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Kinetic modelling techniques in industrial wastewater treatment using nanocellulosic adsorbents: A Review of batch and column operations

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Abstract

The design of a satisfactory adsorption system for the removal of toxic metallic ion requires the knowledge of its kinetics where information on sorption rate at variable experimental conditions, adsorbent capacity and mass transfer mechanisms can be extacted is vital. Flowrates, complexity of sorbent surface, sorbate concentration as well as bed height in column operations are some of the factors that can influence adsorption kinetics. Lagergren pseudo first order and pseudo second order models or Thomas, Yoon-Nelson and Dose-Response models are some of the frequently encountered kinetic models that enhance the prediction of sorbate-nanocellulosic adsorbent interactions in static or dynamic adsorption systems respectively. The robustness of the models can be determined by the application of linear or non-linear regression analysis to assess its goodness of fit index. However, the dynamic behavior of the column depends on the characteristic pattern of the breakthrough curve in response to the variables under investigation with the relevant models, whereas the highest correlation coefficients for batch processes were obtained from pseudo second order kinetic model.

1. Introduction

One of the important separation process techniques employed in industrial effluents and water treatment is adsorption. This is because of the simplicity of its methodology, easy maintenance, overall process economics, high efficiency, the possibility of adaptation of several natural, low cost and eco-friendly adsorbent types, insensitivity of process to toxic pollutants, zero hazardous sludge generation and zero additional chemical compound requirement, except where chemical modification of the adsorbent is involved [1-4].

In general, study of adsorption kinetics is vital for the description and evaluation of reaction pathways/ mechanisms and adsorbate uptake rate at the solid-solution interface. Thus, on the basis of an empirically determined rate law which satisfactorily describes the sorption system, it is possible to predict the rate at which pollutants can be depurated from aqueous solution in order to design appropriate treatment systems.

2. Kinetic modeling in batch or static operation

The necessary information for adsorption kinetic modeling of the batch operation is usually established alongside the adsorption equilibrium isotherm. The design of an effective and reliable adsorption system is dependent upon the ability to predict the adsorption kinetics for the system to a large extent. Consequently, various kinetic models had been proposed based on fundamental concepts such as shrinking core concept, intra-particle surface diffusion theory or interfacial kinetics subject to verification processes with numerous adsorption kinetic systems. Examples of such kinetic models include pseudo-first order, pseudo-second order [5] and Elovich, Avrami and intra-particle diffusion model [2, 6-7]. Information from these models that are essential in process plant design, optimization and control, include rate of sorbate uptake, mechanism of reaction pathway and factors that determine the rate-controlling step. However, the most frequently used kinetic models to correlate sorption data of toxic metallic pollutants on nanocellulose adsorbent and its various modified composites are the pseudo-first and pseudo-second order kinetic models. During such investigations, mass of pollutants adsorbed with respect to time is documented, from where the kinetic profile as well as the rate controlling step can be determined [8-13].

2.1. Pseudo-first order kinetic model

This model was first proposed by Lagergren based on the concept of interfacial kinetics in 1898 [14]. Its differential form of its given as

$$\frac{dq}{dt} = K_1(q_e - q)$$

where q_e = adsorbed amount or adsorbent loading measured in unit of (mg) or (g) of adsorbate (solute) per g adsorbent (solid) at equilibrium, q corresponds to adsorption capacity (mg/g), while t is time(min) and k_1 represents rate constant (1/min).

By an integration operation constrained with the restrictions that at time (t) = 0, ⇒ q = 0 and at time (t) = t, ⇒ q = q, then equation can be linearized as,

$$\ln(q_e - q) = \ln q_e - K_1 t$$

Therefore, the unknown kinetic parameter can be deduced from the plot of the linear dependence of $\ln(q_e - q)$ with respect to time (t) [2,9,15]. The difficulty encountered with the separation of the lumped variable can be overcome by a trial-and-error estimation of the adsorption capacity of the system at equilibrium (q_e) till a satisfactory regression value is obtained. However, solving the above non-linear expression yields;

$$q = (q_e - e^{-k_1 t})$$

where q_e and k_1 can be obtained by non-linear fitting of the plot of q versus t.

