VARIOUS ISOTHERM MODELS FOR MULTICOMPONENT ADSORPTION: A REVIEW

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ABSTRACT

Adsorption is considered as the efficient method for the removal of pollutant from wastewater. The wastewater contains single pollutant as well as multi-pollutants. In case of wastewater having various pollutants, interaction and competition among the adsorbate molecules plays an important role in the adsorption process. The adsorption mechanism will be complicated for these systems. Therefore for understanding the mechanism, different single component isotherm models are modified to multi-component systems. Various isotherm models such as non-modified Langmuir, extended Langmuir, modified Langmuir model, extended Freundlich, Redlich-Peterson model, Sheindorf–Rebuhn–Sheintuch equation and extended Sips isotherm model were studied in order to understand the interaction among the pollutant molecules. Therefore, the current study reviews the different isotherm models used for multicomponent adsorption.

Keywords: Adsorption, isotherm, multicomponent system, competition, interaction.


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1. INTRODUCTION

Due to the increasing industrial activities, there is a growing interest on environmental protection. The wastewater coming out of industries contains different pollutants such as phenol, heavy metals, dyes and suspended matter [1]. As per the environmental protection agency these chemicals are considered as priority pollutants. [2]. The release of these pollutants into the environment causes harmful effects on the aquatic life and the surrounding environment [3]. Various treatment methods like biodegradation, adsorption, membrane separation process, pervaporation, distillation, extraction and advanced oxidation processes are used for the treatment of the pollutant. Adsorption using adsorbent is considered as one of the effective method for the treatment of the pollutant. Adsorbent can be produced from non-renewable materials and also from agricultural waste materials. The removal of the pollutant from wastewater can be found by determining the adsorption capacity of the adsorbent. Adsorption can be carried out with the wastewater having single component or various pollutants. Since the wastewater generally contains various pollutants, there is a need to study
on the removal of the different pollutants from wastewater using various adsorption isotherm models.

2. MULTICOMPONENT ADSORPTION

The concept of multicomponent adsorption is of high importance in wastewater treatment. This is because wastewater having high concentration of pollutants leads to interactions between the components present in the wastewater. It is also required to estimate the movement of the pollutants and to study the influence of competitive interaction among the pollutants on the overall adsorption process. The adsorption of a pollutant on an adsorbent may be affected by the other component because of properties such as surface charge, structure, size, the functional groups of the component and also on the porosity and active sites present on the adsorbent surface [4, 5]. Hence it is required to study the relationships between the adsorption capacity of a component and the concentration of the other pollutants present in wastewater with the help of multicomponent isotherm models.

3. MODELS USED FOR MULTICOMPONENT ADSORPTION

Various isotherm models like Freundlich, Langmuir, Redlich–Peterson and Sips are used to discuss the equilibrium behavior of single-component adsorption. Freundlich model assumes that adsorption occurs on a heterogeneous surface and heat of adsorption is distributed in a non-uniform manner. While the Langmuir model assumes that adsorption happens at homogeneous active sites on the adsorbent surface [6]. The wastewater containing various components results in competition and interaction among the pollutants. Therefore the models used for single component system are not applied to multicomponent system. This is because of the reason that multicomponent adsorption involves a complicated mechanism and more thorough complex models have been employed. Therefore the single component isotherm models are modified to multicomponent system and are discussed below.

3.1. Extended Langmuir Isotherm

The extended Langmuir isotherm for multicomponent adsorption is developed based on the assumptions that all the active sites on the adsorbent are uniform in nature, all the adsorbent sites are equally available to all the adsorbates, the adsorbates in the multicomponent system have non interacting effect and all the pollutant molecules in the wastewater adsorb on identical active sites [7, 8]. The model also assumes that the active sites have uniform energy of adsorption [9]. The model can be represented in the form

\[ q_{e,i} = \frac{q_{m,i}b_{L,i}C_{e,i}}{1+\sum_{j=1}^{N}(b_{L,j}C_{e,j})} \]  

where, \( q_{e,i} \) equilibrium adsorption capacity for component \( i \) (mg/g), \( C_{e,i} \) the equilibrium concentration (mg/L), \( b_{L,i} \) Langmuir constant for component \( i \) (L/mg), \( q_{m,i} \) monolayer adsorption capacity for component \( i \) (mg/g), \( N \) total number of components in the solution.

The above equation can be modified depending on the number of components. For a solution containing two components, the adsorption capacity \((q_{e,1}, q_{e,2})\) can be calculated using the following equations.

\[ q_{e,1} = \frac{q_{m,1}b_{L,1}C_{e,1}}{1+b_{L,1}C_{e,1}+b_{L,2}C_{e,2}} \]  
\[ q_{e,2} = \frac{q_{m,2}b_{L,2}C_{e,2}}{1+b_{L,1}C_{e,1}+b_{L,2}C_{e,2}} \]
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The parameters $q_{m,1}, b_{L,1}$ and $b_{L,2}$ were evaluated for a set of experimental values of $q_{e,1}$ and $C_{e,1}$ by minimizing the error in non-linear regression analysis or by using solver function of non-linear regression in Microsoft excel [7, 10, 11, 12].

