DESIGN OF FIXED BED COLUMN FOR THE REMOVAL OF METAL CONTAMINANTS FROM INDUSTRIAL WASTEWATER

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Abstract: *A mathematical model for fixed bed adsorption column was developed and solved numerically by implicit backward Euler finite difference method. The model was simulated using MATLAB R2012a. The paper was able to consider the design and the operation of fixed bed adsorption column for the removal of water contaminants from industrial wastewater in a concise manner, having been able to obtain the breakthrough curve. The parametric study carried out on the model revealed that smaller bed porosity reduces the solute residence time in the bed and consequently increases the adsorption rate and that decrease in particle diameter decreases the breakthrough time. However, increase in flow rate increases the adsorbate concentration ratio more rapidly. The observations recorded in this study agree excellently with the general observations in other literatures of similar works. Hence, the developed model is suitable and applicable to study the fixed bed adsorption column performance under isothermal conditions.*

INTRODUCTION

Heavy metals are dangerous for living organisms because of their stability, toxicity and tendency of accumulating in the environment. The industrial wastewaters are considered to be the main source of heavy metal impurities [1]. Hence, purification of these wastewaters prior to their discharge into a recipient (i.e. water bodies like stream, river, ocean), becomes necessary.

Metals can be distinguished from other toxic pollutants since they are non-biodegradable, and they show an extreme tendency of accumulating in living organism, causing many diseases [2]. Apart from environmental issues, technological aspects of metal recovery from industrial wastewaters must also be considered. Metals are non-renewable, and natural reserves are becoming depleted; so, the removal of these heavy metals avails us the opportunity of recycling them for further industrial processes where

necessary. High concentration of heavy metals in the industrial wastewater can be removed by employing different techniques ranging from precipitation, chemical oxidation and reduction [3]. However, these conventional methods often cannot achieve the quality of effluent according to the maximum allowable values, so it is necessary to apply tertiary treatment methods such as ion exchange resin, adsorption and membrane filtration (ultra-filtration, reverse osmosis, nano-filtration and electrolysis) [4, 5].

Fixed bed adsorption is widely used for purifying liquid mixture, especially industrial waste effluents. In a little over two decades, activated carbon was extensively used for waste and water treatment. In recent year it has been applied increasingly to large-scale separation [6]. Mathematical models can be developed and simulated to predict breakthrough curves of adsorption system, which are widely employed in riding

industrial wastewater of organic pollutant [7]. To design a fixed bed adsorption process, detailed analysis of the fixed-bed dynamics and rate data are required. Raghavan *et al.,* [8] considered an isothermal adsorption column packed with porous spherical particles, which was subject at time zero, to a small change in the concentration of an absorbable species in the carrier. Several assumptions were made to simplify the model which was then solved by orthogonal collocation. They considered linear isotherm to describe the liquid-solid equilibrium relationship. Suresh *et al* [9] had also considered the effect of various operating variables on the process of fixed bed adsorption. They studied the kinetic using a mathematical model that takes into account of both the external and internal mass transfer resistance, non-ideal plug-flow along the column and variation of fluid velocity along the column.

Industrial wastewater is one of the pollution sources in the pollution of the water environment. During the last century, a huge amount of industrial wastewater was discharged into rivers, lakes, and coastal areas [5]. This results into serious pollution problems in these water bodies and impacts the eco-system and human life negatively.

On a global scale, environmental pollution by food or related industries via effluent discharge has become a threat to plants and animals, and may ultimately threaten the quality of Human life [10]. In 1956, cases of minimata disease were reported in Japan, which affects the brain and which will instantly lead to death, as a result of pollution of water by industrial effluents containing methyl mercury [10]. Also, the increasing rates of industrial wastewater are thought to be higher in the

developing countries of which Nigeria is a part, than those in developed countries [11]. This fact predicts that industrial wastewater pollution as a major pollution problem has moved from developed countries to developing countries. Therefore, the demand for water of high quality calls for further investigation into alternative methods of treatment, which is dynamic in approach and complete in practice such that the various waste products of our modern technology can be adequately treated for safe discharge into the environment. Physico-chemical method of treatment such as the fixed bed column technique does this efficiently and effectively.