According to Putro *et al*. [16], only a handful of adsorption kinetic processes were consistent with the Lagergren pseudo first order model. For instance, the removal of Cr^{3+} and Cr^{6+} from inorganic wastewater using succinated nanocrystalline cellulose and animated nanocrystalline cellulose respectively. Also, the separation of U^{6+} from synthetic wastewater with the aid of cellulose camphor soot nanofibers was in conformity with pseudo-first order kinetic model, even at high solute concentration [17].

Hao *et al.* [18] noted that the kinetic regression analysis of the adsorption of Cu^{2+} ions by polyethylenimine and ferric iron coated spent coffee powder (Coffee-PEI-Fe) fits with the pseudo first order model. Neeli *et al.* [19] reported that using non-linear regression analysis, the uptake of Cu^{2+} from synthetic wastewater using magnetic iron-carbon nanoadsorbent synthesized from cellulose was consistent with the pseudo first order kinetic model.

2.2. The pseudo-second order kinetic model

The Pseudo-second order model is typically a curvilinear function and can be expressed in a differential form as;

$$\frac{dq}{dt} = K_2(q_e - q)^2$$

If an integration within the confines of the restrictions that at time (t) = 0, ⇒ q = 0 and at time (t) = t, ⇒ q = q is performed, several dissimilar linear but related transformations [20-23] of the pseudo-second order models can be derived, viz;

$$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$$

$$\Rightarrow \quad \frac{q}{t} = \frac{k_2 q_e^2 q_e}{q_e + t k_2 q_e^2}$$

$$\Rightarrow \quad q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

$$\text{or} \quad \frac{t}{q} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$$

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

$$q = q_e - \left[\frac{1}{k_2 q_e}\right]\frac{q}{t}$$

$$\frac{q}{t} = k_2 q_e^2 - k_2 q_e q$$

$$\text{and} \quad \frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t$$

Therefore, the distribution of the error function which is required to assess the robustness of the pseudo second order kinetic model depends on the particular linearization technique adopted for the non-linear form due to its effect on experimental data as indicated in **Table 1**.

The inferences drawn in column 3 and column 4 indicate that a researcher may be misled by the results of the kinetic model parameters which can be positively or negatively distorted by the transformation of non-linear kinetic equation to linear expressions due to the corresponding change that may accompany the error distribution of the regressive model.

However, Bujdák [23] indicated that the popularity ascribed to the linearized functions is because it enhances much better fitting of experimental data even though few reports are critical of the technique and advised caution in the use of linear regression for linearized non-linear expressions.

This opinion is also collaborated by Kajjumba *et al.* [24] who reported satisfactory result by applying the a linearized model. Thus, the plot of t/q versus t can yield the unknown kinetic parameters namely, k_2 and q_e. Presently, the preferred evaluation approach is based on its non-linear form which can be determined by non-linear regression analysis with input variables represented by empirical data with the aid of 'Ceres-solver' library [25] or 'origin' software version 2017 [23].

In an extensive review, Putro *et al.* [16] and Hubbe *et al.* [26] submitted that majority of cellulosic and nanocellulosic adsorption studies are in convergence with the pseudo second order kinetic model. Furthermore, the primary mechanism for the bonding of pollutant molecules and functional groups onto the surfaces of the nanocellulosic adsorbent is chemisorption.

Table 1: The various forms of linearized pseudo second order kinetic model (PSOKM) and effects on correlation coefficients.

Linearized Forms of PSOKM	**Plot**	**Effects of linearization**	**Formulae for computing kinetic parameters (s = slope, I = intercept, r = initial sorption rate)**
$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$	t/q vs t	(i) Inversion of relative weights of data points arising from corresponding reversal of the adsorption capacity in the dependent variable (ii) Presence of t on both sides of the expression can result in doubtful correlation	q_e= 1/s K_2 = s^2 /I r = 1/I
$\frac{1}{q} = \frac{1}{q_e} + (\frac{1}{K_2 q_e^2})\frac{1}{t}$	$\frac{1}{q}$ vs $\frac{1}{t}$	(i) Inversion of relative weights of data points owing to corresponding inversion of the adsorption capacity in the dependent variable (ii) The independent variable 1/t can lead to misrepresentation of the error distribution	q_e = 1/I K_2 =I^2/s r =1/s
$q = q_e - \frac{q}{K_2 q_e t}$	q vs $\frac{q}{t}$	(i) The presence of q on both sides of the equation can result in doubtful correlation (ii) The appearance of q in the independent variable (q/t) introduces experimental error which contradicts the basic assumptions of least squares method (iii) The existence of 1/t in independent variable can lead to the misrepresentation of the error distribution	q_e= I K_2 = -1/(I×s) r= -I/s
$\frac{q}{t} = k_2 q_e^2 - k_2 q_e q$	$\frac{q}{t}$ vs q	(i)The existence of q in both dependent and independent variables can lead to defective correlation (ii) The appearance of q in the independent variable introduces experimental error which contradicts the basic assumptions of least squares method	q_e = -I/s K_2 =s^2 /I r = I
$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t$	$(q_{e,exp} - q)^{-1}$ vs t	The need for prior experimental value for $q_{e,exp}$ is a potential source of error variance violation as well as its presence in both dependent and independent variables	q_e = 1/I K_2 =s r = -1/s

