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Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent

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ABSTRACT

The aim of this study was to investigate how basic adsorption isotherms could be applied to predict removal efficiency or required adsorbent mass under given sets of initial conditions. The intrinsic parameters of the Langmuir and Freundlich adsorption isotherms were experimentally obtained and subsequently utilized to predict removal efficiencies for other sets of initial solute concentrations, solution volumes, and adsorbent masses, or to estimate the adsorbent mass required to remove solute at a desired removal efficiency. This was accomplished by combining the isotherms with mass balance of solutes between liquid solution and solid adsorbent phases.

Introduction

Q3 Adsorption technology has been widely utilized in water and wastewater treatment processes because it is a fast, effective, and relatively inexpensive method [1]. Organic and inorganic constituents in the water phase are effectively removed by adsorption technology [2–8]. Activated carbon such as granular and powdered activated carbon (GAC and PAC) have been widely used as adsorbent for water treatment [9–12], but because of considerable operating costs associated with regeneration and/or repeated injection, various alternative adsorbents have been studied [13–15]. Oyster shell powder containing calcium carbonate is one such alternative. Large amounts of waste oyster shells are continuously generated in some countries, which offers a reliable source for them to be used as a cheap adsorbent material [16,17]. It was reported that the removal of orthophosphate by adsorption onto oyster shell powder was comparable to that onto calcium carbonate [18].

In most adsorption studies, adsorption models such as Langmuir and Freundlich isotherms have been widely used to evaluate adsorption phenomena [10,19]. Generally, experimental data were fitted to adsorption isotherm models, and the best-fitted model was used to characterize equilibrium adsorption. As the appropriate adsorption model was selected, the adsorption parameters of the model were obtained and used to describe the adsorption characteristics. Langmuir-type adsorption is considered to be a monolayer process. The maximum adsorption capacity per unit adsorbent mass is determined along with the Langmuir constant showing the solute affinity to the adsorbent. Freundlich-type adsorption is considered to be a multi-layer process in which the amount of adsorbed solute per unit adsorbent mass increases gradually. Freundlich parameters were also used to characterize the adsorption process.

It should be pointed out that, in the adsorption isotherms, the amount of adsorbed solute per unit adsorbent mass (dependent variable) is expressed as a function of the solute concentration at equilibrium (independent variable), not a function of initial concentration. This implies that the model equation would only be utilized when the solute concentration at equilibrium is known. However, in many practical adsorption studies and industrial applications, it might be more desirable to predict the removal efficiency for the given initial set of experimental conditions (initial solute concentration, solution volume, and adsorbent mass), or to estimate the adsorbent mass required to remove the solute for a desired removal efficiency. Najm et al. [20] reported the effect of initial di- and trichlorophenol concentration on adsorption isotherm. Knappe et al. [21] developed a method to predict PAC capacity for trace organic compounds from initial solute concentration at a given adsorbent dose. Bolster [22] predicted adsorbed solute concentration as

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a function of initial solute concentration. However, few studies have sought to directly predict removal efficiencies of adsorption processes as functions of both initial solute concentration and adsorbent mass—information that could be conveniently applied to real adsorption processes.

The objective of this study was to demonstrate how basic adsorption isotherms combined with simple mass balance can be applied to predict removal efficiency or required adsorbent mass under given sets of initial conditions. The intrinsic parameters of Langmuir and Freundlich adsorption isotherms were first obtained by fitting experimental data for the adsorption of orthophosphate and methylene blue onto oyster shell powder and PAC, respectively. Even though only one isotherm for each adsorption experiment need be determined for the predictions, experimental data for different sets of initial adsorption conditions were obtained to be compared to the predicted values. Finally, contour plots of predicted removal efficiencies were generated using both initial solute concentration and adsorbent mass as independent variables.

Model development

Langmuir isotherm

The Langmuir isotherm, which assumes monolayer adsorption onto an adsorbent surface, can be expressed by the following equation [10]:

$$q_e\left(\frac{K_L \times C_e}{1 + K_L \times C_e}\right) \times q_{\max} \tag{1}$$

where C_e is the solute, or so-called adsorbate, concentration in the solution at equilibrium (mg/L), q_e the solute mass adsorbed per unit adsorbent mass at equilibrium (mg/g), K_L the constant of the Langmuir isotherm (L/mg), and $q_{\max}$ relates to the maximum adsorption capacity (mg/g). The above equation may be reformulated in the form of the following linear equation:

$$\frac{1}{q_e} = \left(\frac{1}{K_L \times q_{\max}}\right) \times \frac{1}{C_e} + \frac{1}{q_{\max}} \tag{2}$$

In any adsorption experiments, C_e can be measured and q_e can be calculated for a series of different conditions. Then $1/q_e$ can be plotted as a function of $1/C_e$. Note that most of the adsorption experiments have utilized the above linear form of the equation to evaluate whether or not the adsorption process satisfies the Langmuir isotherm. If the resulting plot shows appreciable linearity, the adsorption process may be deemed to follow the Langmuir adsorption isotherm. Consequently two parameters (K_L and $q_{\max}$) can be obtained by using the slope and the intercept to characterize the adsorption process.

