A Novel approach of the modified BET Isotherm towards continuous column study

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Adsorption can be used to treat wastewater containing pollutants even at the low concentration in a very effective manner. The significance of the Langmuir, Brunauer Emmet Teller Isotherm was investigated for the perfect correlation with the experimental data. A theoretical one dimension dynamic model was proposed to understand the behavior of fixed bed with the assumption of straight through run mode of operation. The limitations associated with the application of classical Brunauer Emmet Teller to the liquid phase modeling were represented. The results were correlated using the theory and experimental observation available in the recently published literature through Mathematical derivation and MATLAB. The present study reveals that the modified Brunauer Emmet Teller isotherm posses the potential towards the applicability as Monolayer Langmuir adsorption isotherm under the condition of number of layer is equal to one.

Keywords: wastewater, optimization, fixed bed column, multilayer isotherm.

Introduction

The wastewater from washes basins, laundry machines, bathtubs and kitchen sinks have low level pollutant concentration of nitrates, chlorides, phosphates and sulphates termed as the grey water. Usually the grey water contaminants are removed through sand filters. The parameters like adsorption characteristic of the pollutants in the different soil layers, flow rate and the residence time plays a vital role in determining the adsorption of solutes in the soil. The direct use of the classical BET equation to liquid phase adsorption has been observed with ambiguous and erroneous results. By close examination of the development of the classical equation, the causes of misunderstandings were elucidated and the suitable form of the BET equation for liquid phase adsorption was developed. The experiment of single solute adsorption isotherm and developed a mathematical model and compared with the experimental results. A theoretical one dimensional dynamic model (convexion dispersion equation) is used to predict dispersive coefficient. Above simulation, was based on Langmuir isotherm obtained from the experiments. The nitrate transport modeled through the unsaturated soil bed by the adsorption techniques. A simple advection and dispersion equations were used in the case analytical modeling. The experiment carried out for the determination of single solute and competitive adsorption isotherm. Those experimental results were compared with classical equilibrium theory. The main focus was set on dynamic methods analyzing concentration profiles that could be detected at the outlet of fixed-beds packed with the stationary phase of interest. A novel adsorption model developed based on multi-layer adsorption reactions and the heterogeneity of adsorbents, which is more general and provides a more complete insight into the adsorption phenomena in comparison of the Do and Do's model. The fixed bed adsorption holds major practical applications than the batch adsorption in terms of the mathematical models of isotherm and kinetic behavior.

Materials and Methods

Adsorption isotherm

In order to optimize the design of an adsorption system to remove pollutant from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems (or for varied experimental conditions) within any given systems.
The Langmuir Isotherm model

This model describes quantitatively about the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. The Langmuir represents the equilibrium distribution of adsorbate between the solid and liquid phases. The Langmuir adsorption isotherm based on the following hypotheses:

1. Monolayer adsorption
2. Once a pollutant occupies a site; no further adsorption can take place in that site
3. Adsorption takes place at specific homogeneous sites within the adsorbent
4. The strength of the intermolecular attractive forces is believed to fall off rapidly with distance
5. Adsorption energy is constant and does not depend on the degree of occupation of an adsorbent’s active centre
6. The adsorbent has a finite capacity for the pollutant (at equilibrium, a saturation point is reached where no further adsorption can occur)
7. All sites are identical and energetically equivalent
8. The adsorbent is structurally homogeneous
9. There is no interaction between molecules adsorbed on neighboring sites
10. Langmuir adsorption parameters were determined by transforming the Langmuir equation into different linear form.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter \( R_L \), a dimensionless constant, referred to as separation factor or equilibrium parameter.

Development of modified BET equation for the liquid phase adsorption

The subtlety of application of BET isotherm for liquid phase adsorption has been presented. It has been shown that direct use of the classical BET equation (which was developed for gas phase adsorption) to liquid phase adsorption leads to ambiguous and erroneous results. Some cases of misuse of BET equation for liquid phase adsorption have been revisited. By close examination of the development of the classical equation, the causes of misunderstandings were elucidated and the suitable form of the BET equation for liquid phase adsorption was developed.

BET isotherm is one of the most successful isotherm models to express adsorption phenomena. This equation has a sound theoretical basis and provides a good understanding about the nature of adsorption phenomena. Multilayer adsorption behavior, monolayer adsorption capacity and heat of adsorption at various adsorption layers are among the parameters of adsorption that can be determined using this isotherm model. Mainly because of these powerful features, BET isotherm model has found widespread application in determination of surface area and pore size distribution of adsorbents and catalysts. The linear form of BET equation is given as follows:

\[
x = \frac{1}{q(1-x)} + \left(\frac{c-1}{q_m c}\right)x
\]

... (1)

Where, \( q \) is the adsorbate per unit of absorbent (mg/g), \( q_m \) is monolayer adsorption capacity (mg/g), \( c \) is a constant parameter, \( x \) is the BET adsorption constant.

