



# A simple method to separate phosphorus sorption stages onto solid mediums



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## ABSTRACT

The sorption of phosphorus (P) onto solid mediums (soil, sediment and P removing materials) is characterized by a rapid sorption phase followed by a slow phase. No studies have yet attempted to quantitatively distinguish between the two stages. In this study, efforts are made to develop a method that can separate the sorption process into fast and slow stages. According to the geometrical shape of P sorption curves, a maximum curvature value points (MCVP) algorithm is presented as the change point based on the most widely used P sorption models (Langmuir and Freundlich isotherm equation, first-order, second-order and Elovich kinetic equation). Results showed that the MCVP successfully separates the sorption process into a fast stage and then a relatively slow one. General analysis formulas of the MCVP for the most commonly used models are described in this paper. Two steps are recommended before the MCVP calculation: first, independent and dependent variables should be plotted in the same order of magnitude (1:1 is the best), free from the axis scale effect; second, the model that best describes the data points should be used to quantify the MCVP. With the MCVP, it is easy for researchers to obtain the change point by substituting the parameters of sorption models, particularly for materials that have been tested before. The significance of this study is that it allows for optimization of the reaction time in P removal technology and furthers our understanding of P distribution characteristics in soil or sediment.

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## 1. Introduction

Numerous studies have confirmed the close association between elevated phosphorus (P) concentrations in water bodies and decreases in surface water quality. More attention is currently being paid to P sorption reactions, as P is a highly particle reactive element and has no significant atmospheric fluxes. P sorption onto solid materials has received widespread investigation because of three aspects: (1) an important process “fixing” fertilizer P into an “unavailable” form in cultivated soils (Froelich, 1988); (2) sorption reactions can buffer water column P levels and facilitate P retention in bed sediments and (3) phosphorus removal from wastewater is closely associated with the filter material (Özacar, 2006; Vohla et al., 2011). The economic and ecological impetuses of these aspects have promoted a long-term effort to understand sorption reactions of P onto solid mediums.

Sorption experiments are conceptually simple. The most commonly used technique is the batch equilibration method. Solids of known mass are added to a solution of known P concentration, shaken or stirred for some time under a given temperature, and separated from solution (Cucarella and Renman, 2009; Froelich, 1988; Graetz and Nair, 2000). The difference between the initial and final P concentration is the amount of phosphorus adsorbed. These experiments are performed to study two basic phenomena: (1) the phosphorus concentration effect, i.e., sorption isotherm, which focuses on the relationship between sorption quantities and so-called “equilibrium concentration” under constant temperatures; and (2) the time effect, i.e., kinetics, which investigates the function of sorption quantities (the dependent variable) and the time span (the independent variable). A sorption model is fit to the data to obtain sorption parameters for the solid phase. The commonly used models are the Langmuir and Freundlich equations for isotherm description (Huang et al., 2012; McGechan and Lewis, 2002; Vohla et al., 2011) and the first-order, Second-order and Elovich equations for the study of kinetic processes (Chien and Clayton, 1980; McGechan and Lewis, 2002; Özacar, 2003). The parameters obtained from these models provide a shorthand

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synopsis of P retention ability of a solid medium, such as maximum sorption capacity in the Langmuir equation and rate constants in the kinetic models.

From the shape of the apparent P sorption process, it is generally accepted that there are at least two stages: a fast sorption phase followed by a slower reaction rate for P. The explanations can be summarized as follows: (1) the two phases could be better regarded as belonging to a continuum, as both can occur simultaneously (Addiscott and Thomas, 2000; Ruttenberg and Sulak, 2011); (2) the fast process accounts for a higher proportion only for a relatively short time (almost instantaneously), and thereafter, slow sorption becomes the main sorption; (3) the fast process takes place at external surface sites and forms monolayer sorption; in comparison with fast sorption, slow sorption occurred in the interior of the particles (a depth below the surface of the particles) (McGechan and Lewis, 2002); and (4) the fast process is assumed to be reversible, whereas the slow process is largely irreversible (Makris et al., 2004; Ruttenberg and Sulak, 2011). The reasons for the two-stage sorption are well documented and can be ascribed to the following: (1) low-energy sites associated with the fast reaction where ligand exchange is believed to be the major sorption mechanism (Makris et al., 2004; Ruttenberg and Sulak, 2011); and (2) surface precipitation reactions, or intraparticle diffusion into micropores, related to the slow reaction (Barrow, 1983; Froelich, 1988; Makris et al., 2004).