Yu *et al*. [31] observed that decontamination of Pb^{2+} from synthetic wastewater by carboxylated nanocellulose crystals conformed to pseudo-second order kinetic model whereas the decontamination of Cr (VI) by calcium hydroxyapatite / microfibrillated cellulose from wastewater was satisfactorily represented by pseudo-second order kinetic model [29].

Also, Hao *et al.* [18] published that the removal of As(V) and P(V) ions by polyethylenimine and ferric ion coated spent coffee powder from aqueous solution obeyed pseudo second order kinetic model.

Similarly, the uptake of Cu^{2+}, $Cd^{2+}$and Pb^{2+}ions onto cellulose/ chitosan composite adsorbent [32] as well as the removal of Pb^{2+} and Cd^{2+} by an adsorbent synthesized from S-ligand tethered cellulose nanofiber [33] were also in conformity with the pseudo second order kinetic model. Also, the decontamination of Pb^{2+} and Cu^{2+} using an adsorbent synthesized from nanofiber hydrogel composites-based chitosan-g-poly (acrylic acid) filled with cellulose nanowhiskers from wastewater obeyed the pseudo second order kinetic model [34].

In another report, Song *et al*. [35] established that the kinetic regression analysis of the adsorptive remediation of Cr^{3+} ions from wastewater by carbon quantum dot/nanofibrilated cellulose composite aerogel adsorbent using green chemical synthesis correlate suitably with the pseudo second order model. Neeli *et al.* [19] reported that the non-regression analysis of the decontamination of Cr^{6+}, As^{5+} and Pb^{2+} from wastewater with the aid of magnetic iron-carbon nanoadsorbent synthesized from cellulose biochar was duly correlated by pseudo second order kinetic model.

The major difference between these two types of models is that pseudo-first order kinetic model was constructed on the Langmuir model which is based on 'one-site occupancy adsorption hyothesis'. Thus, the adsorbate molecule can only react with one site of the adsorbent. It is a physisorption process whereby the rate limiting step is the external diffusion [36]. The pseudo-second order kinetic model involve two site occupancy surface assimilation where one molecule of the adsorbate can react with more than one site, usually by chemisorption which may involve covalent bonding and ion exchange. Here, intra-particle diffusion is the limiting step [36-37].

3. Kinetic models for column adsorption systems

In order to translate the batch-wise wastewater treatment process to an industrial scale operation, the effectiveness of the adsorbate-adsorbent system must be validated through a dynamic type or continuous flow study in which the adsorbent is continuously in contact with fresh feed. Examples of such columns include fixed bed, moving bed and fluidized bed. These types of columns are also capable of accommodating recycling and regeneration operations investigations. Usually, the residence time of most sorption flow processes may not be sufficient for the attainment of equilibrium as it is in batch process resulting in the lack of correspondence between the information obtained from the two processes. Therefore, the data gathered from batch mode operation is mainly useful in the determination of the effectiveness of the adsorbate-adsorbent system and in the preliminary screening of adsorbent candidates for economic reasons but inappropriate for the industrial-type scale-up purposes [38, 28]. Other factors for the incongruity on the data from column operation include the lack of appropriate technique to determine the chemical or biological changes within the adsorbent based on existing isotherms, the near-inexhaustible tendency of micro-range particulate adsorbents during large-scale operations [39] and the response of process variables at any cross-sectional flow area on the basis of the operating limits of the column [40]. Outlined below are some of the established non-mass-transfer-based mathematical models developed for the estimation of the relevant adsorptive kinetic coefficients as a function of the characteristic pattern of the breakthrough curve by certain.

