Mathematical Modelling of Fixed Bed Adsorption Column for Liquid Phase Solute: Effect of Operating Variables

[1]Yusuff A. S., [2]Popoola L. T., [3]Omitola O. O., [4]Adeodu A. O., [5]Daniyan I. A.

[1, 2]Department of Chemical and Petroleum Engineering,

[3]Department of Computer Engineering

[4,5]Department of Mechanical Engineering

Afe Babalola University, Ado Ekiti, Ekiti State Nigeria.

[1]adeyinkayusuff@yahoo.com, [2]popoolalekantaofeek@yahoo.com,
[3]omitolasegun@yahoo.com, [4]femi2001ng@yahoo.com, [5]afolabiilesanmi@yahoo.com

Abstract

A mathematical model for pseudo one component adsorption on a fixed bed is developed. The model takes into account of external and internal mass transfer resistances with non ideal plug flow behaviour. In the present study, the Langmuir equilibrium isotherm is used to represent liquid-solid equilibrium relationship. The model consists of a set of couple partial differential equations, and the differential equations representing the mass balances of both fluid and pore phases are solved by the implicit backward Euler finite difference method and compared with previous models reported in literature. The effects of various important and influencing parameters such as flow rate, particle radius and bed porosity in breakthrough curve are studied in detail. Hence, the proposed model is suitable and applicable to study the fixed bed adsorption column performance under isothermal condition.

Keywords: Adsorption, Modelling, Langmuir isotherm, fixed bed, operating variables, Euler finite difference method, liquid- solid equilibrium.

Word count: 140

INTRODUCTION

Adsorption can be defined as the preferential partitioning of substances from the gaseous or liquid phase onto the surface substrate. In an industrial application, adsorption separation typically, involved a column, packed with a suitable adsorbent, in which a fluid stream containing specifically undesired adsorbates is passed in order to achieve separation. This process is usually fixed

bed operations, but the moving bed process also exists. The fixed bed process essentially consists of two steps. The adsorption and desorption steps. Desorption operation is usually performed either by raising the temperature or by reducing the total pressure. The former characterizes the thermal swing adsorption (TSA) process while the latter is applied in a pressure swing adsorption (PSA) [4, 9]. 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 [10]. For instance, 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 [4]. To design a fixed bed adsorption process, detailed analysis of the fixed-bed dynamics and rate data are required [2].

A lot of studies concerning the mathematical modelling and prediction of adsorption process, adsorption equilibrium and breakthrough curves or mass transfer resistances had been published. Raghavan et al [5] 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 [1] 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.

In this research work, a study to ascertain the extent to which many solutes from a flowing liquid stream are adsorbed using a fixed bed system is considered using a mathematical description. The effects of various operating variable such as particle radius, fluid flow velocity and bed porosity on breakthrough curve are also considered.

MATHEMATICAL MODEL

The mathematical model is developed to describe some important properties of fixed bed adsorber. Included in the model are factors to describe the external film mass transfer rate, nonlinear adsorption

equilibrium and major contribution to isothermal effects.

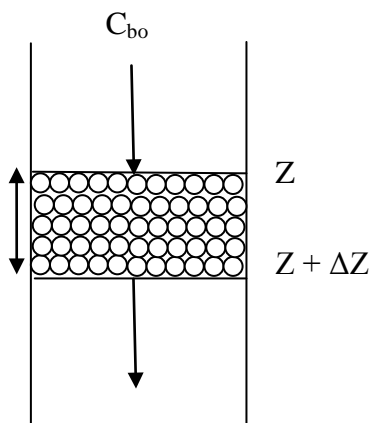Considering an elemental volume of a bed in a fixed bed adsorption column.

Figure 1. Mass balance in element of a fixed bed

Applying 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 accumulation of material + Rate of loss   by   adsorption   (1)

In order to develop a mathematical model for this system, the following assumptions were made:

[1] The system operates under isothermal condition.

[2] The adsorption equilibrium relationship is non linear described by Langmuir isotherm.

[3] Intra particle mass transport 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 transfer coefficient, K_f.

[5] The adsorbent particles are spherical and homogeneous 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 Liquid Phase Solute.

