Critical of linear and nonlinear equations of pseudo-first order and pseudo-second order kinetic models

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Abstract

The experimental adsorption equilibrium of Cd(II) onto chitosan (Cd(II)/CS) and methyl orange onto bentonite (MO/Bt) were studied in batch adsorption experiments at room temperature for an initial concentration of 236.5 mg/L for Cd (II) (pH = 5) and 33 mg/L for MO (pH = 3). The adsorption rate increases rapidly for t < 30 min, and the equilibrium is reached after this contact time for both systems. The values of the experimental maximum amount of Cd(II) and MO adsorbed are $q_e = 56.70$ and 56.55 mg/g for Cd/CS and MO/Bt, respectively. The obtained experimental data were analysed using the linear and the nonlinear forms of pseudo-first and pseudo-second order kinetic models (LPFO, NLPFO, LPSO, NLPSO). The appropriate model to describe the adsorption kinetics of each system was determined based on the comparison of R^2 and the standard deviation Δq (%). It was found that the adsorption process of Cd(II)/CS followed NLPFO and that of MO/Bt can be described by both of NLPSO and LPSO. The results show that the nonlinear forms (NLPSO and NLPFO) are suitable for describing the kinetics adsorption reactions in the liquid phase and the LPSO ($q_t = f(1/t)$ model can also be suitable for some systems, depending on the experimental conditions. Because of q_t values, determined from these models correspond well to the experimental data as confirmed by the error analysis values of R^2 and Δq (%), it is noticed that the determination of R^2 alone is insufficient to decide among the kinetic models.

1. Introduction

Environmental degradation due to the release of different pollutants into receiving environments by industrial and agricultural activities has become of great importance. Thus, to maintain our environment in

a good condition, industrial wastewater must be treated before it is discharged. Among several methods cited in the literature for treatment of wastewaters [1—3], the adsorption is the most widely used method, in comparison to other ones, to eliminate both organic and inorganic pollutants [4,5], because it has several advantages regarding cost, efficiency and ease of use [6,7]. Generally, whatever the nature of the used adsorbents and the pollutants to be treated, the adsorption process is always controlled by two important aspects: kinetics and thermodynamics. In order to better

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Nomenclature

C_0	Initial concentrations in liquid solution $(mg.L^{-1})$
C_e	Equilibrium concentrations in liquid solution $(mg.L^{-1})$
q_e	Amount adsorbed at equilibrium $(mg.g^{-1})$
q_t	Amount adsorbed at time t $(mg.g^{-1})$
V	Volume of the solution (L)
m_{ads}	Mass of the adsorbent (g)
$q_{t,exp}$	Adsorbed amounts experimental
$q_{t,cal}$	Adsorbed amounts calculated
k_n	Rate constant for a kinetic with order n
k_1	Rate constant for a kinetic of the pseudo first order (min^{-1})
k_2	Rate constant for a kinetic model of pseudo second order $(g.mg^{-1}.min^{-1})$
t_{eq}	Equilibrium time (min)
NLPFO	Nonlinear pseudo first order model
LPFO	Linear pseudo first order model
NLPSO	Nonlinear pseudo second order model
LPSO	Linear pseudo second order model
SD	Standard deviation

understand the interactions between adsorbents and adsorbates at equilibrium, several parameters (q_t: adsorbed amount, t_{eq}: equilibrium time, q_e: adsorbed amount at equilibrium, and E_a: activation energy) were, thus, determined, using various kinetic and isothermal models, especially those of Lagergren, and Blanchard et al. (1984) and Ho for pseudo-first order (PFO) and pseudo-second order (PSO), respectively [8–10]. Langmuir and Freundlich models [11,12], which are based on the solution concentration, were commonly used to describe adsorption isotherms.

In most cases, the kinetic and the isothermal parameters were deduced by a simple confrontation of the experimental data with the linearized equations of these models. Accordingly, the constants can be obtained from the slope and the intercept of a straight t line plot, and the appropriate model which fits the experimental data is the one whose coefficient of determination (R^2) is close to the unity. However, several articles related to this field [13–17], have shown that the incorrect application of the linear equations for the kinetic models of PFO and PSO lead to the erroneous values of the intrinsic kinetic parameters. This problem was related to the various used mathematical expressions and to the unknown value of q_e [14,18]. Plazinski et al. [19] portrayed that PSO's

wide applicability over PFO does not necessarily stem from a physical basis, but from a mathematical one. On the other hand, The PFO model has been demonstrated to be valid only at the initial stage of adsorption [20].

Similarly, in the case of adsorption isotherms, criticisms have been reported concerning the application of the linear equations of the Langmuir and Freundlich isotherms, which are the most often used to predict the maximum adsorption capacity (q_m) at equilibrium and the affinity of the adsorbents for the adsorbates. Vasanth Kumar and Sivanesan [21] recommended that the use of equilibrium data covering the complete isotherm was the best way to obtain the parameters in isotherm expressions; equilibrium data with a partial isotherm was insufficient. Moreover, for the best fit of experimental kinetic and isotherm data, both in batch and column experiment or in other systems involving the transfer of fluids, several studies [22–28] have displayed that the application of the nonlinear method is more suitable than the linear one [22,23,29–35], because it allows a better adjustment of the different parameters. Recently, the inconsistencies of linearized forms of different models, and their negative impact on parameter values, involved in the liquid phase adsorption process were reviewed [14,29].

The aim of this work is to compare the two forms of the usually used kinetic models (PFO and PSO) for a better interpretation of batch adsorption experiments of Cadmium (Cd (II)) onto chitosan (CS) and methyl orange (OM) onto bentonite (Bt). The results were discussed to support the different criticisms appeared in literature concerning these two models.

2. Experimental part

2.1. Material and methods

The chitosan used in this study was obtained from the deacetylation of chitin extracted from shrimp shells collected in Morocco. Its degree of deacetylation is 76% as it was described in the previous work [36]. Bentonite was purchased from Rhône-Poulenc (France) and used without any pre-treatment. The salt $Cd(NO_3)_2$ was purchased from Across Organics (USA) and methyl orange (99%) from Fisher Scientific International Company. All working concentrations of solutions of each pollutant were prepared with distilled water.

A mass m = 0.1 g of each adsorbent, CS or Bt, was first mixed with V = 20 mL of a synthetic solution of $Cd(NO_3)_2$ or MO, with initial concentrations C_0 = 236.5 and 33 (mg/L) respectively. Then, the mixture was agitated during a given contact time t and