3.1. Bed Depth Service Time (BDST) model

This model, often called Bohart-Adams model was proposed by the pair in 1920 [41] to represent the intrinsic relationship between normalized adsorbate concentration and time with reference to the adsorption of chlorine by charcoal [40]. It has now been extensively applied to several continuous flow liquid/solid pollutant sorption systems [39, 41]. It is based on the premise that (i) the surface assimilation of the adsorbate and the residual capacity of the sorbent material are the basic determinants of the sorption rate (ii) equilibrium does not occur rapidly, which implies that the obtained experimental data can only satisfactorily depict the initial region of the breakthrough curve and (iii) the adsorbate uptake rate is controlled by external mass transfer which is promoted by surface reaction of pseudo-second order kinetics. However, despite the above restrictions, this model is regarded as the simplest and most rapid approach for the prediction of adsorbent behavior in the assessment of continuous flow adsorption systems for design purposes [39].

Essentially, the BDST model describes the linear relationship between the bed depth (z) and column service time (t) in accordance with the following equation;

$$\mathrm{Ln}\left(\frac{c_t}{c_0}\right) = \mathcal{k}_{BA} c_0 t - \frac{\mathcal{k}_{BA} z N_0}{v_o}$$

which can also can be rearranged as

$$\mathrm{Ln}\left(\frac{c_0}{c_t} - 1\right) = \frac{\mathcal{k}_{BA} N_0 z}{v_0} - \mathcal{k}_{BA} c_0 t$$

where c_0 is equivalent to inlet or influent concentration at time t = 0 ($\mathrm{mg\,L^{-1}}$), c_t effluent concentration at time t = t ($\mathrm{mg\,L^{-1}}$), $\mathcal{k}_{BA}$ corresponds to the kinetic rate constant for the Bohart-Adams' model ($\mathrm{L\,mg^{-1}min^{-1}}$), z is length of the column bed (cm) while N_0 represent the adsorbent saturation concentration ($\mathrm{mg\,L^{-1}}$) and v_0 is the linear velocity influent liquid ($\mathrm{cm\,min^{-1}}$) which is the quotient of the volumetric flow rate and the cross sectional area of the bed. Moreover, bed height can be replaced by the adsorbent mass (g) since the values of the breakthrough time determined for various bed heights can be incorporated into the BDST model [28]. By the evaluation of linear dependence of different bed heights (z) versus breakthrough times (t) at constant flowrate and initial adsorbate concentration, N_0 and $\mathcal{k}_{BDST}$ can be deduced from the gradient and intercept respectively. However, if the $\mathrm{Ln}\left(\frac{c_0}{c_t} - 1\right)$ is plotted against t, $\mathcal{k}_{BA}$ can be deduced from its gradient.

3.2. Thomas model

This model was developed in 1944 based on the consideration that the dynamic plug flow characteristics of the fixed bed is subject to the fact that (a) axial dispersion does not occur within the column during the sorption process (b) Langmuir isotherm for adsorption-desorption system does apply (c) it is coupled on pseudo second order reversible kinetics (d) the rate controlling step is the interface mass transfer step which is restricted to chemisorption [28, 42].

The data obtained from these studies provide information for the evaluation of the maximum solid phase concentration of the sorbate on the sorbent and its rate constant. Thomas model is often expressed as:

$$\mathrm{Ln}\left(\left(\frac{c_0}{c_t}\right) - 1\right) = \frac{\mathcal{k}_{TH} q_0\, m}{Q} - \mathcal{k}_{TH} c_0\, t$$

where $\mathcal{k}_{TH}$ corresponds to Thomas model constant ($\mathrm{L\,min^{-1}mg^{-1}}$), q_0 is equivalent to the maximum solid-phase concentration of the solute or maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$) while Q represents the volumetric flow rate (mL min^{-1}) while m is the mass of the sorbent material packed as fixed bed (g). By maintaining a constant flow rate, k_{TH} and q_0 can be obtained from the graph of Ln $[(\frac{C_0}{C_t}) - 1]$ versus t (ν_{eff}/Q), where ν_{eff} is the effluent volume (mL) [43-44].