In the classical form of the BET equation which was originally developed for gas phase adsorption, the gas phase concentration was expressed as relative concentration, i.e. the ratio of the partial pressure of the adsorbate to its saturation partial pressure at the system temperature \( (x = P/P_S) \). In this case, the equation has two degrees of freedom in the form of two parameters of \( q_m \) and \( k_L \). When applying BET equation to liquid phase adsorption; one may simply substitute liquid phase concentration, \( C \) for partial pressure of the adsorbate, \( P \) in the classical BET equation. However, difficulty arises in replacing the saturation partial pressure \( P_S \), with the corresponding term in liquid phase.

In the classical BET equation, if we replace \( 1/P^S \) with the equilibrium constant of upper layers \( k_s \) and \( P \) with the liquid phase equilibrium concentration \( C \), the BET isotherm equation can be modified for liquid phase adsorption as:

\[
q = q_m \frac{k_s C \left[1 - (N+1)(k_i C)^N + N(k_i C)^{N+1}\right]}{(1-k_i C) \left[1 + \left(\frac{k_s}{k_i} - 1\right) k_i C - \frac{k_s}{k_i} (k_i C)^{N+1}\right]}
\]

... (2)

The equation (2) becomes the normal BET equation for liquid adsorption at \( N = \infty \) and becomes the Langmuir isotherm at \( N = 1 \).

It is obvious that in case of liquid phase adsorption the BET isotherm equation has three degrees of freedom \( (q_m, k_s, k_i) \), while it has two degrees of freedom \( (q_m, k_s) \) in the case of gas phase adsorption. In fact one of the three parameters of the equation \( (q_m, k_s, k_i) \) fixed by expressing the adsorbate concentration in the form of relative concentration.
(by equating $1/ k_l = P_S$ ) and reduced the number of parameters to two ($q_m, k_s$) for the purpose of developing the equation in linear form for ease of linear regression of the experimental data.

**Modeling and Simulation studies**

The adsorption process is analyzed from an elemental material balance viewpoint and then a mathematical model, which describes our process, is derived. Further, the method of simulation is also dealt with. Here using the experimental data in the frontal analysis of various species, we try to obtain the adsorption isotherm (BET) and using that isotherm we try to predict the model frontal curve in the species uptake during adsorption. The purpose of this simulation is to estimate the mass transfer coefficient for different adsorbents, their adsorption isotherm or equilibrium relation and the transport properties like dispersion coefficient. By getting the mass transfer coefficient we can estimate the life of the filter bed.

There are few assumptions involved here which are stated as:

1. Flow is one-dimensional and vertical flow.
2. The bed is fully saturated with liquid.
3. The equilibrium adsorption relation is given by BET model.
4. There is almost no mass transfer resistance on the liquid side.
5. The mass transfer resistance on the surface of adsorbent is linear.
6. For model in which mass transfer resistance is neglected, assumption is that the effect of all transport properties can be combined to give an effective dispersion co-efficient.

**Model for Continuous Process**

**Straight through mode**

We consider the continuous straight through mode of adsorption in the bed when the feed concentration to the bed is a constant. Based on the solute transport equation equation and the equilibrium law, mass transfer equation is used for this model. In this case the optimized parameter values (dispersion coefficient and mass transfer coefficient) from with mixing model are used to predict the experimental and theoretical curves. The nodes are considered from the bottom 1 to n. as seen in the following diagram.

**Approach towards the problem**

Here, the approach adopted towards studying the process of adsorption is experimental followed by numerical solution to the process and find the various adsorption parameters that play a significant role. Consider a packed adsorption tower of length L. Now consider the differential element of an adsorbent bed Fluid enter at point ‘z’ and leaves at ‘z+dz’. In this section adsorption of solute occurs. Fluid leaves the upper section with lower concentration of solute. A mass balance for bulk liquid phase is applied in that small section. The differential element of a continuous fixed bed adsorption column through straight run mode operation has been represented in the figure 1.

Accumulation = input - output + generation

Where $C$ is the concentration of solute in bulk fluid phase (mg/L), $q$ concentration in solute in liquid phase (mol/gm), $D$ is the Dispersivity ($m^2$/s), $\epsilon$ - Void space and $u$ – Actual velocity (m/s) are the notations used in material balance. Dividing the material balance equation by $A, \Delta Z, \Delta t$ and tending $\Delta Z$ and $\Delta t$ to zero we get one-dimensional solute transport model which governs the adsorption of a solute in a fixed bed. This is also called convection-dispersion equation (CDE).

This is a non-linear parabolic partial differential equation and describes how the liquid phase concentration $C$ varies with $Z$ and time. It contains two dependent variables, $C$ and $q$. Hence, one more relationship is needed to formally solve the problem. This relationship between $C$ and $q$ is given by the adsorption isotherm.

The relationship is assumed as the modified BET isotherm equation in our work. This is characterized...

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**Fig. 1—Differential element of a continuous adsorption bed through straight run mode operation**
by three parameters $k_s$, $k_l$, and $q_m$. These parameters depend on the choice of the solute as well as the particles used as an adsorbent.

Solving the one dimensional transport equation with adsorption isotherm equation we will lead to the expression in this form,

$$\frac{\partial^2 C}{\partial t^2} = -u \frac{\partial C}{\partial Z} + D \frac{\partial^2 C}{\partial Z^2} \frac{g(C)}{g(C)}$$

... (3)

Where $g(C)$ will be different for different situation.