Subject to equation 1 and assumptions stated above, the material balance for fluid phase in the column is given by:

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

Introducing appropriate dimensionless variables:

$$\overline{C_b} = \frac{C_b}{C_{b_0}}, \qquad X = \frac{z}{L}, \qquad \tau = \frac{U_0 t}{L}, \qquad \overline{q_p} = q_p, \qquad \overline{u} = \frac{u}{u_0}$$

and substitute them into equation (1)

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

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

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

$$\ell_s \frac{\partial q_t}{\partial t} = \frac{3k_f}{a_p}\left(c_b - c_s\right) \; [1] \qquad (4)$$

Where $\ell_p \left(1 - \varepsilon_p\right)\ell_s$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad (5)$

Put equation (1) and (2) together, we have

$$\frac{\partial q}{\partial t} = \frac{3k_f\left(1-\varepsilon_p\right)}{\ell_p a_p}\left(c_b - c_s\right) \qquad (6)$$

Introducing those appropriate dimensionless variable stated above, we have

$$\frac{\partial \overline{q}}{\partial t} = \frac{3k_f L\left(1-\varepsilon_p\right)}{U_0 a_p \ell_p}c_{b_o}\left(\overline{c_b} - \frac{c_s}{c_{b_0}}\right) \qquad (7)$$

The adsorption equilibrium is described by Langmuir Isotherm:

$$q_s = \frac{q_m bc}{1+bc} \qquad (8)$$

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:

$$c_s = \frac{q_s}{\left(q_m b - q_s b\right)} \qquad (9)$$

put equation (9) into equation 3, we have

$$-\frac{1}{p_e}\frac{\partial^2 \overline{c_b}}{\partial x^2} + \frac{\partial \overline{c_b}}{\partial x} + \frac{\partial \overline{c_b}}{\partial z} + \frac{3k_f L\left(1-\varepsilon_p\right)}{\varepsilon U_0 a_p}\left(\overline{c_b} - \frac{q_s}{c_{b_0}\left(q_{mb} - q_{sb}\right)}\right) = 0 \qquad (10)$$

Initial and boundary condition

The initial and boundary condition to be employed for fluid phase model are in the following forms:

Initial condition:

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

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

Boundary condition:

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

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

Material balance for pore diffusion control phase:

Subjects to these aforementioned assumptions and equation (1), the material balance for diffusion into a spherical pellet is written as:

$$D_p \varepsilon_p \frac{\partial}{\partial r}\left(\frac{\partial c}{\partial r}\right) = \varepsilon_p \frac{\partial c}{\partial r} + \left(1 - \varepsilon_p\right)\ell_p \frac{\partial q}{\partial t} \quad [6,7,8] \tag{15a}$$

or

$$\frac{D_p}{r^2}\varepsilon_p \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) = \varepsilon_p \frac{\partial c}{\partial t} + \left(1 - \varepsilon_p\right)\ell_p \frac{\partial q}{\partial t} \tag{15b}$$

Differentiating the left hand side term, we have:

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

Assuming instantaneous equilibrium

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

By substitutions and rearrangement, we have:

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

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

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

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

put equation (19)into equation (18), we have:

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

Equation (19) represents the pure diffusion control phase model.

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

Initial condition:

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

Boundary condition:

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

$K_f(C_b - C_s) = D_p \dfrac{\partial c}{\partial r}$, r = a_p, t $>$ 0

SIMULATION TECHNIQUE

Since nonlinear adsorption equilibrium is considered, the preceding sets of partial differential equations were solved numerically by a reduction to set of ordinary differential equation using the implicit Backward Euler finite difference method. This finite difference procedure was employed due to its stability and the nature of boundary condition which is Neumann. A mathematical algorithm to solve these coupled equations was developed and implemented into a computer program using MATLAB software. The same parameters reported by Bautista et al [2003] were used for simulation in this study and are given in the table 3.0 below.

Simulation Parameter

The model parameters for simulation [1] are summarised:

Table 1. Used parameters in simulations of fixed bed adsorption column.

Parameter	Unit	Values
Bed porosity (ε)	-	0.58
Axial dispersion coefficient (D_L)	m^2 / s	5.9 x 10^{-10}
Particle porosity (ε_p)	-	0.53
Particle density (ℓ_p)	kg/m^3	1970
Maximum adsorption capacity (q_m)	mg/g	45.4
Saturated adsorption capacity *	mg/g	35.2
Langmuir Isotherm constant (b)	ml/mg	0.84
Pore diffusivity (D_ρ)	m^2/s	2.4 x 10^{-11}
External mass transfer coefficient (k_f)	m/s	8.2 x 10^{-6}
Bed diameter (d) *	m	0.016
Initial adsorption concentration (C_{b0}) *	mg/l	1.2
Column length (l) *	m	1.00

Note: The values of those parameters with asterisk (*) are assumed.