3.3. *Yoon and Nelson model*

The Yoon and Nelson model though, advanced to describe the uptake of gaseous adsorbate onto activated coal, had been observed to accord satisfactory results to liquid-solid adsorption systems by various researchers [45-46]. This model is based on the hypothesis that the chances of the uptake of each pollutant molecule decreases at a rate directly proportional to the probabilities of both the pollutant molecule uptake and its breakthrough on the sorbent material. It is not as complicated as other models because detailed data are neither required on the characteristics of adsorbent and adsorbate, nor on the physical properties of the adsorption bed. Consequently, the Yoon-Nelson model is often valid for rough estimation of process variables for industrial scale adsorption [28, 46-47]. Its linearized form can be represented by

$$\mathrm{Ln}(\frac{C_t}{C_0 - C_t}) = k_{YN}t - k_{YN}\tau,$$

where k_{YN} stands for the Yoon-Nelson rate constant (min^{-1}), t represents the processing time (min) and τ refers to the length of time (min) necessary for the attainment of 50% initial adsorbent concentration in the effluent stream. The product of these two variables is constant for a particular adsorbent-adsorbate system and independent of both the flow rate and the initial adsorbate concentration [39]. If the experimental data describes the model accurately, then k_{YN} and τ can be evaluated from the gradient and the intercept of the graph of $\mathrm{Ln}(\frac{C_t}{C_0 - C_t})$ versus t at different bed masses or heights, flow rates and initial concentrations.

3.4. *Clark model*

This model is hinged upon two fundamental hypothesis (a) column adsorption is driven by the combination of mass transfer phenomena and the consistency of its profile within the confines of the Freundlich adsorption isotherm. It should be noted that during mass transfer axial dispersion is neglected such that the shape of the mass transfer zone is constant relative to amount of adsorbate adsorbed, (b) fluid flow through the column is assumed to be similar to piston flow. Thus, by the evaluation of the material balance of the differential element in the fixed bed, coupled with Freundlich equilibrium isotherm for solid-liquid system a set of equations were derived, which by rearrangement and simplification can be represented in a linearized form as

$$\mathrm{Ln}[(\frac{C_0}{C_t})^{n-1} - 1] = -rt + \mathrm{Ln}\ A$$

Where r (min^{-1}) and A are Clark model parameters while n represents Freundlich constant or the inverse of the slope of Freundlich isotherm to be determined on the basis of batch experiment from its equation namely

$q_e = K_F C_e{}^{1/n}$

Thus, the graph of $\mathrm{Ln}[(\frac{C_0}{C_t})^{n-1} - 1]$ versus time (t) allows parameter r and A to be evaluated from the slope and intercept respectively. However, A can also be evaluated from the equation :

$$A = \left(\frac{c_{in}^{n-1}}{c_b^{n-1}} - 1\right) e^{r t_b}$$

Where c_{in} corresponds to constant influent value on adsorbent bed, c_b corresponds to breakthrough concentration and t_b service time.

3.5. *Wolborska model*

This model portrays the adsorption dynamics based on film diffusional equation, which governs the concentration profile at the lower range of the break through curve [46-47]. Its functional form is written as

$$\mathrm{Ln}\left(\frac{c_t}{c_0}\right) = \frac{\beta_\alpha c_0}{N_0} t - \frac{\beta_\alpha z}{\nu_0}$$

where β_α represents the kinetic coefficient of the external mass transfer (min^{-1}) while ν_0 stands for linear velocity ($cm\ min^{-1}$) and N_0 is equivalent to saturation concentration or adsorption capacity ($mg\ L^{-1}$). The parameters of Wolborska`s model viz; β_α and N_0, can be evaluated from the linear dependence of $\mathrm{Ln}\left(\frac{c_t}{c_0}\right)$ versus time. However, if the value of the ratio β_α/N_0 is equivalent to k_{BA} then the Wolborska solution will be similar to Bohart-Adams solution [50].

3.6. Dose-Response model (DRM)

Yan et al. [51] introduced the DRM model to provide a better presentation of continuous fixed bed adsorption operation than is obtainable from earlier models, particularly in the aspect of minimizing the error observed at the lower and upper regions of the rupture curve of the Clark model. The DRM equation is a function of both volume and time and is given as

$$\frac{c_t}{c_0} = 1 - \frac{1}{1 + (c_0 V_{ef}/q_0 m)^{\alpha}}$$

where c_t/c_0 correspond to the response while V_{ef} correspond to the dose and α is known as the DRM model parameter. This equation can be rewritten in a linear form for ease of application as

$$\frac{c_0}{c_0 - c_t} - 1 = \left(\frac{c_0 V_{ef}}{q_0 m}\right)^{\alpha}$$

$$\Rightarrow \mathrm{Log}\left(\frac{c_t}{c_0 - c_t}\right) = \alpha \mathrm{Log}(c_0 V_{ef}) - \alpha \mathrm{Log}(q_0 m)$$

Thus, a graph of $\mathrm{Log}({}^{c_t}/_{c_0} - c_t)$ versus $\mathrm{Log}(c_0 V_{ef})$ can be developed to evaluate the unknown values.