3.2. Non Modified Competitive Langmuir Isotherm

The model is applied for the competitive adsorption of component $i$ in a solution containing $n$ number of components. The adsorption capacity of a component can be calculated when it is present in association with other components [5, 9]. The model is expressed as

$$q_{e,i} = \frac{q_{m,i}b_{L,i}C_{e,i}}{1 + \sum_{j=1}^{n}(b_{L,j}C_{e,j})}$$

(4)

where $q_{m,i}$ and $b_{L,i}$ are monolayer adsorption capacity for component $i$ (mg/g) and Langmuir constant for component $i$ (L/mg) respectively calculated from the experimental data of individual Langmuir isotherms. Then for a set of $C_{e,i}$ values the corresponding values of $q_{e,i}$ can be evaluated [7, 8, 11, 12, 13, 14].

3.3. Modified Competitive Langmuir Isotherm

The parameters calculated from the single component adsorption isotherm model does not explain how the interaction takes place between the individual components in a solution. Therefore an interaction term is introduced to describe the nature of adsorption process. The interaction factor shows the competitive effect of adsorbates in the solution. It is a characteristic parameter of a component which depends on the concentration of the other components present in the solution [5, 6, 8, 15, 16]. It is represented in the form

$$q_{e,i} = \frac{q_{m,i}b_{L,i}(C_{e,i}/\eta_{L,i})}{1 + \sum_{j=1}^{n}(b_{L,j}(C_{e,j}/\eta_{L,j}))}$$

(5)

$q_{e,i}$ the equilibrium adsorption capacity for component $i$ (mg/g), $C_{e,i}$ the equilibrium concentration (mg/L). The constants $q_{m,i}$ the monolayer adsorption capacity for component $i$ (mg/g) and $b_{L,i}$ Langmuir constant for component $i$ (L/mg) are evaluated from the experimental data of individual Langmuir isotherms. The interaction factor $\eta_{L,i}$ which is dependent on the concentration of other components. The parameter $\eta_{L,i}$ for various components were calculated for a range of experimental values of $q_{e,i}$ and $C_{e,i}$ by reducing the error in non-linear regression analysis in Microsoft excel. By adding the correction factors the isotherm model fits better to the experimental data and the accuracy of the results can be improved [5, 10, 12, 15, 17].

3.4. Extended Freundlich Equation

The mono-component Freundlich equation can be applied to binary systems to develop extended Freundlich isotherm model. The model is used for heterogeneous systems when interaction is happening among the adsorbed molecules [17]. The equation for multicomponent system can be represented as

$$q_{e,1} = \frac{k_{F,1}C_{e,1}^{(1/n_1)+x_1}}{C_{e,1}^{x_1+y_1C_{e,2}^{x_1}}}$$

(6)

$$q_{e,2} = \frac{k_{F,2}C_{e,2}^{(1/n_2)+x_2}}{C_{e,2}^{x_2+y_2C_{e,2}^{x_2}}}$$

(7)
\( q_{e,1} \) and \( q_{e,2} \) the equilibrium adsorption capacity for component 1 and 2 (mg/g), \( C_{e,1} \) and \( C_{e,2} \) the equilibrium concentration of component 1 and 2 (mg/L). The values of Freundlich constants \( k_{F,1} \), \( k_{F,2} \) and adsorption intensity \( n_1 \) and \( n_2 \) are obtained from the experimental data of individual Freundlich isotherms. The constants \( x_1, y_1, z_1 \) and \( x_2, y_2, z_2 \) were obtained for a set of experimental values of \( q_{e,1} \) vs \( C_{e,1} \) and \( q_{e,2} \) vs \( C_{e,2} \) respectively, by minimizing the error in non-linear regression analysis [6, 8, 17, 18].

3.5. Non Modified Competitive Redlich Peterson Isotherm

Redlich–Peterson isotherm is derived by combining both the Langmuir and Freundlich isotherm models and the model equation is developed by taking all the model constants. The equation developed shows that the model is linearly dependent on concentration in the numerator term and exponentially dependent in the denominator term. It facilitates the model can be used to validate the equilibrium data over a wide variety of concentration. The equation approaches towards Freundlich model at higher concentration for the \( \beta \) value equal to zero. It gets modified to Langmuir equation at lower concentration when \( \beta \) value is tending to one [19, 20, 21]. The equation can be given as

\[
q_e = \frac{k_{PR,C_e}}{1 + a_{PR,C_e}^\beta} \quad (8)
\]

\( k_{PR} \) Redlich–Peterson constant (L/g)

\( a_{PR} \) model constant (L/mg) \( \beta \) (L/mg)\( ^\beta \)

\( \beta \) exponent varying from 0 and 1.

