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Prediction of arsenic breakthrough in a pilot column of polymer-supported nanoparticles

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ABSTRACT

Adsorption is an important process for arsenic removal from drinking water supplies. Fixed bed column processes are the preferred mode of operation owing to their simplicity and proven performance. Mathematical models can facilitate the design and optimization of fixed bed adsorbers. For systems exhibiting linear isotherm behavior over the relevant concentration range, their performance can be predicted using models that are amenable to analytical solutions. The predictive utility of an asymptotic solution of the homogeneous surface diffusion model (HSDM) and an approximate solution of a linear driving force model (LDFM) under linear isotherm approximation was evaluated in this study. A previously published pilot test on arsenic breakthrough in a fixed bed adsorber of polymer-supported nanoparticles was modeled. Model parameters were estimated on the basis of some easily determined batch measurements. The pilot test yielded 27,000 bed volumes at 10 μg/L arsenic. The two analytical solutions predicted 24,200 and 27,100 bed volumes. Despite the simplicity of the HSDM and LDFM solutions, their predictions agreed well with the experimental data. These analytical solutions are very straightforward, easy to apply, and provide acceptable modeling power.

1. Introduction

Adsorption processes offer an efficient means for arsenic removal from contaminated drinking water. Their performance depends in large parts on the nature of the selected adsorbent [1,2]. In recent years several types of polymer-based nanoadsorbents have been synthesized for environmental applications [3–5]. For example, polymer supports impregnated with different types of nanoparticles have proven to be efficient adsorbents for the removal of arsenic from contaminated water [6–13]. These hybrid nanoadsorbents offer the benefits of excellent mechanical strength, favorable adsorption capacity and kinetics, no back-washing requirement under normal operating conditions, and regenerability. Commercial polymer beads impregnated with nanoparticles of iron oxide/hydroxide for the removal of arsenic from drinking water include ArsenX^{np} and Lewatit FO 36.

ArsenX^{np} is a hybrid nanoadsorbent developed by SolmeteX [8]. It consists of hydrous iron oxide nanoparticles impregnated into a polystyrene-based strong base anion exchange resin (~25% iron dry weight). The particle size for ArsenX^{np} ranges from 0.3 to 1.2 mm. The performance of ArsenX^{np} for removing arsenic from drinking water has been evaluated at several field test sites. For example, a pilot plant trial performed at Rio Rancho, New Mexico, USA, showed that no breakthrough was observed after about 33,000 bed volumes of water with arsenic concentrations between 16 and 23 μg/L were passed through a fixed bed column of ArsenX^{np} [8]. Another field test was performed at Chandler, Arizona, USA, treating water with arsenic concentrations between 12 and 13 μg/L. These rather low influent arsenic concentrations allowed ArsenX^{np} to maintain the effluent arsenic concentration below the WHO drinking water standard of 10 μg/L for about 80,000 bed volumes [8].

ArsenX^{np} has also been tested under field conditions by Sandia National Laboratories at a number of locations in New Mexico, USA. For example, at the town of Socorro Springs (influent arsenic = 40–45 μg/L), arsenic breakthrough to 10 μg/L was observed at about 27,000 bed volumes [14]. ArsenX^{np} performance data for water treatment systems with a lead-lag configuration [15] as well as point-of-entry (POE) and point-of-use (POU) devices [16] have been reported. Fixed bed columns of ArsenX^{np} operating in remote villages of West Bengal, India, ran for more than 20,000 bed volumes before breakthrough of 50 μg/L [17].

The commercial nanoadsorbent Lewatit FO 36 is marketed by LANXESS. It is a polystyrene-based weak base ion exchanger (mean bead size = 0.35 mm) that contains nanoparticles of iron oxide in its pores [18]. The iron content is about 15% by weight. Field test data

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suggest that the arsenic removal ability of Lewatit FO 36 was similar to that of ArsenX^{np} [18] but the former was more effective than the latter for the removal of arsenic from geothermal water [19].

Field pilot tests are the most accurate method to predict nanoadsorbent performance in fixed bed adsorbers. However, pilot testing is time consuming, requires large amounts of challenge water and incurs significant costs. As an alternative to pilot testing, mathematical models may be used to predict nanoadsorbent performance. A myriad of mathematical models with varying degrees of complexity have been proposed for the design, scale-up and optimization of fixed bed columns. In the field of water treatment, the homogeneous surface diffusion model (HSDM) has seen great success in predicting adsorption of organic contaminants on granular activated carbon [20,21]. Some success with the prediction of arsenic removal in fixed bed adsorbers using the HSDM has also been achieved [22–27].