3.7. The modified BDST model

The BDST model leverages on the linear dependence of the normalized concentration versus the service time of the fixed bed to evaluate a specified bed depth (z) where constant slope is a given. From equation (xiv), it can be deduced that the parameters governing the behavior of the BDST slope consists: - initial adsorbate concentration, bed capacity and influent linear velocity during operation [39]. However, Lee *et al.* [52] portrayed the possibility of inconsistencies in the slope values despite constant values of linear flow velocity within the column, initial adsorbate concentration and cross-sectional area. This occurrence was inferred as the manifestation of corresponding increment in bed adsorption capacity with service time. Thus, the modified BDST model was proposed to evaluate the correlation between these constant parameters and the observed inconsistencies on the values of the slope. The authors decided that such correlation is dependent upon the square root of the bed service time in correspondence with the diffusion controlling step of the process [31] and the bed capacity at different service time expressed as;

$$N_t = N_0[1 - \exp(-\alpha\sqrt{t})]$$

where N_t correspond to the variation in bed capacity at different bed service time. Thus, Bohart-Adams' model can be rewritten to expressly portray the connection between the bed capacity and the operational service time as,

$$t = \frac{N_0 z}{v_0 C_0} - \frac{1}{k_{BA} C_0} Ln(\frac{C_0}{C_t} - 1)$$

The modified BDST model equation can be derived by logical manipulation of the equation of the bed capacity at different service time and the rearranged BDST equation as;

$$t = \frac{[N_0[1 - \exp(-\alpha\sqrt{t})]}{c_0 v_0} z - \frac{1}{k_{BA} c_0} Ln(\frac{c_0}{c_t} - 1)$$

This is a non-linear function but can be rearranged into;

$$t = m'(1 - \exp(-\alpha\sqrt{t}))\, z + b$$

where $m' = \frac{N_0}{c_0 v_0}$, $\alpha = \frac{N_t}{c_0 v_0}$ and $b = -\frac{1}{k_{BA} c_0} Ln(\frac{c_0}{c_t} - 1)$.

Thus, m' corresponds to the slope parameter of the BDST graph when bed capacity has attained equilibrium capacity threshold value and □ can be found from the gradient arising from the transformation of the modified BDST equation to the form;

$$t = m'z + b$$

Furthermore, the modified BDST model can also be represented in the form;

$$z = \frac{t - b}{m'(1 - \exp(-\alpha\sqrt{t}))}$$

Hence, the modified slope parameter (m') and the modified intercept b can be deduced given the graph of bed depth (z) against service time (t) using a trial-and-error minimization method of the sum of squared estimate of errors (SSE) :

$$SSE = \sum (t_{cal} - t_{exp})^2$$

Although dynamic adsorption studies involving cellulose nanocomposites are relatively scarce, their breakthrough curve fitting suitability based on Yoon-Nelson, Thomas and Bohart-Adams models for the prediction of column performance had been reported severally in the literature [2, 16, 24, 28, 40,44, 53- 58, 39, 59- 62].

The primary aim of any fixed bed kinetic experimentation is to obtain data wherefrom the profile of the breakthrough curve can be established. It is represented by a graphical representation of the normalized adsorbate concentration versus the time or effluent volume of the fixed bed column which is vital in the generation of information for the design of its industrial-scale counterpart [62]. Information such as appropriate throughput or solid phase loading requirement on the basis of column size (L/D), bed height, operation lifespan, recycling index, and regeneration time is generated. In this case parametric studies can be conducted on initial adsorbent concentration, column bed height, flowrate of influent fluid, particle size of adsorbent, pH of adsorbate and system temperature in correlation with the breakthrough curves; which is normally denoted by a characteristic s-curve with fluctuating degree of inclinations [40, 55]. Nonetheless, reliable results can be obtained when only the first three variables outlined here are applied.