SIMULATION RESULT AND DISCUSSION

The simulation of the model gives a solution for the dimensionless concentration of adsorbate against time at different operating conditions and concentration of solute in the liquid phase inside the pores against radial distance and obtained results are compared with previous models reported in the literature, which agree reasonably well with them. This present model is studied by varying different important parameters such as particle diameter, bed porosity and fluid flow rate.

Effect of fluid flow rate on simulated breakthrough curve.

The result for three different feed flow rates plotted. During this simulation, other parameters are kept constant; figure [2] shows that as flow rate increases, the breakthrough curve becomes steeper, so 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.
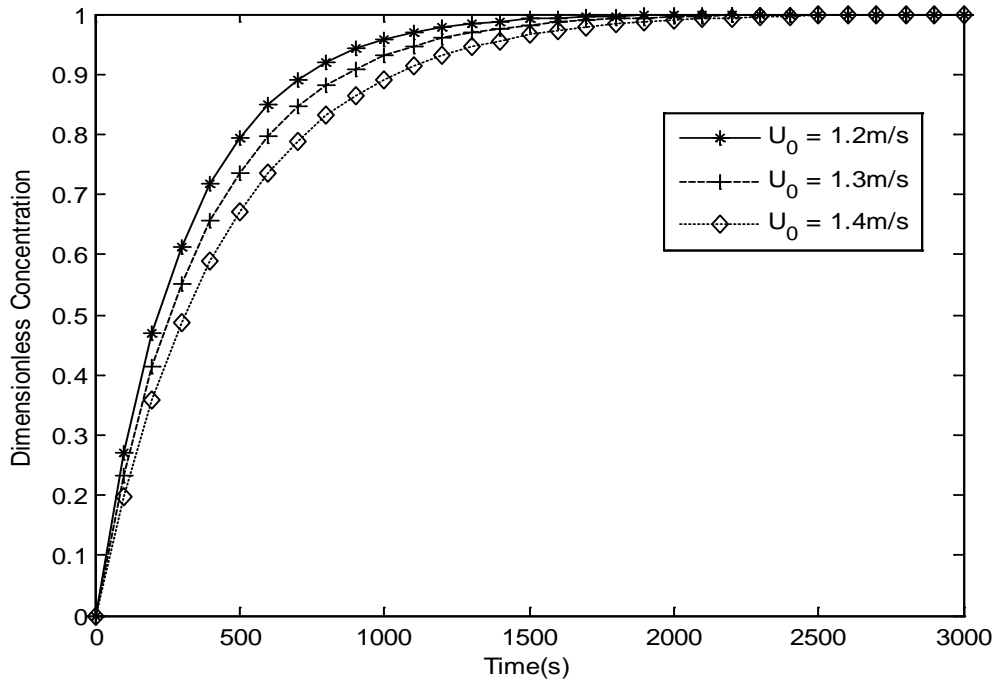
Figure 2. Effect of feed flowrate on simulated breakthrough curve

