Chemical Engineering Journal 146 (2009) 370–376

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents

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ARTICLE INFO

Article history:
Received 27 October 2006
Received in revised form 2 June 2008
Accepted 21 June 2008

Keywords:
Adsorption
Isotherm models
Linear and non-linear regression
Microporous polymeric adsorbents
Adsorption kinetics

ABSTRACT

Adsorption mechanism of a natural compound, alizarin (1,2-dihydroxyanthraquinone), onto three types of microporous polymeric adsorbents (XAD-4, XAD-7, XAD-16) has been proposed using Langmuir, Freundlich and Redlich–Petersen isotherms. Adsorption capacity and optimum adsorption isotherms were predicted by linear least squares and non-linear regression method. Adsorption kinetics was proposed by pseudo-first and second second order models. The adsorption capacity of XAD-16 was the highest at 0.0424 mg/mg, with initial alizarin concentration of 200 mg/L. Pseudo-second-order kinetics was more appropriate in explaining the adsorption mechanism than pseudo-first-order. Over the studied concentration ranges, only XAD-4 adsorption can be reasonably described by the three isotherms. XAD-16 data is only best-fitted to Langmuir and Redlich–Petersen isotherms. Non-linear method proved a better way to predict the equilibrium isotherm parameters. The combination of parameters, such as specific surface area, pore diameter, polarity of the network of the resins, the solubility and polarity of the adsorbate, are the significant parameters for optimum adsorption process.

1. Introduction

Adsorption process involves separation of a substance or adsorbate from one phase, followed by its accumulation onto the surface of the adsorbing phase or adsorbent [1,2]. The sorption ability of different sorbents is strongly dependent on the available surface area, polarity, contact time, pH and the degree of hydrophobic nature of the adsorbent and adsorbate [3,4]. Equilibrium condition is attained when the concentration of the solute remains constant, as a result of zero net transfer of solute adsorbed and desorbed from adsorbent surface. The equilibrium adsorption isotherms describe these relationships between the equilibrium concentration of the adsorbate in the solid and liquid phase at constant temperature [1–3], and also propose the involved interactive forces in the process.

As the isotherm indicates the adsorption capacity of the sorbent, it enables the evaluation of adsorption performance, the involved mechanisms, and parameters to be improved, which are of critical importance in optimizing the use of the adsorbents [2,5]. The prediction of adsorption kinetics is also necessary for the design of sorption systems. While chemical kinetics explains the rate of chemical reaction and the factors affecting the reaction rate, measurement of sorption rate constants could evaluate the basic qualities of a good sorbent such as the time required for a sorbent to remove particular compounds or the efficacy of the sorbents. Pseudo-first- and second-order models are the most common models being used to explain the adsorption kinetics [3,6].

The analysis of experimental equilibrium data by fitting into different isotherm models is an important step to propose suitable model for process design [1]. The most widely applied isotherms for data modeling are the Langmuir and Freundlich, which are developed based on thermodynamic equilibrium [7–9]. Other empirical adsorption models are the Redlich–Petersen [10] and Radke and Prausnitz isotherms [11]. Non-linear method has been suggested a better way to obtain the equilibrium isotherm parameters, but linear regression is most frequently used to investigate the most fitted isotherm [12]. Depending on the way the isotherm equations are linearized, the error distribution changes can either be the best or the worst [13].

In this study, a theoretical model (Langmuir isotherm) and two empirical models (Freundlich and Redlich–Petersen isotherms) were utilized to describe the adsorption of a natural compound, alizarin (1,2-dihydroxyanthraquinones), onto three types of Amberlite polymeric adsorbents—XAD-4, XAD-7 and XAD-16. Anthraquinones (AQs) are natural products that occur in higher plants especially in Rubiaceae family, and also in bacteria, fungi and lichens. AQs and alizarin are used in the production of dyes, and have been reported to exhibit interesting bioactivities, such

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doi:10.1016/j.cej.2008.06.018