This paper shows the strategic steps in the design and the operation of fixed bed column used for the removal of metal contaminants from industrial wastewater which when untreated is detrimental to the eco-systems and human life. The paper also shows the effects of various important and influencing parameters such as flow rate, particle radius and bed porosity on the breakthrough curve, hence, the proposed model is suitable and applicable to study the performance of a fixed bed adsorption column under isothermal condition. In this paper, we will focus on activated carbon as our choice of adsorbent. Activated carbon can be manufactured from carbonaceous material including coal (Bituminous and Lignite), Peat, Wood, or Nutshells (i.e. coconut).The manufacturing process consists of two phases; carbonization and activation [12].

MATHEMATICAL MODEL DEVELOPMENT

In this paper, a mathematical model for the fixed bed column is developed by incorporation of important parameters such as the linear velocity variation along the

bed which significantly affects the design of the adsorption column. The proposed model can be extensively used to understand the dynamics of the fixed bed adsorption column for the adsorption of organic and inorganic (metal ions) compounds.

Currently, a variety of mathematical models have been used to describe and predict the breakthrough curves of a column adsorption system in liquid or gaseous phase. To model a liquid-solid column adsorption, it is necessary to divide it into four (4) basic steps [13]:

1. Liquid phase mass transfer including convective mass transfer and molecular diffusion,

2. Interface diffusion between liquid phase and the exterior surface of the adsorbent (i.e. film diffusion),

3. Intra-pellet mass transfer involving pore diffusion and surface diffusion and

4. The adsorption-desorption reaction

Let us consider the Fig. 1 to develop a mathematical model to describe the dynamism of a fixed bed adsorption column.
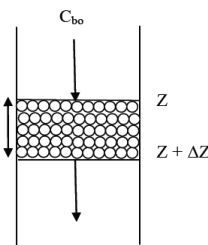

Fig. 1: Mass Balance in the Elements of a Fixed Bed

From the principle of conservation of mass to fluid and pore phases in the column; we have:

Rate of material in – Rate of material out
± Rate of material generation by adsorption =
Rate of material accumulation

However, the development of the mathematical model for the system above is based on the following assumptions:

1. The system operates under isothermal condition

2. The Adsorption equilibrium relationship is non-linear described by Langmuir Isotherm

3. Intra particle mass transfer is due to Fickian diffusion and it is characterized by the pore diffusion coefficient D_P

4. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external film mass coefficient; R

5. The adsorption particles are spherical and homogenous in size and density

6. The Flow pattern in the bed can be described by an axial dispersion plug flow model

7. The axial velocity does not change from place to place

8. A pseudo one-component adsorption is assumed.

Material Balance for Adsorption Column

Subject to the assumptions above, the following parameters can be deduced from the system:

a. Convective Mass transfer across the boundary layer is given by: $-U\frac{\partial C_b}{\partial z}$

Where; U = Superficial Velocity, ms^{-1}

C_b = Adsorbate concentration in the mobile phase, mgL^{-1}

Z = Axial coordinate, m

b. Axial dispersion is given by: $D_L\frac{\partial^2 C_b}{\partial z^2}$

Where; D_L = Axial dispersion coefficient, m^2s^{-1}

c. Materials absorbed by the adsorbent is given by: $(1-\varepsilon)\rho_a\frac{\partial q_t}{\partial t}$

Where; ε = Bed porosity

ρ_a = Density of adsorbent or particle, kgm^{-3}

q_t = Average solid phase adsorbate concentration, mgg^{-1}

t = Time, sec

d. Accumulation of the adsorbate is given by: $\varepsilon\frac{\partial C_b}{\partial t}$

From the four different groups of parameters obtained as shown above, an overall material balance for the column can be formulated through the application of the principle of conservation mass as stated earlier. This therefore gives rise to the equation 1:

$$\varepsilon\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} + (1-\varepsilon)\rho_a\frac{\partial q}{\partial t} = D_z\frac{\partial^2 C}{\partial z^2}, \qquad (1)$$

Where initial and boundary conditions are:

$$t = 0 \rightarrow C(z,t) = 0,$$
$$t = 0 \rightarrow q(z,t) = 0,$$
$$Z = 0 \rightarrow C_b(0,t=0), C_b(0,t>0) = C_{b0}$$

$$z = H \rightarrow \frac{\partial C}{\partial z} = 0.$$

When the axial dispersion is ignored, equation 1 becomes:

$$\varepsilon\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} + (1-\varepsilon)\rho_a\frac{\partial q}{\partial t} = 0.$$

The initial and boundary conditions turn to:

$$t = 0 \rightarrow C(z,t) = 0,$$
$$Z = 0 \rightarrow C_b = C_{b0} + \frac{D_{zz}\partial C_b}{U\partial Z}$$
$$z = H \rightarrow \frac{\partial C}{\partial z} = 0.$$

Where ε is the bed porosity, t is the time, ρ_a or ρ_p the particle or adsorbent density, C_{b0}, H is the bed height.

