.

3.5 Sum of normalised errors (SNE)

Different error functions yield different value of goodness fit—thus it may be difficult to select the best model fit. SNE provide a normalised value of the different error functions, making comparison very easy. SNE is done by dividing the error value of the different functions by the highest error for a given kinetic model.

3.6 Misuse of fitting index

The assessment of adsorption kinetics using error function has been misused in almost all adsorption papers. The problem arises when error function of linearized equations of non-linear functions are expended to determine the suitability of a model. In some linearized models, to reduce the error factor, log or square root transforms are applied if the error increases with the dependent factor. And if the error variance decrease with increasing dependent factor, then exponential or square alters are applied. However, the use of R^2 or SSE does not detect the biasness of the parameters.

The dependent variable in adsorption kinetic is not entirely linear over the given values of the independent variable. Eq. (7) shows the linearized form of PSO. The inverse of data weights $\left(1/q_t\right)$ and the presence of independent variable (t) in both dependent and independent sides causes false correlation. The inversing of variables on both sides of Eq. (8) distorts the error distribution over the entire data. In the third form of PSO (Eq. (9)), the presence of dependent parameter $\left(q_t\right)$ in both the independent and dependent section leads to spurious correlation. While in Eq. (10), the presence of independent variable violates the least squares assumption [18]. R^2 is a very sensitive parameter that can cause spurious conclusions. R^2 varies with the range of independent parameter—if the range is big, R^2 will be fit; and if the range is small, fit will be poor. Adding more data points decreases the degree of freedom of a system; this favours model fit. Therefore, making conclusions solely basing on R^2 can be misleading to the industry of adsorption mechanism.

4. Linear and non-linear fitting application

4.1 Dyes

Dyes are organic substances that cause a permanent or temporary change in colour of a material; they are resistant to detergents. Dyes are widely employed in leather, food, textile, paper, rubber, and plastic industries. When dyes are released in the hydrosphere, they can block sunlight penetration, thus affecting the marine life. In addition, they give unpleasant colour to water making it unsafe for human consumption. To reduce the impact of dyes on the ecosystem, adsorption method has been employed to remove dyes from wastewater. Different kinetic models have been employed to study the adsorption of dyes from solution, these include; PFO, PSO, Elvoich, and IP models. The suitability of any model depends on error functions. **Table 2** summarises the non-linear adsorption kinetics of different adsorbent.

Adsorbent	Solute	Error function	Kinetic	Ref.
Activated carbon	Acid red	R^2	PFO, PSO*	[19]
Activated carbon	Methylene blue	R^2	PFO*, PSO*	[20]
Activated carbon	Methylene blue	R^2, NSD	PFO*, PSO	[21]
Mn_2O_3 nanofibres	Methylene blue, malachite green, Basic red 46	R^2, X^2	PFO, PSO*, IP	[22]
Sugarcane bagasse	Auramine-O, Safranin-T	R^2, X^2	PFO, PSO*, IP, Elovich*	[23]
Polyhedral oligomeric	Crystal violet	R^2	PFO*, PSO*	[24]
MWCNTs hydrogel	Methylene blue	R^2, X^2, NSD	PFO*, PSO	[25]
$Mg_3Si_2O_5(OH)_4$	Rhodamine B	R^2	PFO*, PSO*	[26]
$Fe_3C/Fe_3O4/C$	Methylene blue	R^2	PFO, PSO*	[27]
Clinoptilolite	Pb	NSD, R^2, SSE	PFO*, PSO Elovich*	[28]
Clinoptilolite	Pb	R^2	PFO, PSO*	[29]
Wheat straw	Cu	R^2, X^2	PFO, PSO* Elovich	[30]
Fruit peels	Cu	R^2	PFO*, PSO Elovich	[31]
Chitosan	Cu	R^2, ARE	PFO, PSO* Elovich	[32]
Rape straw	Cu	R^2, X^2	PFO, PSO*, IP	[33]
Nano-TiO_2	As	NSD, R^2	PFO, PSO*	[34]
Nano-iron	As	NSD, R^2, SSE ARE	PFO, PSO* Elovich	[35]
Graphene oxide	As	R^2, X^2	PFO*, PSO, IP, Elovich	[36]
Nanocellulose	Hg	R^2, X^2	PFO, PSO*	[37]
MCM-41	Hg	R^2, RMSE, ARE	PFO, PSO*, IP, Elovich	[38]
Almond shell	Hg	R^2, ARE	PFO, PSO*, IP,	[39]
Chitosan	P	R^2	PFO*, PSO*	[40]
Tourmaline	P	R^2	PFO, PSO*	[41]
Zn-Al	P	R^2, RMSE	PFO, PSO* IP	[42]
Iron	N	R^2, SSE	PFO*, PSO IP, Elovich	[43]
Chitosan-Fe	N	R^2, X^2, NSD	PFO, PSO* IP	[44]
Cellulose	N	R^2, ARE	PFO, PSO*, Avrami	[2]
Quintinite	F	R^2, X^2, SSE	PFO, PSO*, Elovich	[45]
Mg-Al-Fe	F	R^2, RMSE	PFO*, PSO, IP	[46]
Manganese carbonate	F	R^2, NSD	PFO, PSO*	[47]
Coconut	Carbofuran	R^2, ARE	PFO, PSO*	[48]
AC	Carbofuran	R^2, RMSE	PFO, PSO*	[49]