If the adsorption isotherm is nonlinear, a numerical method is usually needed to solve the HSDM. However, in many cases it is possible to approximate the nonlinear isotherm by a linear isotherm over relatively low concentration ranges. Given that typical arsenic concentrations under field conditions are <100 μg/L, it is not uncommon for a fixed bed adsorber to operate within the linear range of a nonlinear isotherm. Under this condition, the breakthrough behavior may be predicted using fixed bed models with a linear isotherm approximation which permits the models to be solved analytically. This paper explores the feasibility of using an asymptotic solution of the HSDM and an approximate solution of a linear driving force (LDF) model under linear isotherm approximation to predict arsenic breakthrough in a pilot column packed with the commercial nanoadsorbent ArsenX^{np}. The benefit of using these analytical solutions is their tractability and the ease with which they can be programmed in Excel spreadsheets. So far, however, there has been little discussion on the use of the two analytical solutions examined here for predictive modeling. The predictive modeling approach utilizes equilibrium and kinetic information extracted from independent batch tests to provide a priori predictions of fixed bed breakthrough behavior.

2. Mathematical models

2.1. Fixed bed adsorber models

The homogeneous surface diffusion model (HSDM) has been used extensively to predict the performance of fixed bed adsorbers packed with porous media. Since this model has been reported in detail elsewhere [20,28], only a brief description is given here. The HSDM treats a porous adsorbent as a homogeneous matrix regardless of its porous structure. Two mass transport resistances are considered: film diffusion resistance in the fluid outside the adsorbent particle and surface diffusion resistance inside the adsorbent particle. The HSDM is given by

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \tag{1}$$

where D_s is the effective surface diffusion coefficient, q is the solid phase concentration of adsorbate at each radial position in the adsorbent particle, and r and t are the radial and time coordinates, respectively. A film transfer coefficient appears in one of the boundary conditions. The differential mass balance equation in the fixed bed adsorber can be written as

$$\frac{\partial C}{\partial t} + \nu\frac{\partial C}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_p\frac{\partial \bar{q}}{\partial t} = D_a\frac{\partial^2 C}{\partial z^2} \tag{2}$$

where C is the liquid phase adsorbate concentration, ν is the interstitial velocity, ε is the bed void fraction, ρ_p is the adsorbent particle density, $\bar{q}$ is the average concentration of adsorbate in the adsorbent, D_a is the axial dispersion coefficient, and z is the axial coordinate.

If the isotherm is nonlinear, Eqs. (1) and (2), together with proper initial and boundary conditions, are usually solved numerically. For linear isotherm systems, analytical expressions for the breakthrough curve may be derived. Eqs. (1) and (2), together with the assumptions of plug flow and linear isotherm ($q = KC$; K is Henry's constant), have been solved by Rosen [29]. Unfortunately, Rosen's full solution is not very tractable because it is given in the form of complicated integrals. In a subsequent paper, Rosen [30] derived an asymptotic solution from the full solution. If surface diffusion is the dominating transport resistance, Rosen's asymptotic solution for sufficiently large bed length is given by

$$\frac{C}{C_0} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\tau_R - \xi_R}{2\sqrt{\xi_R}}\right)\right] \tag{3}$$

In the above equation

$$\tau_R = \frac{15D_s}{R^2}\left(t - \frac{L}{\nu}\right); \quad \xi_R = \frac{15D_s\rho_p K}{R^2}\frac{L}{\nu}\left(\frac{1-\varepsilon}{\varepsilon}\right)$$

where C_0 is the adsorbate concentration in the feed solution, L is the bed length, R is the particle radius, and τ_R and ξ_R are dimensionless time and bed length, respectively. Here, we refer to Eq. (3) as the Rosen solution.

Several mathematically simpler versions of the HSDM have been proposed. For example, the linear driving force model (LDFM) proposed by Glueckauf and Coates [31] is frequently used to describe intraparticle diffusion. The LDFM is given by

$$\frac{d\bar{q}}{dt} = k(q^* - \bar{q}) \tag{4}$$

where q^* is the solid phase adsorbate concentration in equilibrium with the bulk solution and k is the effective LDF mass transfer coefficient. The LDFM lumps the rate limitations of intraparticle diffusion and external mass transfer into a single rate coefficient. With the assumptions of linear isotherm and negligible axial dispersion, Eqs. (2) and (4) have been solved by several researchers. Like Rosen's full solution of the HSDM, these analytical solutions are also rather complex. There have been several approximations proposed. One of the approximate solutions, proposed by Klinkenberg [32], is given below.

$$\frac{C}{C_0} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\sqrt{\tau_K} - \sqrt{\xi_K} + \frac{1}{8\sqrt{\tau_K}} + \frac{1}{8\sqrt{\xi_K}}\right)\right] \tag{5}$$

$$\tau_K = k\left(t - \frac{L}{\nu}\right); \quad \xi_K = k\rho_p K\frac{L}{\nu}\left(\frac{1-\varepsilon}{\varepsilon}\right)$$

where τ_K and ξ_K are dimensionless time and bed length, respectively. Eq. (5) is valid if the dimensionless bed length ξ_K is >2 [32]. Eq. (5) is referred to as the Klinkenberg solution in this paper.

2.2. Batch adsorber models

For adsorption in a batch adsorber, the HSDM (Eq. (1)) or LDFM (Eq. (4)) is solved in conjunction with the following mass balance equation, along with appropriate initial and boundary conditions.

$$m\frac{dq}{dt} = -V\frac{dC}{dt} \tag{6}$$

where m is the amount of adsorbent and V is the volume of solution. If the isotherm is linear, analytical expressions may be