Table 1
Typical properties of Amberlite polymeric adsorbents

Adsorbent	Chemical nature	Polarity	Surface area (m^2/g)	Average pore diameter (Å)
XAD-4	Polystyrene-divinylbenzene	Non-polar	725	40
XAD-7	Methylacrylate ester	Intermediate polarity	450	90
XAD-16	Polystyrene-divinylbenzene	Non-polar	800	100

as antimicrobial, antifungal, hypotensive, analgesic, antimalarial, antioxidant, antileukemic and mutagenic activities [14]. Alizarin is used as a reference compound in the spectrophotometric determination of AQs contents from *Morinda elliptica* cell culture [15]. The adsorption capacity and the optimum equilibrium adsorption isotherm parameters for adsorption of alizarin onto XAD-4, XAD-7 and XAD-16 were estimated by linear least squares and a trial and error non-linear method using Langmuir, Freundlich and Redlich–Petersen isotherms. A comparison was made between these two methods of estimating the isotherm parameters. The adsorption kinetics was proposed based on pseudo-first- and second-order models.

2. Materials and methods

2.1. Adsorbents

Amberlite polymeric adsorbents, XAD-4, XAD-7 and XAD-16 resins (Rohm and Haas Inc., USA), were dried overnight in an oven at 70 °C. The adsorbents were left in a desiccator to reach ambient temperature before sieving to sizes 0.1 cm × 0.1 cm to obtain uniform size distribution. The properties and characteristics of these adsorbents are reported in Table 1.

2.2. Adsorption equilibrium study

The binding capacity of each adsorbent was determined using 0.1 ± 0.02 g adsorbent/30 ml solution of Alizarin in Erlenmeyer flasks. Alizarin was dissolved in dichloromethane to achieve concentration range 20–200 mg/L. The flasks were sealed airtight with aluminium foil and shaken on an orbital shaker (120 rpm) at 24 ± 2 °C. From contact-time experiment, the equilibrium condition was reached within 7–9 h. The pH of the solution throughout the experiment was found consistent at pH 6.5. Adsorbents were incubated in 30 ml alizarin solution at respective concentration. The concentration of alizarin before incubation and at equilibrium was determined spectrophotometrically (Jenway 6300, UK) at 420 nm. The adsorption capacity, q_e (mg/mg), was calculated using

$$q_e = \frac{V_i C_i - V_e C_e}{W} \tag{1}$$

where C_i and C_e are the initial concentration and concentration at equilibrium (mg/L), respectively. V_i and V_e are the initial volume and equilibrium volume (L), respectively, and W is the mass of adsorbent (mg).

The adsorption efficiency was calculated as follows [1]:

$$\text{Adsorption (\%)} = \frac{A_0 - A}{A_0} \times 100 \tag{2}$$

where A_0 and A are the initial and final absorbance (nm) of the solution, respectively.

2.3. Adsorption kinetics

In order to observe the sorption process of alizarin onto the adsorbents, two kinetic models, pseudo-first- and second-order models, were proposed.

2.3.1. Pseudo-first-order Model

The pseudo-first-order equation can be written as

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3}$$

where q_t (mg/g) is the amount of adsorbate absorbed at time t (min), q_e (mg/mg) is the adsorption capacity in equilibrium, and k_f (min^{-1}) is the rate constant for pseudo-first-order model. After integration and by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_f t}{2.303}\right) \tag{4}$$

2.3.2. Pseudo-second-order Model

The pseudo-second-order model can be presented in the following form:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{5}$$

where k_s is the rate constant of pseudo-second-order model (in g/mg min). By definite integration of Eq. (5) for boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$, the following form of equation is obtained:

$$\frac{t}{q_t} = \frac{1}{(k_s q_e^2)} + \left(\frac{1}{q_e}\right) t \tag{6}$$

The initial sorption rate constant, h (mg/g min), at $t = 0$ can be defined as

$$h = k_s q_e^2 \tag{7}$$

2.4. Adsorption isotherm models

The equilibrium adsorption of alizarin onto XAD-4, XAD-7 and XAD-16 resins was analysed using Langmuir, Freundlich and Redlich–Petersen isotherms.

2.4.1. Langmuir isotherm

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites. It is originally developed to represent chemisorption on a set of distinct, localized adsorption sites. Langmuir has developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface due to the pressure of the gas. The equation is applicable to homogeneous adsorption where adsorption process has equal activation energy, based on the following basic assumptions:

(i) molecules are adsorbed at a fixed number of well-defined localized sites,
(ii) each site can hold one adsorbate molecule,
(iii) all sites are energetically equivalent,
(iv) there is no interaction between molecules adsorbed on neighbouring sites.

The general Langmuir equation is as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{8}$$