Effect of bed porosity on simulated breakthrough curve

Based on the figure 3, as the bed porosity increases from 0.48 - 0.68, 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.
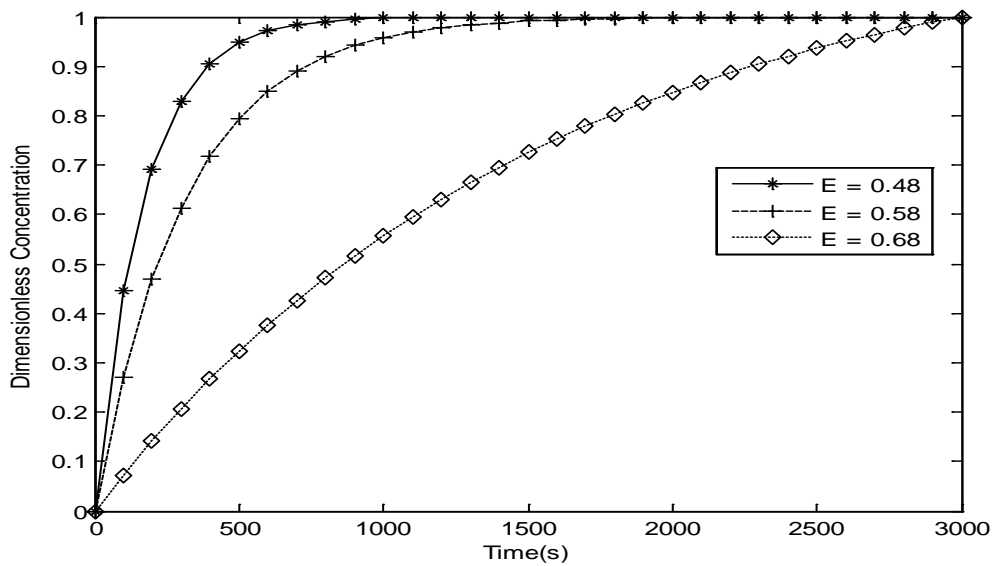

Figure 3. Effect of bed porosity on simulated breakthrough curve

Effect of particle radius on simulated breakthrough curve.

The effect of particle on effluent concentration is shown in figure 4. During these simulations, other parameters such as flow rate, and bed porosity are kept constant. Figure 3 shows that as the particle radius increases from 0.0003 to 0.0005m, the steepness of the breakthrough curves decreases. Also, as

the diameter of the particle increases, the thickness of stagnant film around the particles increases and the total length of the path inside the pore increases. Under these conditions, the overall kinetics of the process is slow because the time for molecules of adsorbates to reach the adsorption site is more as the diffusion path along the pores is large.
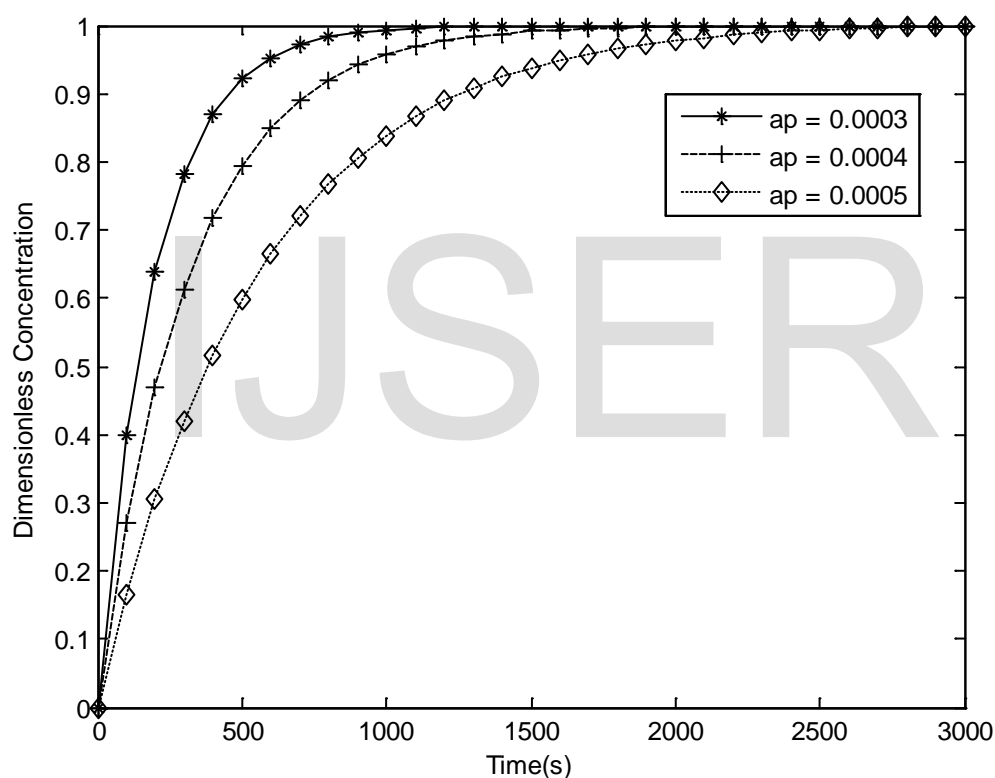

Figure 4. Effect of particle radius on simulated breakthrough curve

Concentration profile of PCAS in the solid phase.