Equation (3) is solved subject to the following initial and boundary conditions.

The initial conditions are $C(t=0)=0$; for $0 < z < L$

Since the bed is assumed to have no solute at the start of the experiment.

The boundary conditions are, at $Z = 0$ (entry),

$$uC_{in} = -D \frac{\partial C}{\partial Z} + uC$$

... (4)

This is called the closed Danckwerts boundary condition. Here, we neglect the dispersion in the distributor section just upstream of the test section. Here, $C_{in}$ is the concentration of the solution entering the bed. In our case this is a constant equal to $C_{feed}$.

At $Z = L$ (exit)

$$uC(L^+) = -D \frac{\partial C(L^-)}{\partial Z} + uC(L^-)$$

... (5)

Imposing continuity of concentration at the exit of the bed we obtain

$$uC(L^+) = uC(L^-)$$

... (6)

The parabolic partial differential equation (3) is solved using method of lines. The concentration in the bed is discretized in the spatial direction. The bed is divided into (n-1) grids. The grid points are numbered from 1 to n as we vary $Z$ from 0 (entrance) to $L$ (exit). the evaluation of the concentration with time in each node is modeled through ordinary differential equations. The concentration evolution with time was obtained using a variable step-size Runge-Kutta algorithm in MATLAB. A grid independence study was performed by increasing the number of grids. It was found that the numerical results did not vary significantly when the no of grids was increased beyond 40.

Optimization

The parameters occurring in the governing equations can be classified into two groups, first which can be measured independently as velocity, porosity, feed concentration and second those which have to be estimated like $q_m$ – monolayer adsorption capacity; $D$ – dispersion coefficient. The former are used as fixed parameters in simulations. The latter are specific to the system being investigated and are estimated by comparing the predictions of the model with the experimental data.

Result and Discussion

Multilayer adsorption model for continuous process (straight run mode) A model for multilayer adsorption has been developed in straight run mode assuming modified BET isotherm for liquid phase adsorption. The code has been verified with experimental data, and simulation results reported in literature, break through curve has been obtained. The initial conditions that were used were as following:

Salt: sodium Chloride, Molecular wt (mw) = 58.44 gm/mol, Length of bed, $L= 0.3048$ m, Porosity of the bed $\epsilon =0.42$, Fixed bed material: sand and brick (1:1), Density of bed particle, $\rho =1805$ kg/m$^3$, $C_{feed} =2000$ ppm=2000/mw=34.22 mol/Kg and Dispersion coefficient= 4.6387x10$^{-5}$ m$^2$s. Break through Curve for the Concentration $C_{feed}$: 2000 ppm (n tends to 10) was represented in the figure 2.

Optimization (Fig.2) has been done taking N tends to infinity to get unknown parameter $q_m$, $k_s$, $k_l$. Then

![Fig. 2—Break through Curve for a Concentration $C_{feed}$: 2000ppm](image-url)
again using these values breakthrough curves have been drawn for experimental and theoretical data (obtained by model) for various values of n and a satisfactory agreement between these two is observed for n=1. Experiment performed in fixed bed observed that experimental data fits best to Langmuir isotherm and concluded that there is only monolayer adsorption (n=1) is taking place based on the literature study. In the current study it is summarized that Langmuir isotherm is a specific case of BET when n=1 so our model should be valid for this experimental data when study performed for n=1. By Fig.2 we can clearly observe that the data are best fit for n=1 which conclude that our model is valid.

Then again using these values breakthrough curves have been drawn for experimental and theoretical data (obtained by model) for various values of n and a satisfactory agreement between these two is observed for n=1. According to literature study experiment performed in fixed bed observed that experimental data fits best to Langmuir isotherm and so concluded that there is only monolayer adsorption (n=1) is taking place. But the present study summarized that Langmuir isotherm is a specific case of BET when n=1 so our model should be valid for this experimental data when study performed for n=1. By Figure.3 the data are best fitted for n=1 which conclude that our model is valid. So taking two different feed concentrations the modeling is validated and for both case it is giving satisfactory results, which conclude the model is well developed.

**Conclusion**

The inapplicability of classical BET for liquid phase modeling has been highlighted and the modification to be done for its applicability has been reported. The literature survey involved a thorough study of many research journals and papers related to the, modeling of adsorption phenomena, use of different adsorption isotherm. A wide perspective on the theory behind the modeling and nature of the isotherm was obtained. The various models like Langmuir and BET describing the phenomena of adsorption was learnt. The governing equation, the mode of operation which plays a prominent role in the modeling of adsorption process taking place in system was studied. It was concluded that the use of classical BET isotherm for Liquid phase adsorption lead to erroneous result. Hence corrected BET was used in our model and comparing our results with experimental data, concluded that our model is valid to govern the adsorption phenomena in fixed bed. The modified BET isotherm under the condition of n=1 becomes the Langmuir adsorption isotherm therefore the novel generated modified BET isotherm has its own applicability towards the monolayer adsorption isotherm-Langmuir isotherm.

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