**2.9 Some Kinetic models for column adsorption systems**

Kinetic models for column adsorption systems are mathematical expressions used to describe the rate at which adsorption takes place in a packed bed or column. These models are essential for understanding and optimizing the performance of adsorption processes, particularly in continuous flow systems, such as fixed-bed adsorbers. Kinetic models help to predict the breakthrough time, adsorbent bed saturation, and overall efficiency of the adsorption process over time.

**2.9.1 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 (Patel 2019, Yunnen et al, 2017).

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:

Ln = kTHq0 m -

kTHC0 t

Q

where kTH corresponds to Thomas model constant (L min-1mg-1), q0 is equivalent to the maximum solid-phase concentration of the solute or maximum adsorption capacity (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, kTH and q0 can be obtained from the graph of Ln [() – 1] versus t (νeff/Q), where νeff is the effluent volume (mL) (Ostovar et al, 2017, Zheng et al, 2018).

**2.9.2 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 (Bhaumik et al, 2013, - Kopsidas, 2016). 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 (Patel, 2019, Kopsidas, 2016, Dutta and Basu, 2014). Its linearized form can be represented by

Ln= kYN t - kYN Ʈ,

where kYN stands for the Yoon-Nelson rate constant (min-1), t represents the processing time (min) and Ʈ 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 (Franca and Oliveira, 2010). If the experimental data describes the model accurately, then kYN and Ʈ can be evaluated from the gradient and the intercept of the graph of Ln () versus t at different bed masses or heights, flow rates and initial concentrations.

**2.9.3 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. (Dardouri et al., 2017) 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

Ln [ (n-1 – 1] = - rt + LnA

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;

qe = KFCe1/n

Thus, the graph of Ln [(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:



Where Cin corresponds to constant influent value on adsorbent bed, Cb corresponds to breakthrough concentration and tb service time.

**2.9.4 Weibull Function Model**

The Weibull cumulative distribution function, formulated for adsorption, may be written (Weibull, 1951).

= 1 – exp [ -]

Where c is the effluent concentration at any time t, c0 is the feed concentration, a > 0 is a rate parameter, and b > 0 is a shape parameter. The Weibull function generates S-shaped curves for b > 1. Its two unknown parameters, a and b, can be easily determined using a spreadsheet program with a built-in optimization routine. Because the two parameters lack physical significance, their values are usually extracted from breakthrough data. It is not possible to determine the two parameters from independent sources (e.g., engineering correlations). The Weibull function can be transformed into linear form and linear regression can then be used to estimate its parameters. One version of the linearizing transformation is given by

In [-In(1 - )] = bIn(t) – b In(α)

If this equation is obeyed, plots of its left-hand member against ln(t) should give a straight line. However, fitting the linearized Weibull function to breakthrough data by linear regression to estimate its parameters is a procedure fraught with statistical problems.

**2.9.5 Yan model**

A high accuracy statistical base model of Yan to an experimental data with some simplifications was represented by:

Where:

is the maximum uptake capacity (mg/g),

a is an empirical parameter that decides the slope of the regression function and M is the dry weight of the sorbent (g).

The values of qo and a can be estimated by the non-linear fitting of Equation to the experimental data of the breakthrough curves. This model is well known in many literatures as the Dose-Response model (DR). (Yan, et al., 2009).

**2.9.6 Bed Depth Service Time (BDST) model**

This model, often called Bohart-Adams model was proposed by the pair in 1920 (Barros et al, 2013) to represent the intrinsic relationship between normalized adsorbate concentration and time with reference to the adsorption of chlorine by charcoal (Chowdhury et al, 2015). It has now been extensively applied to several continuous flow liquid/solid pollutant sorption systems (Oliveira et al, 2010, Barros et al, 2013). 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 (Franca & Oliveira, 2010). Essentially, the BDST model describes the linear relationship between the bed depth (z) and column service time (t) in accordance with the following equation;

Ln = kBA C0t - kBAzN0

V0

which can also be arranged as

Ln = kBAN0 z - kBA t

V0 vv

where C0 is equivalent to inlet or influent concentration at time t = 0 (mgL-1), Ct effluent concentration at time t = t (mgL-1), kBA corresponds to the kinetic rate constant for the Bohart-Adams’ model (Lmg-1min-1), z is length of the column bed (cm) while N0 represent the adsorbent saturation concentration (mgL-1) and v0 is the linear velocity influent liquid (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 (Patel, 2019). By the evaluation of linear dependence of different bed heights (z) versus breakthrough times (t) at constant flowrate and initial adsorbate concentration, N0 and kBDST can be deduced from the gradient and intercept respectively. However, if the Ln ( – 1) is plotted against t, ***k***BA can be deduced from its gradient.

**2.9.7 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 (Kopsidas, 2016, Dutta and Basu, 2014). Its functional form is written as:

Ln = βα  - βα

t

N0

V0

where βα represents the kinetic coefficient of the external mass transfer (min-1) while ν0 stands for linear velocity (cm min-1) and N0 is equivalent to saturation concentration or adsorption capacity (mgL-1). The parameters of Wolborska`s model viz; βα and N0, can be evaluated from the linear dependence of Ln () versus time. However, if the value of the ratio βα /N0 is equivalent to then the Wolborska solution will be similar to Bohart-Adams solution (Madan et al, 2019).

Breakthrough curves after fitting Wolborska model are displayed in the images below.