4. Breakthrough curve analysis

The primary purpose of the fixed bed column operation in adsorption is to minimize the concentration of the adsorbate in the its effluent stream in tandem with the predetermined lower boundary of the breakthrough value known as the breakthrough point. This is often fixed at the maximum permissible adsorbate concentration based on acceptable standard for disposable limit or as dictated by effluent stream processing requirement. The rate of change of the influent concentration depends on the composition of the feed stream, the nature of the adsorbent, pH of the influent stream and the operating conditions of the system, whereas its mechanism is a function of the convection of intraparticle diffusion resistance, film diffusion resistance and axial dispersion, as driven by the departure from equilibrium. Normally, dynamic equilibrium is encountered in column studies unlike its batch counterpart, due to the continuous passage of influent and effluent streams while the unsteady-state condition prevails. Adsorption occurs from the inlet to the outlet of the column until the offset of saturation. Regeneration for reuse can occur after adsorbent exhaustion. A typical diagram of the adsorption profile of a fixed bed column operation is illustrated in Figure 1. Here, the adsorption zone or saturation zone refers of the used portion of the adsorbent (SZ); the mass transfer zone (MTZ) is where most the change in adsorbate concentration occur. It is equivalent to the difference between saturation and breakthrough times.

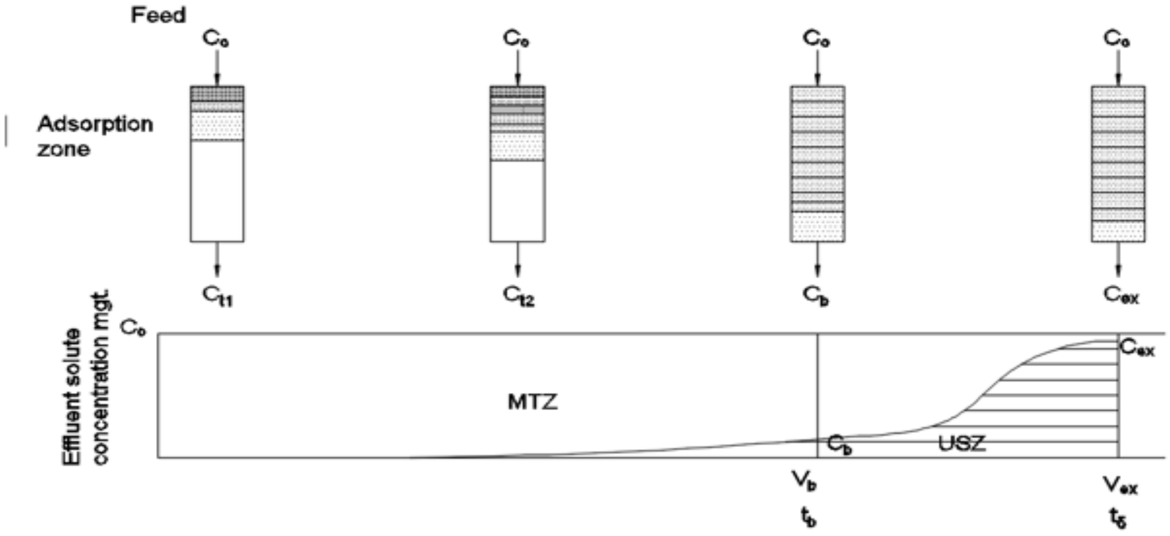

Figure 1: Adsorption profile of fixed bed column operation.

However, excluding the temperature parameter, it is problematic to measure the fluid progress within the MTZ online. Consequently, measurement of adsorbate concentration is performed as the treated fluid exit the fixed bed column. The unsaturated zone comprises the unused portion of the adsorbent (USZ). Also, C_b and V_b correspond to the breakthrough point concentration and volume respectively, which is frequently set at $C_t \approx 0.05\%$ of C_0 or $C_t/C_0 = 0.05$ [1]. This figure represents the maximum adsorbate concentration on adsorbent that can be discarded. Thus, the effluent stream concentration remains near zero until the mass-transfer zone approaches the column exit at time t_b when its outlet concentration (C_b) begins to increase rapidly.