Having known that, the material balance for fluid phase in the column is given by [6]:

$$-D_L\frac{\partial^2 C_b}{\partial z^2} + U\frac{\partial C_b}{\partial z} + \frac{\partial C_b}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\ell_p\frac{\partial q_t}{\partial t} = 0 \qquad (2)$$

We can introduce some dimensionless variables for conveniences as shown below;

$$\overline{C_b} = \frac{C_b}{C_{b_0}}, \qquad X = \frac{z}{L}, \qquad \tau = \frac{U_o t}{L}, \qquad \overline{q_p} = q_p, \qquad \overline{u} = \frac{u}{u_0}$$

Substitute the dimensionless variables into the equation (2), we have:

$$-\frac{1}{P_e}\frac{\partial^2 \overline{C_b}}{\partial x^2} + \frac{\partial \overline{C_b}}{\partial x} + \frac{\partial \overline{C_b}}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\ell_p}{C_{b_0}}\frac{\partial \overline{q_p}}{\partial y} = 0 \qquad (3)$$

where P_e = Peclet number $\left(\frac{ul}{D_L}\right)$

The interphase mass transfer rate may be expressed in terms of the concentration driving force across the bounding film to give:

$$\ell_s \frac{\partial q_s}{\partial t} = \frac{3k_f}{a_p}(c_b - c_s) \quad [1] \tag{4}$$

Where $\ell_p(1-\varepsilon_p)\ell_s$ (5)

Substituting equation (4) into (5) gives:

$$\frac{\partial q}{\partial t} = \frac{3k_f(1-\varepsilon_P)}{\ell_p a_p} \tag{6}$$

Introducing the appropriate dimensionless variables stated above, we have:

$$\frac{\partial \bar{q}}{\partial t} = \frac{3k_f L(1-\varepsilon_p)}{U_0 a_p \ell_p} c_{b_s} \left(\bar{c_b} - \frac{c_s}{c_{b_s}} \right) \tag{7}$$

The adsorption equilibrium is described by Langmuir Isotherm [9]:

$$q_s = \frac{q_m bc}{1+bc} \tag{8}$$

Where $c = c_s$ (fluid phase concentration in equilibrium with q_s on the surface of the pellet)

After re-arrangement and substitution of c_s for c, equation 8 becomes:

$$c_s = \frac{q_s}{(q_m b - q_s b)} \tag{9}$$

Put equation 9 into equation 3, we have:

$$-\frac{1}{p_e}\frac{\partial^2 \bar{c_b}}{\partial x^2} + \frac{\partial \bar{c_b}}{\partial x} + \frac{\partial \bar{c_b}}{\partial z} + \frac{3k_f L(1-\varepsilon_p)}{\varepsilon U_0 a_p}\left(\bar{c_b} - \frac{q_s}{c_{b_s}(q_{mb} - q_{sb})} \right) = 0 \tag{10}$$

Initial and boundary condition
The initial and boundary condition to be employed for fluid phase model are:

Initial condition:

$$\tau \leq 0; \ X = 0; \ \bar{c_b} = 1 \tag{11}$$

$$\tau \leq 0; \ 0 < X \leq L; \ \bar{c_b} = 0 \tag{12}$$

Boundary condition:

$$1 - \bar{c_b} + \frac{1}{P_e}\frac{\partial \bar{c_b}}{\partial x} = 0; \ X = 0, \tau > 0 \tag{13}$$

$$\frac{\partial \bar{c_b}}{\partial x} = 0; \ X = L, \tau \geq 0 \tag{14}$$

Material Balance for Pore Diffusion Control Phase [10]:

Subject to the aforementioned assumptions and equation 1, the material balance for diffusion into spherical pellet is written as:

$$\frac{D_P}{r^2}\varepsilon_p \frac{\partial(r^2 \partial c)}{\partial r} = \varepsilon_p \frac{\partial c}{\partial t}(1-\varepsilon_p)\rho_p \frac{\partial q}{\partial c} \tag{15}$$