The above phenomenological classification is based on pure observation and does not identify the point that leads to different sorption shapes. Therefore, identification of the sorption stages based on a quantitative method is still unclear. This is of particular importance in P sorption studies, where sorption stages are commonly used to ascertain P retention efficiency, which is used in land and water management decisions. To better characterize the changes in the P sorption rate of solid materials, researchers have presented models to describe the time-dependent sorption process. Van der Zee and Van Riemsdijk (1991) described fast sorption based on the differential form of the Langmuir model; Hansen et al. (1999) proposed a piecewise function to fit the experimental data; Barrow (1974) described the slow reaction effect with an empirical rate equation, in which the Arrhenius equation was applied to quantify the coefficients. As stated by McGechan and Lewis (2002), the complexity and parameters, which are unknown for many soils, have limited the applicability of the above models. Instead, the Langmuir, Freundlich, first-order, second-order and Elovich kinetic equations are simple forms and widely used (Cucarella and Renman, 2009; Özacar, 2006, 2003). Can we use these simple models to quantitatively distinguish sorption stages? A few researchers have introduced a method to separate the sorption stages by plotting the logarithm of dissolved phosphorus concentrations against time, each of which had a distinct slope representing a specific sorption stage (Appan and Wang, 2000; Lai and Lam, 2009). Nevertheless, a transformation of data required for linearization can result in differences in fitted parameters between linear and non-linear regression due to modification of the error structure, and therefore, transformation of the models is not recommended by many researchers (Bolster, 2008; Bolster and Hornberger, 2007; Schulthess and Dey, 1996). More importantly, the divided criteria of the adjacent lines were not reported by these authors. Without an exact algorithm to find the change points, the standard would be arbitrarily set and the results can often not be compared and misleading.

How can we divide the two sorption stages more accurately? Based on the shape of the sorption curve, the point with the most bending could be used for this purpose. Thus, the discrimination of sorption stages would be reduced to finding the maximum curvature in the sorption curve. Here, a qualitative approach will be

replaced by a quantitative study using mathematical methods to solve curvature. According to the mathematic form of the Langmuir, Freundlich, first-order, second-order and Elovich equations, all of these functions have a second-order derivative and thus have curvature, in theory.

In this study, we will use the concept of curvature to determine the change points that are used to discriminate each stage of the sorption process. Based on the most widely used models, the objective of this study is to determine the sorption stage by finding maximum curvature value points (MCVP). This will enable us to better understand P distribution in soil and sediment and the optimum time to renew filter material for higher P removal efficiency.

## 2. Theory and method

### 2.1. Equilibrium models of sorption

The most popular Langmuir and Freundlich isotherm models have found successful application in many real sorptions (Fitter and Sutton, 1975; Mead, 1981; Olsen and Watanabe, 1956). To separate different stages in these two models, a lumped analysis of the function form is presented below.

#### 2.1.1. Langmuir model

The widely used Langmuir isotherm (Cucarella and Renman, 2009; McGechan and Lewis, 2002; Özacar, 2006) is expressed as:

$$Q = Q_m \left( \frac{k_L C_e}{1 + k_L C_e} \right) \quad (1)$$

where  $Q$  is the sorption amount at equilibrium concentration  $C_e$ ,  $Q_m$  corresponds to the maximum sorption capacity (saturation), and  $k_L$  is the Langmuir coefficient.

#### 2.1.2. Freundlich model

The well-known Freundlich isotherm (Fitter and Sutton, 1975; Huang et al., 2012; Tellinghuisen and Bolster, 2010) is often used for heterogeneous surface energy systems. The Freundlich equation is given as:

$$Q = k_F C_e^{1/n} \quad (2)$$

where  $k_F$  is the Freundlich constant and  $n$  is the Freundlich exponent.

### 2.2. Kinetic models of sorption

Sorption equilibrium is a description of dynamic balance at the interface of adsorbents and solution. From the kinetic analysis, the P sorption rate, which determines the reaction time required for completion of the sorption reaction, may be computed.

#### 2.2.1. First-order kinetic model

Phosphorus sorption could be described by the first-order equation (Özacar, 2006, 2003). The differential equation is the following:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where  $q_t$  and  $q_e$  are the amounts of phosphorus adsorbed at time  $t$  and at equilibrium, respectively, and  $k_1$  is the rate constant of first-order sorption.

After integration by applying the boundary conditions  $q_t = 0$  at  $t = 0$ , Eq. (3) changes to

$$q_t = q_e - q_e \exp(-k_1 t) \quad (4)$$

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