Adsorbent	Solute	Error function	Kinetic	Ref.
AC	Carbofuran	R^2	PFO, PSO[*]	[50]
AC	2,4-D	R^2, ARE, NSD	PFO, PSO[*], IP	[51]
MIEX resin	2,4-D	R^2, RMSE	PFO, PSO[*], IP	[52]
Sibunit	2,4-D	R^2	PFO[*], PSO[*],	[53]
AC	2,4-D	R^2, RMSE	PFO, PSO[*]	[54]
Peanut	Atrazine	R^2	PFO[*], PSO[*]	[55]
MWCNT	Atrazine	R^2, ARE	PFO, PSO[*], IP	[56]
Biochars	Atrazine	R^2	PFO, PSO[*], IP, Elovich[*]	[57]
Trimethylsilylated	Gemfibrozil	R^2, SE	PFO, PSO[*]	[58]
Photocatalytic	Indomethacin	R^2, SE, SSE	PFO, PSO[*]	[59]
Human hair	Tetracycline	R^2, ARE	PFO[*], PSO, IP	[60]

[*]*Best model, NSD: normalised standard deviation, X^2 : chi-square, SE: standard error, SSE: sum of error squared, ARE: average relative error, RMSE: root-mean-square error, AC: activated carbon, 2,4-D: 2,4-dichlorophenoxyacetic acid.*

Table 2.
Non-linear adsorption kinetics.

While using a linear model of kinetics, based on R^2, it was evident the adsorption of Rhodamine B by $Mg_3Si_2O_5(OH)_4$ followed second order system; however, expending non-linear analysis, R^2 of PFO jumped from 0.67 to 0.99 [26]. Using non-linear approach to analyse the kinetics of dye adsorption, the goodness fit of PFO increases drastically to an average of 0.90. The fitting of $R^2 \geq 0.9$ is statistically good and can be used to make conclusions. Most error functions have been based on R^2—this has forced researchers to conclude that both PFO and PSO explain the adsorption of dye. However, further analysis using different error functions can help to solve the puzzle. The adsorption of Methylene blue onto activated carbon fitted PFO and PSO well ($R^2 > 0.9$); however, the analysis of NSE, PFO had the least value [21]—thus the adsorption of methylene blue is best described by PFO. Linearization of PFO worsens the adsorption parameter—to have a better fitting of PFO during dye adsorption, the non-linear model should be used while studying dye adsorption. Therefore as more dye adsorption studies are being carried, non-linear model and error functions should be explored to avoid misleading conclusions. Similar trends have been observed by different research groups working on dye adsorption [61–65].

4.2 Other organic materials

A number of organic material have been classified as emerging contaminates, these include; pesticide, pharmaceuticals, disinfection by-products, fertilisers, and biological toxins. All these organic materials affect our ecosystem in a diverse way. The cheap and effective method of removing these materials from the solution is adsorption; however, there has been mixed results about the adsorption kinetics of these pollutants. Carbofuran is a pesticide, ranked among the most dangerous carbamate insecticides. Albeit its bioaccumulation is less, its mammalian toxicity potential is high. When consumed for a prolonged period of time at elevated concentrations (more than 0.09 mg/L), it disrupts the endocrine, breathing, development and reproduction systems [50]. This necessitates its removal from

wastewater. The adsorption kinetics of carbofuran have been studied in almost every adsorption study. The analysis of non-linear and linear kinetic functions using the error parameters—the adsorption of carbofuran generally follows PSO. The experimental data for adsorption of carbofuran on coconut were almost in perfect correlation with PSO model [48]. Therefore, PSO should be given a priority while designing adsorption system for carbofuran adsorption.