Differentiating the left hand side term, we have:

$$\frac{D_p}{r^2}\varepsilon_p\left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right] = \varepsilon_p\frac{\partial c}{\partial t}+(1-\varepsilon_p)\ell_p\frac{\partial q}{\partial t} \tag{16}$$

Assuming instantaneous equilibrium

$$\frac{\partial q}{\partial t} = \frac{\partial c}{\partial t}x\frac{\partial q}{\partial c} \quad [1] $$

By substitution and rearrangement, we have:

$$D_p\varepsilon_p\left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right] = \frac{\partial c}{\partial t}\left[\varepsilon_p + (1-\varepsilon_p)\ell_p\frac{\partial q}{\partial c}\right] \tag{17}$$

$$\frac{\partial c}{\partial t} = \frac{1}{\left[1+\ell_p\left(\frac{1-\varepsilon_p}{\varepsilon_p}\right)\frac{\partial q}{\partial c}\right]}D_p\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{18}$$

Where $\frac{\partial q}{\partial c}$ is the derivative of adsorption isotherm differentiating Langmuir Isotherm (equation 8).

$$\frac{\partial q}{\partial c} = \frac{q_m b}{(1+bc)^2} \tag{19}$$

Substituting equation 19 into equation 18, we have:

$$\frac{\partial c}{\partial t} = \frac{1}{\left(1+\ell_p\left(\frac{1-\ell_p}{\varepsilon_p}\right)\frac{q_m b}{(1+bc)^2}\right)}D_p\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{20}$$

Equation 19 represents the pure diffusion control model.

For this kind numerical problem, initial and boundary condition were defined as follows:

Initial condition:

$$C = 0; \ 0 < r < a_p, \quad t = 0$$

Boundary condition:

$$\frac{\partial c}{\partial r} = 0; r = 0, t > 0$$

$$K_f(C_b - C_p) = D_p, r = a_p, t > 0$$

Equation 20 represents the mathematical model developed for the study of fixed bed performance under isothermal condition.

RESULTS AND DISCUSSION

Since nonlinear adsorption isotherm is considered, the preceding sets of partial differential equations (1) to (20) were solved numerically by a reduction to set of ordinary differential equation using the Implicit Backward Euler Finite Difference method. The finite difference was employed due to its stability and nature of boundary conditions. However, a mathematical algorithm to solve coupled equations was developed and implemented into a computer program using MATLAB software. The parameters for the simulation of the model were obtained from Crittenden and Weber [14]. This present model is studied by varying different important parameters such as particle diameter, bed porosity, Initial concentration and fluid flow rate.
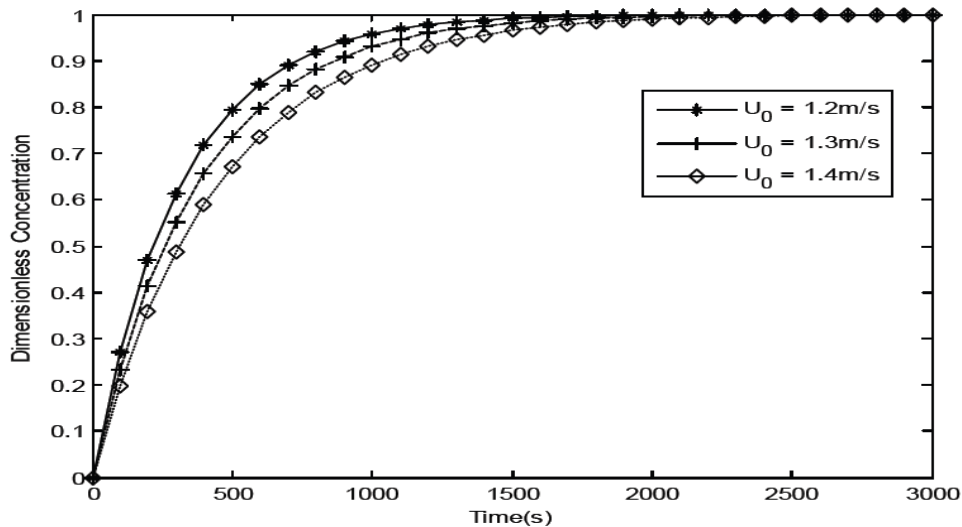

