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New models for kinetics and equilibrium homogeneous adsorption

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ABSTRACT

8 new models, named respectively LK 1, LK 2, LK 3, LEq 1, LEq 2, LEq 3, LEq 4 and LEq 5 are suggested to describe the kinetics and the equilibrium of a homogeneous adsorption. The models, more general than the existing ones, are very useful to describe the different kinetics and isotherms experimental behaviour of many adsorbents. In these new methods, the adsorption is decomposed in 1 or 2 steps, each step following an n order kinetics. The models have scientific, logical and chemical understanding meaning. Some (LK 1, LK 3, LEq 2, LEq 4) can predict the maximum adsorption capacity Q_{max} . LEq 1 and LEq 2 models permit to make the link between the kinetics and the equilibrium results and determine the order of reaction for both the adsorbent and the adsorbate, then, increasing the knowledge of the sorption parameters.

The kinetics and the equilibrium of the adsorption of lead by a commercial activated carbon are studied and these new models are used to fit the experimental data. The kinetics and the equilibrium parameters are determined. The fitting of the kinetics results are compared to those obtained with other existing models, idem for the equilibrium results. Regression results show that the new equilibrium models better fit the experimental data than the existing ones for this sorption process.

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1. Introduction

Many processes exist to purify polluted water: precipitation, membrane technology and adsorption. Adsorption is a simple, an efficient and an economic technic to remove them from waters.

For a part, adsorption kinetics (extent of sorption in function of time) is the most important information in an adsorption process. The kinetics parameters are essential to understand the process, to study the adsorption equilibrium and to design the adsorption equipment.

An adsorption process takes place in 3 steps, first the diffusion of the adsorbate to the adsorbent, then the diffusion of

the adsorbate in the interior of the adsorbent and finally the adsorption itself.

Many models exist to describe the kinetics of adsorption in batch mode when adsorption is considered to be the slowest phase in the adsorption process. The pseudo first order model (Lagergren, 1898), the pseudo second order model (Ho et al., 1996), the pseudo n order model (Ritchie, 1977), the Elovich model (Elovich and Larinov, 1962) and the kinetic Langmuir model (Langmuir, 1918) are ones. Note that in all these cited models, except the Elovich one, the sorption sites are considered to be homogeneous.

The selected model must fit precisely the experimental data to determine the kinetic parameters representative of

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Nomenclature

k_1'	rate constant in the step 1 for reaction 1
k_1	pseudo rate constant in the step 1 for reaction 1
k_{-1}	rate constant in the step 1 for reaction –1
k_2	rate constant in the step 2 for reaction 2
k_{-2}	rate constant in the step 2 for reaction –2
m, m'	partial order for the adsorbate
n, n'	partial order for the adsorbent
K_1	equilibrium constant in the step 1
K_2	equilibrium constant in the step 2
t	time (s)
Q	amount of adsorbent adsorbed at the moment t (mg g^{-1})
Q_{eq}	amount of adsorbent adsorbed at equilibrium (mg g^{-1})
C_t	concentration of adsorbate at the moment t (mg L^{-1})
C_{eq}	concentration of adsorbate at equilibrium (mg L^{-1})

the adsorption process studied and use them after. However, these previously cited models cannot describe all the kinetics behaviours encountered in adsorption. Moreover, with the progress in computer simulation, it is now possible to solve complex kinetics equations being more suitable to represent more precisely an adsorption process.

So, one objective of this paper is to suggest new kinetics equations, when adsorption is the slowest phase in the adsorption process, usable to describe a homogeneous adsorption process in batch mode.

For another part, the study of equilibrium (extent of sorption at the end of the process in function of the quantity of pollutant) is necessary in an adsorption process and permits to know the final state of the process. One of the definitions of adsorption equilibrium is a state of dynamic equilibrium where both adsorption and desorption rates are equal, then new isotherm models can be suggested from the expression of the new kinetics models. Then, presenting new equilibrium models for homogeneous adsorption derived from the new kinetic models is another objective of this paper.

Finally, these new models must be validated by tests with real adsorption experiments. The last objective of this paper is modelling the adsorption of lead by an activated carbon from Coconut shells using these new and efficient kinetics and equilibrium models of homogeneous adsorption, quantifying the kinetics and the equilibrium parameters of these new equations and comparing the new models with already existing models.

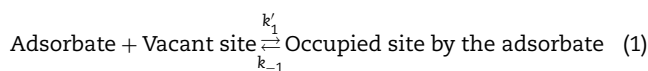
2. The one step models

The one step models assume only one step in the adsorption process according to Eq. (1).

If assuming chemisorption is the lowest rate process, the adsorption reaction takes place between the adsorbate and a vacant site of the adsorbent and leads to the formation of an occupied site by the adsorbate. All the sorption sites are considered to be homogeneous.

At the beginning of the sorption reaction, the active sites are free and their number is relative to the maximum capacity of adsorption of the adsorbent, that is to say Q_{max} .

The progress table of the adsorption reaction is given via Eqs. (2)–(4).



$$t = 0 \quad C_0 \quad Q_{\text{max}} \quad 0 \quad (2)$$

$$t \quad C_t \quad Q_{\text{max}} - Q \quad Q \quad (3)$$

$$t_{\text{eq}} \quad C_{\text{eq}} \quad Q_{\text{max}} - Q_{\text{eq}} \quad Q_{\text{eq}} \quad (4)$$

The differential equation obtained according to the table progress is:

$$\frac{d(Q)}{dt} = k_1'(C_t)^m(Q_{\text{max}} - Q)^n - k_{-1}(Q)^n \quad (5)$$

If considering C_t constant, the equation becomes:

$$\frac{d(Q)}{dt} = k_1(Q_{\text{max}} - Q)^n - k_{-1}(Q)^n \quad (6)$$

2.1. The kinetics models

2.1.1. The already existing models

Assuming a first order for reaction (1): that is to say $n=1$ and neglecting reaction (–1) (then, the adsorption is considered irreversible and concerns only one site per adsorbate), the Eq. (6) changes in Eq. (7):

$$\frac{d(Q)}{dt} = k_1(Q_{\text{max}} - Q)^1 \quad (7)$$

The resolve of the Eq. (7) leads to the well-known pseudo first order equation (Lagergren, 1898) given in Table 1.

Resolving the Eq. (6) by assuming a second order for reaction (1): that is to say $n=2$ and neglecting reaction (–1) (irreversible reaction using 2 adsorption sites per adsorbate) leads to the famous pseudo second order equation (Ho et al., 1996) as written in Table 1.

The calculus of the differential Eq. (6) by assuming an n order for reaction (1) and neglecting reaction (–1) leads to the pseudo n order equation (Ritchie, 1977) given in Table 1. Then the adsorption is irreversible and uses n sites.

Taking account a first order for reaction (1) and (–1), the Eq. (6) changes in Eq. (8):

$$\frac{d(Q)}{dt} = k_1(Q_{\text{max}} - Q) - k_{-1}Q \quad (8)$$

The resolving of the Eq. (8) leads to the Langmuir kinetic equation (Langmuir, 1918) and the result of the differential equation is given in Table 1. The theoretical foundation of the Langmuir model is that the adsorption is then reversible and uses only one vacant site per adsorbate.

2.1.2. The new models

Other new kinetics equations can be obtained by resolving the Eq. (6) taking account a second order ($n=2$) for reaction (1) and (–1) or an n order for the both reactions. These new equations are named respectively LK 1 and LK 2 models.

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