In this study, the isotherm equation was combined with a mass balance, which has been generally used in modelling studies on adsorption [10,19]. In a batch system at the given solution volume, the following mass balance should be satisfied:

$$C_0 = C_e + C_e^S \tag{3}$$

where C_0 is the initial concentration of solute in the solution, and C_e^S is the concentration of solute adsorbed onto the adsorbent at equilibrium. The q_e in Eq. (1) can also be expressed in terms of solution volume, V, and adsorbent mass, M, with C_0 and C_e as follows:

$$q_e = \frac{V \times C_e^S}{M} = \frac{V(C_0 - C_e)}{M} \tag{4}$$

Substituting Eq. (4) into Eq. (1) gives the second order function in which C_e is a one argument variable as follows:

$$K_L \times C_e^2 + \left(1 + \frac{K_L \times q_{\max} \times M}{V} - K_L \times C_0\right) \times C_e - C_0 = 0 \tag{5}$$

Note that the resulting equation shown above is a form of quadratic equation if all variables other than C_e are treated as constants, and thus C_e can be explicitly and simply solved by using the following quadratic formula [22,23]:

$$C_e = \frac{-(1 + (K_L \times q_{\max} \times M/V) - K_L \times C_0) + \sqrt{(1 + (K_L \times q_{\max} \times M/V) - K_L \times C_0)^2 + 4K_L \times C_0}}{2K_L} \tag{6}$$

The resulting C_e is a function of C_0 and M for a specific V with parameters K_L and $q_{\max}$. Therefore, once K_L and $q_{\max}$ are obtained from a set of adsorption experiments, equilibrium solute concentrations can be estimated for the given initial solute concentration and the adsorbent mass in a fixed volume, which can differ from the conditions in the experimental set used for determining K_L and $q_{\max}$. If the removal efficiency by adsorption for water treatment is set to R, it can be expressed as

$$R = \frac{C_0 - C_e}{C_0} \tag{7}$$

and thus R is also a function of C_0 and M ($R = R(C_0, M)$) for a specific V.

For the given initial solute concentration and target removal efficiency, the model equation to predict the adsorbent concentration can also be obtained. Substituting Eqs. (4) and (7) into Eq. (1) and arranging for M gives:

$$M = \frac{V \times R}{K_L \times q_{\max} \times (1 - R)} + \frac{V \times R}{q_{\max}} \times C_0 \tag{8}$$

Note that the resulting Eq. (8) is an explicit equation in which M is a function of C_0 and R for a specific V with parameters K_L and $q_{\max}$ ($M = M(C_0, R)$), and thus the required adsorbent mass can be simply predicted from a set of an initial solute concentration and a desired removal efficiency (Fig. 1).

Freundlich isotherm

The Freundlich isotherm, which was originally developed as an empirical model, may be written as follows [10,19]:

$$q_e = K_F \times C_e^{1/n} \tag{9}$$

where K_F is the constant of the Freundlich isotherm ($L^{1/n}$ $mg^{(1-1/n)}$/g), and $1/n$ is the Freundlich exponent. The linear form of the

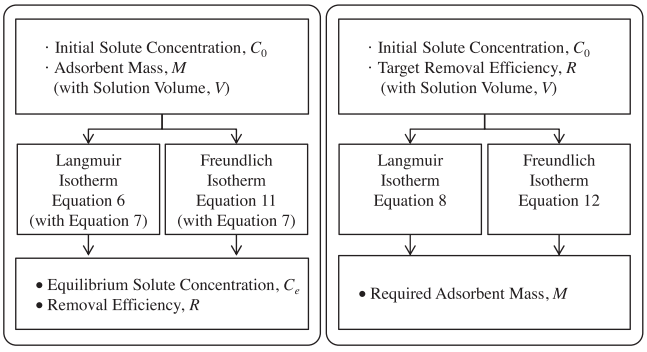

Fig. 1. Simplified flowcharts for the application of adsorption isotherms combined with mass balances to predict removal efficiency or required adsorbent mass.