Fig. 1: Effect of Fluid Flow Rate on Simulated Breakthrough Curve

Fig. 1 shows the result for three different feed flow rates plotted while other parameters are kept constant. As flow rate increases, the breakthrough curve becomes steeper, such that at high flow rate the adsorbate solution leaves the column before equilibrium occurs. Furthermore, a fixed saturation capacity of bed based on the same driving force gives rise to a shorter time for saturation at higher flow rate. The Flow rate of wastewater stream flowing through the column plays a major role in designing an adsorption column because as the flow rate increases, the total percentage removal of the contaminants in fixed-bed operations are found to reduce. Also, the total time corresponding to the stichiometric capacity of the column is also found to be decreasing with an increase in the flow rate.
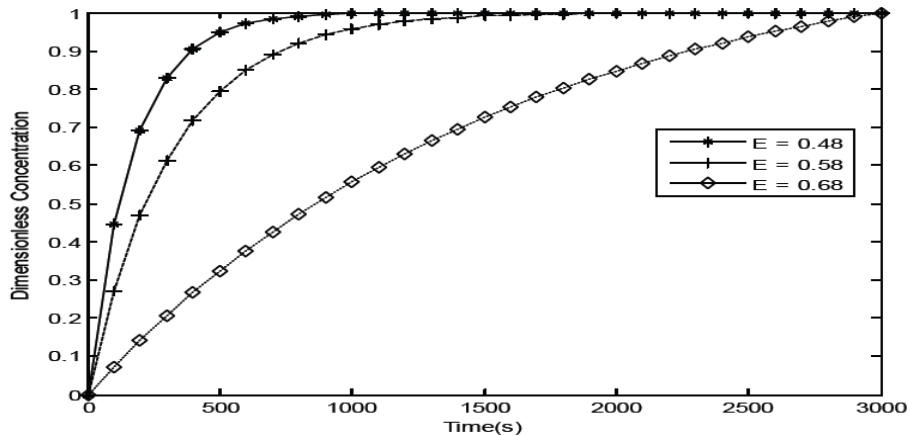
Fig. 2: Effect of Bed Porosity on Simulated Breakthrough Curve

Fig. 2 shows that as the bed porosity increases, the steepness of the breakthrough curve decreases. It signifies that the increment of bed porosity leads to a lower performance in solute removal. Meanwhile, smaller bed porosity reduces the solute residence time in the bed and consequently increases the adsorption rate.
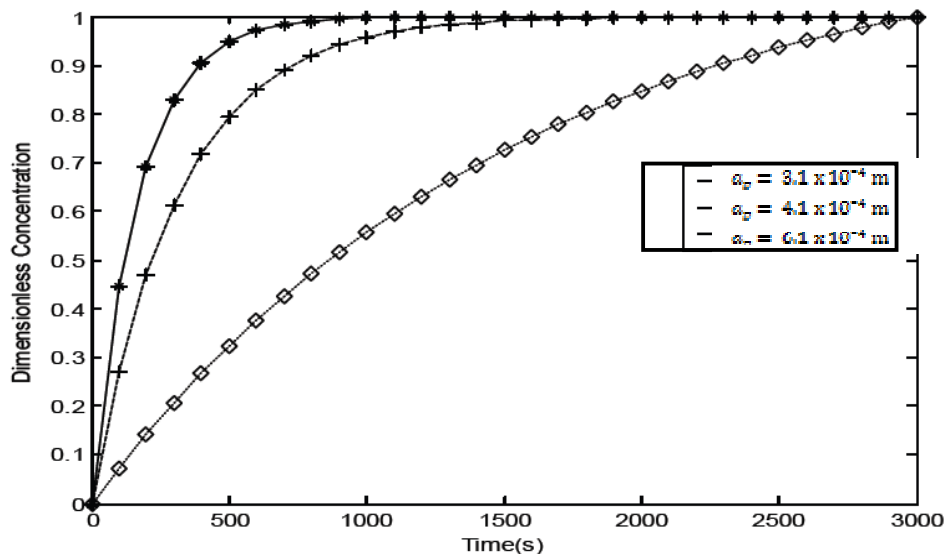