The model used as described above determined 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.
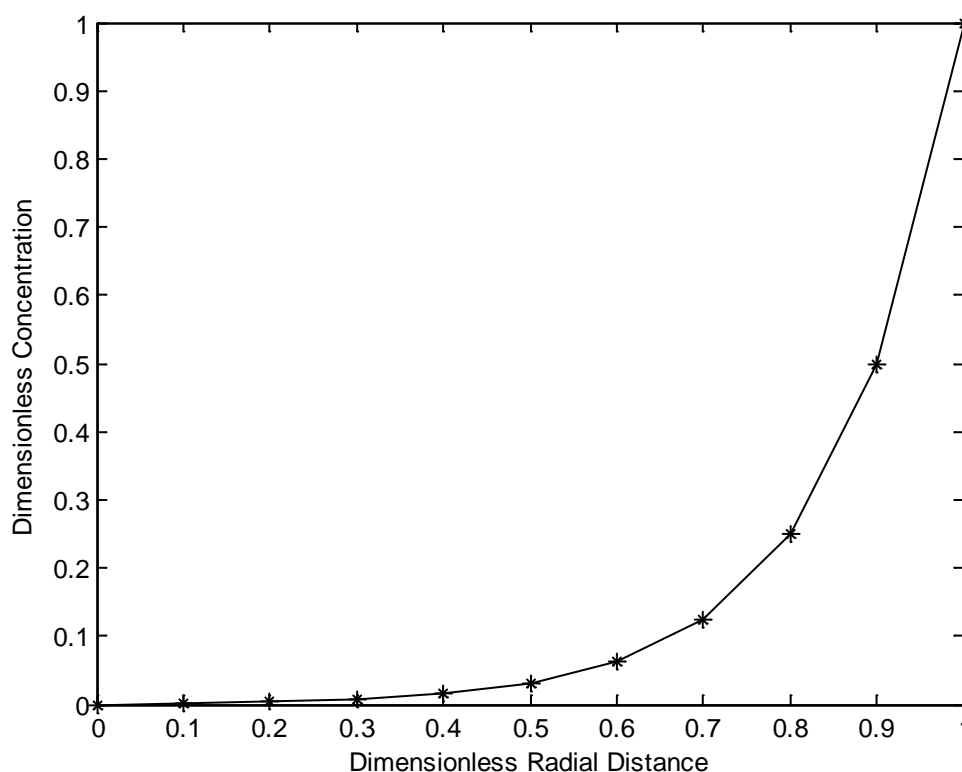
Figure 5. Concentration Profile of MCA in the Solid Phase of the Adsorber

CONCLUSION AND RECOMMENDATIONS

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 programming language. 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. Conclusively, the observations recorded in this study agree excellently with the general observations in the [1,3,5]. Hence, the proposal 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.

Appendix

Nomenclature

a_p	Radius of the adsorbent pellets	m
A	Area of cross section	m^2
b	Langmuir isotherm parameter	l/mg
C	Solute concentration of the liquid phase inside the pore	mg/l
C_b	Bulk phase concentration	mg/l
C_s	Liquid phase concentration in equilibrium with q_s on the surface	mg/l
C_{in}	Inlet adsorbate concentration	mg/l
C_b	Dimensionless concentration of the adsorbate in fluid phase	
D_L	Axial dispersion coefficient	m^2/s
D_p	Pore diffusion coefficient	m^2/s
K_f	External film mass transfer coefficient	m/s
L	Column length	m
g_p	Average adsorbed solute concentration	mg/g
g_m	Langmuir isotherm parameter	mg/g
q_s	concentration on the surface of the pellet	mg/g
r	Radial distance coordinate	m
u	Superficial velocity	m/s
u_o	initial superficial velocity	m/s
$\bar{U}$	Dimensionless superficial velocity	
t	Time	sec
T	Dimensionless time	
x	Dimensionless axial distance	
z	Axial distance coordinate	m
Pe	Peclet number	
Greek letters		
E	Bed porosity	
ε_p	Porosity of the adsorbent	
Pi	Solution density	Kg/m^3

ρ_p	Particle density	Kg/m^3
Δ	Delta	
Subscripts		
o	Initial Audition	
in	Inlet	
p	Particle	
S	Solid phase	
i, j	Cell location in grid	

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