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Extension of classical adsorption rate equations using mass of adsorbent: A graphical analysis

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ABSTRACT

A simple and interesting method is presented for analyzing the effect of adsorbent mass on the rate of adsorption process. In this approach, a graphical method is applied for determination the adsorbent mass order in the rate equation. The proposed analysis is according to the plot of the normalized adsorbed amount $\frac{q_e-q}{q_e}$, versus the normalized time scale $t[m]^n$. In comparison with the limited available methods for describing the adsorbent dosage effect on the adsorption rate, this method needs fewer experiments. The classical adsorption kinetic models were extended by considering mass of adsorbent which provides unique rate coefficient for all experiments.

1. Introduction

Surface reactions play critical roles in a wide range of the industrial applications, involving: petroleum, oil, wastewater treatment and so on [1]. The knowledge of kinetic of these reactions is a paramount of importance in design and operation of the chemical reactors. Therefore, it is really vital and significant to find a simple method to investigate the kinetic of these reactions [2]. Blackmond et al. presented a graphical method RPKA (reaction progress kinetic analysis), for analysis of kinetic of the surface catalytic reactions [3,4]. Recently, Burés presented an interesting graphical approach to find the catalyst order in a catalytic reaction [5]. Although, adsorption is mechanistically different with the catalytic surface reactions, it can be considered as another noticeable and important example of the surface reactions [6–9]. A systematic search among the published articles shows that there are more than twenty thousand research papers about kinetic of adsorption. Although, there are a lot of studies, which tried to explain kinetic of adsorption [10–16], a little attention has been given to the very important parameter i.e. the adsorbent concentration. Only some studies have been devoted to the detailed analysis of the adsorbent dosage effect on kinetic of adsorption [17]. Ho and McKay proposed an empirical complex function to show how the adsorbent dosage affects the rate of adsorption [5].

The aim of this study is to introduce a simple graphical method to determine the order of the adsorbent dosage in the adsorption rate equation. By finding the order of the adsorbent dosage, it is possible to extend the classical adsorption rate equations. Therefore, the mass of adsorbent can be one of the descriptive parameters of kinetic of adsorption.

2. Result and discussion

2.1. Normalized time scale approach

The analysis of kinetic of adsorption is often according to the investigation of the change of the adsorbed amount with time as follow:

$$\frac{dq}{dt} = kf(q) \tag{1}$$

where q is the amount of the adsorbed species per unit mass of the adsorbent, and t is the reaction time. Moreover, k is the rate constant and $f(q)$ is a function of q. It should be noticed that the most popular forms of $f(q)$ are $(q_e - q)$ and $(q_e - q)^2$ in pseudo first order [18] and pseudo second order [17,19] models, respectively, where q_e is the equilibrium value of q. Other forms of $f(q)$ have been reported too [20–25]. Although it experimentally has been proven that the mass of adsorbent affects the rate of adsorption [5], up to now, no explicit function has been introduced in the adsorption rate equation. So, by inspiration of the rate equation for the catalytic reactions, we can introduce the adsorbent dosage effect on the rate equation as follow:

$$\frac{dq}{dt} = kf(q)[m]^n \tag{2}$$

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where $[m]$ is mass of the adsorbent and n is its order. Since, in most rate equations, $f(q)$ is proportional to $(q_e - q)$, and by consideration of this fact that q_e is a constant parameter, Eq. (2) can be rewritten as:

$$\frac{-d(q_e - q)}{dt} = k(q_e - q)^{\alpha}[m]^n \tag{3}$$

where α is the order of adsorption [21,26]. As will be shown later, the basis of our graphical approach for finding the adsorbent mass order (n), is that the variable of the rate equation is a function of the normalized time scale $t[m]^n$. As can be seen in supplementary material file, the variable of Eq. (3), $(q_e - q)$, is a function of the normalized time scale, $t[m]^n$, but the plot of $(q_e - q)$ versus $t[m]^n$ at different adsorbed dosages starts from different points (Fig. S1). Therefore, it is not possible to find (n) by applying the data of this plot. In order to solve this problem, the $(q_e - q)$ variable of the rate equation has been normalized to $(q_e - q)/q_e$, and so Eq. (3) changes to:

$$-\frac{d\left(\frac{q_e - q}{q_e}\right)}{dt} = k\left(\frac{q_e - q}{q_e}\right)^{\alpha}[m]^n \tag{4}$$

For different values of α, the normalized adsorbed amount $(q_e - q)/q_e$ is a function of the normalized time $t[m]^n$.