Fig. 3: Effect of Particle Diameter on Simulated Breakthrough Curve

Fig. 3 reveals that as the particle radius increases the steepness of the breakthrough curve decreases. This means that smaller particle size resins provide quicker kinetic equilibrium and therefore better breakthrough capacity is obtained at higher linear velocities. As the diameter of the particle increases, the thickness of stagnant film around the particles increases, and also the total length of the path inside the pores increases. Under these conditions, the overall kinetics of the

process is slow, because the time for a molecule of adsorbate to reach the adsorption site is more, as the diffusional path along the pores is large. As the particle radius is 3.1×10^{-4} m, the break point time is 1325 sec along the bed. The percentage change in break point time is

17%. For the particle radii 4.1×10^{-4} and 6.1×10^{-4} m, the percentage change in breakpoint time is 22% and 29%, respectively. This shows as the particle radius increases the velocity variation effect on breakthrough curve increases.
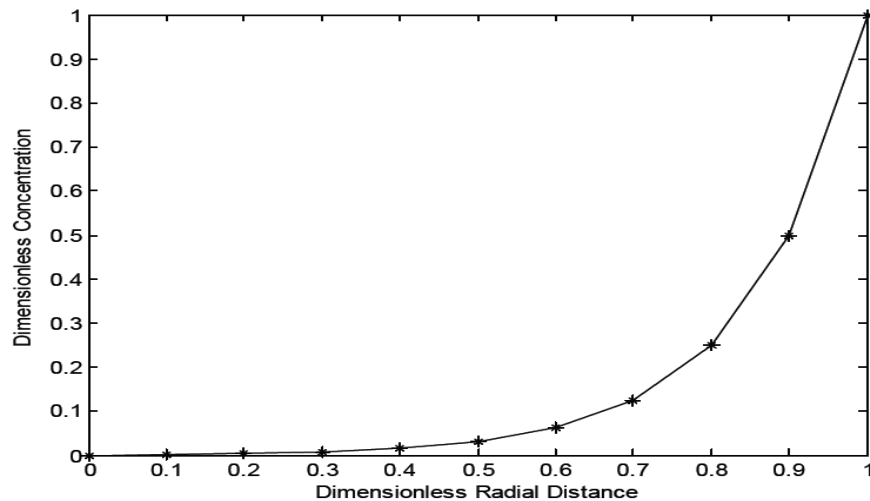

Fig. 4: Concentration Profile of Metal Contaminants

Fig. 4 shows the potency of the model used to describe and determine the outlet adsorbate concentration at different value of radial distances. The graph of dimensionless concentration against dimensionless radial distance was plotted from simulation results obtained which shows an increase in concentration of solute inside the pores as the adsorption progresses.

CONCLUSIONS

This paper showed that the use of dimensionless variables leads to homogeneous and consistent equation settings for various breakthrough curve models. The numerical resolution of the corresponding systems of partial differential equations by MATLAB allowed us to better understand the behaviour of the concentration front before

it reaches a constant shape. These results are useful to interpret breakthrough curves obtained in metal ion contaminants capture through activated carbon based filters.

A mathematical model for a fixed bed adsorption column was developed and solved numerically by implicit backward Euler finite difference method. It was simulated by using MATLAB R2012a. Parametric study carried out on the model reviewed that smaller bed porosity reduces the solute residence time in the bed and consequently increases the adsorption rate and decrease in particle diameter decreases the breakthrough time. However, increase in flow rate increases the adsorbate concentration ratio more rapidly. The observations recorded in this study agree excellently with the general observations in other literatures of similar works.

Hence, the proposed model is suitable and applicable to study the fixed bed adsorption column performance under isothermal conditions. The model developed here could be further tested by applying it to the non-isothermal system as well as non-adiabatic modelling.

This paper has been able to consider the design and the operation of fixed bed adsorption column for the removal of water contaminants from industrial wastewater in a concise manner, having been able to obtain the breakthrough curve. The following are the contribution to knowledge provided by this research work:

- The increase in the steepness of breakthrough curve as the bed porosity decreases, signifies the increase in the removal efficiency of the bed and the vice versa.

- As the flow rate of the influent liquid increases, it leads to the adsorbate leaving the column before the equilibrium, and hence there is higher efficiency in the degree of adsorbate removal.

- Finally, this study has been able to establish the relationship between the dimensionless concentration and the dimensionless radial distance as illustrated by Fig. 4.

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