2,4-Dichlorophenoxyacetic acid (2,4-D) is herbicide that is globally used as a selective regulator of plants. 2,4-D is non-volatile but highly soluble in water. Thus exposure of groundwater to 2,4-D can lead to contamination. Long-time exposure of 100 µg/L of 2,4-D to humans can lead its accumulation in the seminal plasma and follicular mucus—increasing the risk of infertility. The removal of 2,4-D from solution using adsorption technique is mainly dominated by carbon related adsorbents [66]. Although the adsorption of 2,4-D using Sibunit raised a mixed observation as the initial concentration of changed [53], from **Table 2**, the assessment of error functions shows that adsorption of 2,4-D is mainly governed by PSO kinetics. Both non-linear and linear functions sorption kinetics favour PSO model. Another common herbicide expended in broadleaf weeds regulation is atrazine. Because of its high solubility in water, it has been detected in a number of groundwater wells, thus its ban in European countries; however, atrazine is extensively used in developing economies as pre and post-emergent herbicide to control weeds in crops. As 2,4-D, atrazine is an endocrine disruptor [56]. Several non-linear and linear kinetic studies have indicated that the adsorption of atrazine to be PSO in nature (**Table 2**).

Pharmaceuticals are organic compounds used to prevent, treat, and restore organ function. After restoring the damaged organ, they are flashed out of the body into the environment. In addition, pharmaceutical companies release numerous amount of waste into the water streams. The widely employed wastewater treatment technologies cannot remove pharmaceuticals wastes—thus the escalated presence of pharmaceutical products in the environment. Estrone, 17β-estradiol, 17α-ethinylestradiol, estriol, and acetaminophen are among the most alkaloids, steroid hormones and primary estrogens present in wastewater. As pesticides and herbicides, pharmaceuticals danger the nervous system. Most of the pharmaceuticals that are harmful to human nervous system tend to be lipophilic in nature, binding to solids. Nanofiltration, advanced oxidation, and adsorption are some of the main methods that are used to remove pharmaceuticals from wastewater. To effectively remove pharmaceuticals from solution, mesopore adsorbents with considerable surface area must be used. The adsorption kinetics of anionic, neutral, and cationic pharmaceutical onto mesopore trimethylsilylated all followed PSO model [58].

4.3 Metals and anions

In allowable range, metals are vital elements that support human life—without them, life could be impossible. Among all the major contaminants, metals top the list because of their wide applicability in electricity, construction, and medicine. Accumulation of heavy metals in human bodies is dangerous. For example, thallium and manganese damages nervous system, while cobalt and nickel are carcinogenic. Different adsorbents have been developed to remove these metals from wastewater. These include; industrial waste, peat, wood, brown rice, straw, peanut shell, hazelnut shell, soybean filament, cotton seed pulp, sugar beet pulp, leaves. The adsorption of metals is affected by pH of the solution, contact time, the initial concentration of metal and ambient temperature are affected. The adsorption mechanism is evaluated by various kinetic models such as PFO, PSO, Elovich,

Weber and Morris intra-particle diffusion model, Bangham model and Boyd kinetic model.

During metal adsorption, the best kinetic model is evaluated by assessing the error function after plotting linear or and linear model. In addition, qe must match reasonably well with experimental values, qe_{cal} at all initial concentrations of adsorbate with maximum R^2 and minimum χ^2 values. The adsorption of lead by pretreated clinoptilolite using the non-linear kinetics was best described by PFO [28]. Both raw and treated clinoptilolite PFO had R^2 above 0.98 in addition to having the least values of SSE—the experimental values agreed well with the calculated values. The rate constant increased with the increase in the initial solute concentration. Using almost similar adsorbent, bentonite to adsorbed Pb from solution was best described by PSO than any other kinetic model [29]. This observation was based on the linear format of the kinetics—therefore, to make conclusive meaning, both non-linear and linear model should be investigated.

Copper is another mineral that has received considerable attention over the past decades. Copper nanoparticles have been employed in lubricates to reduce the friction, tear and mend torn surfaces. Because of its good charge-discharge property, copper nanoparticles have been used in lithium batteries to improve coulombs efficiency. Due to numerous application of copper, it is mostly likely to enter into human bodies via the food and water chain. Excessive exposer of animals to copper destruct lipid profile, malfunction of the renal, and hepatocirrhosis [33]; this calls its removal from solution before it is consumed by humans. The removal of copper by adsorption process has been studied by different research groups. Although there are some studies that have favoured the adsorption of copper to be PFO nature [31], the assessment non-linear and linear adsorption kinetics of copper favours PSO—regardless of the adsorbent (**Table 2**). Comparing the error functions that determine the suitability of the kinetic model, PSO error parameters possess minimal variations. For example, the adsorption of copper onto chitosan followed PSO mechanism [32].