In the plot of the normalized adsorbed amount $(q_e - q)/q_e$ versus the normalized time scale $t[m]^n$ at different adsorbent dosages, all curves start from the same point, and it is possible to find the order of the adsorbent easily, as will be described later. In our proposed method, the normalized adsorbed amount, in terms of $(q_e - q)/q_e$, has been plotted versus the normalized time, $t[m]^n$. This method is according to the recent work of Burés which investigates the catalyst concentration effect on the catalytic reactions rate [3]; any point of time is multiplied by the used dosage of the adsorbent (or catalyst) which is raised to an arbitrary power. The value of this power is changed until the curves overlay.

The reason for overlaying of the curves is this fact that the mass of adsorbent affects on the time of adsorption (by increasing the effective mass of adsorbent the time of adsorption decreases). Therefore the reduced time (t) is compensated by increased effective mass $[m]^n$ and therefore the normalized time scale, $t[m]^n$, is the same for all sets of experiments.

In the following part, it is shown that how this approach is capable to find the order of the adsorbent in rate equation. At first, it

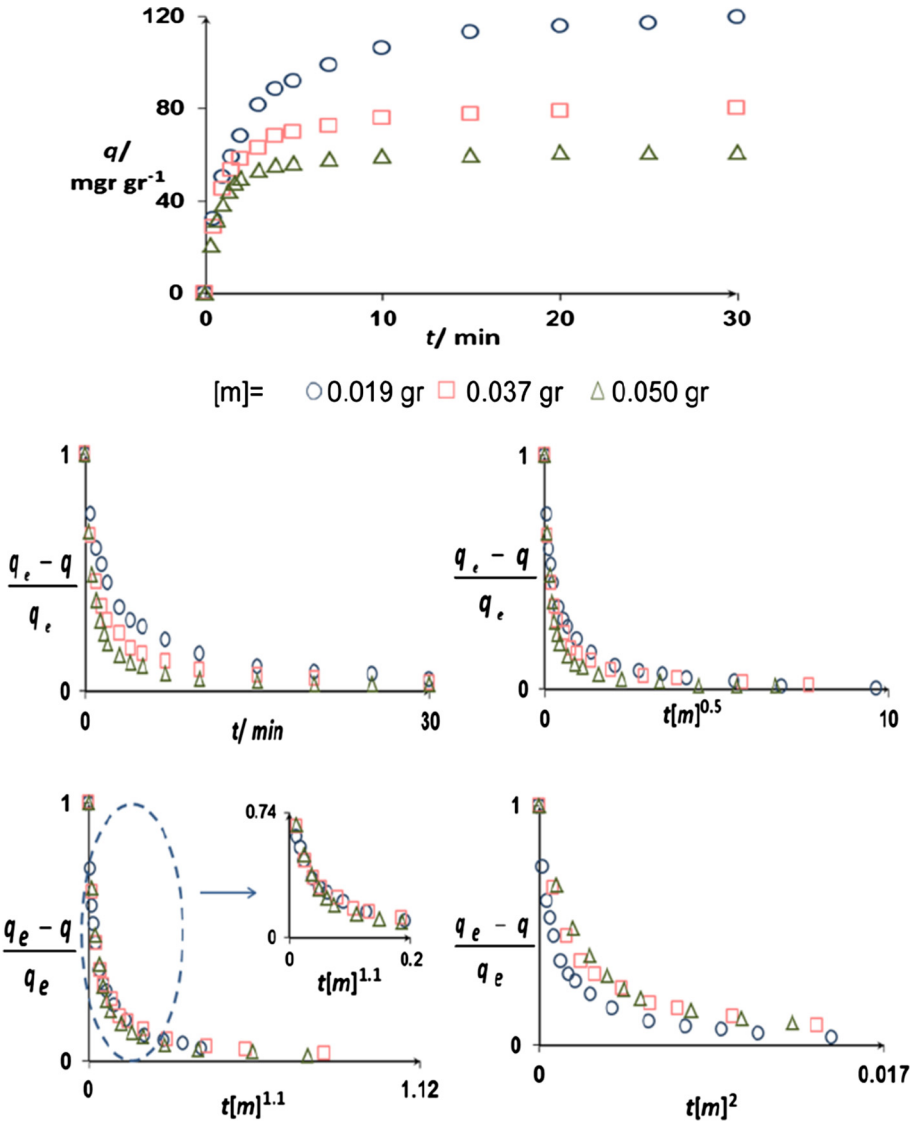

Fig. 1. The application of graphical method to find the order of the adsorbent mass in adsorption of DBT on to ACC. (a) The variation of the adsorbed amount of DBT (500 ppm) on different dosages of AAC as a function of time. (b) The adjustment of the adsorbent order, which brings the curves to overlay.