After the break-point time is attained, the effluent concentration peaks sharply up to point C_{ex}, which is the end of the breakthrough curve where the bed is considered unproductive. C_{ex} and V_{ex} refer to the exhaust point concentration and volume which can be located at the ratio $C_t/C_0 = 0.95$. Scanty adsorption occurs after the breakthrough point since the system is tending towards equilibration; where the normalized concentration ratio is unity [39-40, 63]. Thus, adsorbate concentration on the adsorbent and adsorbate concentration in feed are related by the thermodynamic equilibrium. The representation of the normalized adsorbate concentration in the effluent stream (c_t/c_0) versus time (t) or effluent volume (V_{ef}) profile for a specific depth is known as the breakthrough curve. The economics and practical feasibility of sorption column performance can be verified through the dynamic response of its operation with respect to initial pollutant concentration, specific bed height and flow rate based on the analysis of breakthrough time (t_b), exhaustion time (t_δ) and the characteristic curvilinear shape of the breakthrough curve. Exhaustion time (t_δ) refers to the time necessary for the adsorption front to traverse from the breakthrough point to saturation point, which is equivalent to a constant depth (δ) quite distinct from the actual height of the fixed bed (z). However, the total flow time required by the adsorption front to establish itself and traverse the entire length adsorbent filled region fixed bed can be designated as (t_{total}). It had been recommended that the adsorbent can be replaced when $c_t/c_0 = 0.5$, which is 50% of the breakthrough time $(t_{0.5})$, though adsorption can still proceed to complete exhaustion [28, 62, 64]. The extent to which the adsorbent capacity can be utilized is determined by the degree of steepness of the breakthrough curve which is a function of the length of the adsorption bed in harmony with the Langmuir or Freundlich isotherm models. Given the volumetric flow rate Q (m L/min), the volume of effluent (V_{ef}, mL) can be deduced as;

$$V_{ef} = Qt_{total}$$

While $t_\delta = \frac{V_{ef} - V_b}{Q}$ and $t_{total} = t_f + t_\delta$

where t_f is the time for the adsorption wavefront to develop to break point.

On the basis of the corollary that the depth and time ratios are equivalent when the adsorption front moves at constant rate, it can be inferred that;

$$\frac{\delta}{z} = \frac{t_\delta}{t_{total} - t_f}$$

Thus, at breakthrough point, the fractional capacity f of unused adsorbent material in the adsorption front can be evaluated as;

$$f = 1 - \frac{t_f}{t_\delta}$$

The value of the total mass of solid pollutant recovered (q_{total}, mg) for a given influent stream concentration and a specific flow rate is equivalent to the area under the breakthrough curve which can be obtained from equation :

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} c_{ad} dt$$

where c_{ad} corresponds to the concentration of metal adsorbed (mg L^{-1}).

The saturation capacity of the column which is equivalent to equilibrium adsorption capacity is given by;

$$q_e = \frac{q_{total}}{m}$$

where (m, g) represents the mass of the dry adsorbent in the column.

The total mass of metallic pollutant (m_{total}, mg) received by the column can be evaluated as;

$$m_{total} = \frac{c_0 Q t_{total}}{1000}$$

Equilibrium concentration can be computed from the equation

$$c_e = \frac{m_{total} - q_{total}}{V_{ef}} \times 1000$$

while the percentage recovery of the pollutant (%R) is given by

$$\%R = \frac{q_{total}}{m_{total}} \times 100$$

Conclusion and perspectives

A water-secure world is a critical and necessary step towards a sustainable future.

Adequately treated wastewater is cardinal to the possibility of treated water reuse, conservation of water resource, protection of humans from several debilitating or fatal water related health disorders, protection of the marine life and water quality of surface water bodies for recreation, transportation, agriculture, domestic and various other uses beneficial to man. While there has been an array of other adsorbent candidates, cellulose nanomaterials (CN) serve as an eco-friendly, bio renewable, biodegradable and economical solution which can satisfy this demand with great potential for industrial application.

The fixed bed column breakthrough pilot experiment is crucial to the design and scale-up of an industrial adsorption system with the aid of complimentary batch-wise experimental data for any newly developed adsorbent candidates. More so, the design of an effective and reliable adsorption system is dependent upon the ability to predict the adsorption kinetics for the system with significant level of accuracy. Caution should be applied when transforming non-linear kinetic equations to linear expressions due to the corresponding change that may accompany the error distribution of the regressive model which may sometimes offer less clarity between the predicted and empirical values. The validity of the predictions of the kinetic models for dynamic adsorption become doubtful when there is a deviation from the characteristic s-shape pattern of the breakthrough curve.

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