The Redlich–Peterson model can be applied to multicomponent systems to get different forms such as competitive non-modified and competitive modified Redlich–Peterson isotherm models. The non modified competitive Redlich Peterson isotherm is expressed as

\[
q_{e,i} = \frac{k_{PR,i}C_{e,i}}{1 + \sum_{j=1}^{N}(a_{PR,j}C_{e,j})^{\beta}} \quad (9)
\]

modified competitive Redlich Peterson models. ms to get different forms such as competitive non-modified, competitive modifi

where \( k_{PR,i} \left( \frac{L}{mg} \right) \), \( \beta \) and \( a_{PR} (L/mg)^\beta \) the model constants are obtained from the experimental data of individual Redlich Peterson isotherms. Then for a set of \( C_{e,i} \) values the corresponding values of \( q_{e,i} \) can be evaluated [6, 11].

3.6. Modified Competitive Redlich Peterson Isotherm

The interaction term is added is added in this model in order to show the nature of interaction among the components in a multicomponent solution. The modified competitive Redlich Peterson model can be represented as

\[
q_{e,i} = \frac{k_{PR,i}(C_{e,i}/\eta_{PR,i})}{1 + \sum_{j=1}^{N}(a_{PR,j}(C_{e,j}/\eta_{PR,j})^{\beta+j})} \quad (10)
\]

\( q_{e,i} \) the equilibrium adsorption capacity for component \( i \) (mg/g), \( C_{e,i} \) the equilibrium concentration (mg/L). The constants \( k_{PR,i} \left( \frac{L}{mg} \right), \beta \) and \( a_{PR} (L/mg)^\beta \) the model constants are evaluated from the experimental values of individual Redlich Peterson isotherms. The interaction parameter \( \eta_{PR,i} \) for various components can be calculated for the experimental
values of $q_{e,i}$ and $C_{e,i}$ by minimizing the error in non-linear regression analysis in Microsoft excel. By adding the correction factors the isotherm model can be validated better compared to the non-modified model [12, 14].

3.7. Sheindorf–Rebuhn–Sheintuch (SRS) Equation

The equation is derived for multicomponent systems based on the concept of Freundlich isotherm. The assumptions which are followed in this isotherm are that each component in a solution follows Freundlich isotherm and distribution of adsorption energy takes place for each solute exponentially [6, 13]. The competition coefficient $a_{ij}$ is introduced in order to show how the component $j$ inhibits to the adsorption of component $i$. The competition coefficient values for $a_{ii}$ and $a_{jj}$ are unity [18]. The SRS equation can be given as

$$q_{e,i} = k_{F,i}C_{e,i}(\sum_{j=1}^{N}(a_{ij}C_{e,j}))^{(1/n)}$$

The SRS equation can be given as

$$q_{e,i} = \frac{q_{m,i}k_{S,i}C_{e,i}^m}{1 + \sum_{j=1}^{m}k_{S,j}C_{e,j}^m}$$

The Sips isotherm is used for heterogeneous systems. The modified sips isotherm for multicomponent system is

$$q_{e,i} = \frac{q_{m,i}k_{S,i}C_{e,i}^m}{1 + \sum_{j=1}^{m}k_{S,j}C_{e,j}^m}$$

The Sips constants are taken from the isotherm data of individual components. At lower pollutant concentration for $m$ value of 0, the model approaches Freundlich isotherm. For higher adsorbate concentration for $m$ value approaching 1, the model can be modified to Langmuir isotherm [20, 23].

3.9. Interaction Effect

In a solution containing various pollutants, different types of interactions happen between the adsorbate molecules and are described below. It can be discussed based on the ratio of adsorption capacity of an adsorbent ($Q_m$) in the system having multicomponent to the adsorption capacity of the pollutant ($Q_i$) in a solution containing single component. The following are the interactions among the pollutants.

(a) Synergistic interaction: The adsorption capacity of an adsorbent enhances when it is present in a solution having different pollutants ($Q_m/Q_i > 1$).

(b) Antagonistic interaction: The adsorption capacity of an adsorbent decreases when it is in association with other components ($Q_m/Q_i < 1$).

(c) Non interaction: The adsorption capacity is not influenced whether the pollutant is present alone or if it is present in the multicomponent solution ($Q_m/Q_i = 1$)[10, 12, 24, 25, 26].
4. CONCLUSIONS

Adsorption was found to be effective for the treatment of wastewater containing different pollutants. Multicomponent isotherm models are required to know the interaction among the molecules. The importance of various multicomponent isotherms such as Langmuir, Freundlich, Redlich-Peterson and Sips model were investigated. The model are specific with respect to type of pollutant, surface area of adsorbent, nature of attractive forces, surface charge and concentration of pollutant. The interaction effects shows how the adsorption of a pollutant is affected when it is present in association with other pollutants. Therefore the present review is helpful in understanding the adsorption of a pollutant in multicomponent system.

REFERENCES

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