Ranked in top five among the most dangerous metal, the occurrence of Arsenic in wastewater is on raise due to increased usage of paintings, dyes, mining and smelting activities. The consumption of arsenic contaminated materials (above 10 parts per billion) causes muscle cramping, blood and hair loss—thus it is necessary to remove arsenic from water before it is consumed. The adsorption kinetics of arsenic vary from one experiment to another. While comparing the non-linear and linear kinetics of arsenic adsorption by nano-TiO_2, both non-linear form of PFO and PSO yielded good fit (>0.90) [34]. The linear model of PFO yielded a very poor fit—thus basing on the linear model only can lead to poor judgement. Although there is no clear cut point on the best kinetic model, the recent adsorption studies of arsenic favour PSO (**Table 2**). Mercury is another heavy metal that has been investigated extensively due to its toxicity to animals. Although Hg is widely used in teeth amalgam, consumption of water levels with more 0.01 mg/L of Hg causes neuronal disorders and damages cardiovascular system [67]. This has called the development of cheap and efficient adsorbents to remove Hg from solution. While modelling the linear adsorption of Hg using MCM-41, PFO yielded a poor coefficient; however, when non-linear models were applied, PFO error functions improved [38]. **Table 2** summaries the adsorption kinetics of Hg onto different adsorbents—the non-linear PSO model has been preferred over the other models.

Metals in wastewater are always accompanied by anions like phosphate, sulphate, carbonate, and chloride. Among these, phosphate is the most crucial element. Phosphorus is a vital element in our ecosystem, without it life would be impossible. Phosphorus support bone and tooth growth, nerves and muscles. Phosphorus is vital during the formation and maintenance of DNA and cell membranes. However,

excessive presence of phosphorus in the ecosystem promotes bacteria growth. This affects marine life which in turn disorganises the ecosystem. Also, white phosphorus has been reported to cause stomach cramps, nausea, and drowsiness [68]. Various approaches are used in phosphate removal from wastewater including ion exchange, chemical precipitation, biological, and adsorption. The later has received considerable attention due to its efficiency and cost benefit. The adsorption kinetics of vanadium have been extensively studied in almost every study. There are mixed results about the adsorption kinetics of phosphorus. The adsorption of phosphorus onto tourmaline was best described by linear PSO; however, analysis of the non-linear models produced better fitting for both models ($R^2 > 0.95$) [41]. Thus, before any conclusion is made about the kinetic model, non-linear kinetics should be investigated. There is no clear model that governs the adsorption of phosphorus (**Table 2**).

Nitrates are another ions that affect ecosystem extensively. The mechanisation of agriculture has promoted the use of nitrogen infused fertilisers at large scale. Excessive nitrogen promotes eutrophication—a condition that promotes algal growth. Algal growth cuts off oxygen supply in the aquatic system [69]. Therefore, before nitrate infused wastewater is released into the atmosphere, it must be treated. In addition, elevated amount of nitrate cause blue-baby syndrome. Adsorption has been employed to remove nitrates from wastewater. The adsorption of nitrate onto iron particles was best described by PFO [43]. However, during the adsorption of nitrate onto chitosan-Fe, PSO was favoured model [44]. There is more need to investigate the non-linear kinetics of nitrate adsorption. Fluorine is an essential element in our daily life—it is used in toothpaste to prevent teeth from decay. However, long term consumption of water with over 1.5 mg/L causes fluorosis, a condition that affects teeth, bones ossification, and neurological damage under extreme conditions [70]. To remove fluorine from water, precipitation and adsorption have been employed extensively. The adsorption kinetics of fluoride are complex, they depend on solute-adsorbent interaction. For example, the adsorption of fluoride onto manganese carbonate was second order in nature [47]; however, the analysis of a non-linear model of fluoride adsorption by Mg-Al-Fe, PFO controlled the reaction [46].

5. Conclusion

Since the late C20[th], majority of the adsorption studies have favoured PSO than PFO. This is attributed to the fact that, most of the plots of PSO include values as the system approaches equilibrium—the values of $t/q_t \approx t/q_e$. The incorporation of values close to equilibrium produces a fitting index close to one. For PFO, as the system approaches equilibrium, the $(q_t - q_e)$ slant to zero, thus $ln(q_e - q_t)$ becomes abnormally large at equilibrium reducing the accuracy. In all adsorption studies sampled, R^2 has is used to test goodness fit. However, to have a better comparison of R^2, the scale must be the same. Therefore, to understand the adsorption mechanism of any solute, non-linear models should be applied, and to assess the best fit model, non-linear least squares must be applied. Many linear forms of PFO, PSO and Elovich have been developed, but most of them are based on erroneous assumptions. Consequently, while studying the adsorption kinetics, the above given equations should be used. Using PSO model to conclude that the adsorption kinetics is chemisorption is misleading. The models should also be checked with diffusion models to best describe the adsorption mechanism.

Acknowledgements

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