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Two-phase homogeneous diffusion model for the fixed bed sorption of heavy metals on natural zeolites

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ABSTRACT

In this work, the fixed bed removal kinetics of Pb^{2+}, Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and Cu^{2+} from aqueous solutions on natural zeolites was studied. For this aim, a non-dimensional two-phase homogeneous solid diffusion model including axial dispersion and equipped with a universal double-selectivity equilibrium model is developed and applied. In total 9 isotherms, representing 128 experimental points and 25 breakthrough curves, representing 764 experimental points are used in modeling. The application of the model is satisfactory resulted in an average deviation from the experimental data of 11.19 ± 5.53%. The solid phase diffusion coefficients are between 10^{-7} and 10^{-9} cm^2/s depending on the metal, flow rate and particle size in the decreasing order of Cu > Fe, Cr > Zn, Pb > Mn. The study is supplemented by an extended literature review on fixed bed models and experimentally derived solid phase diffusion coefficients in zeolites.

1. Introduction

Industrial and, in lesser extent, municipal wastewater contains heavy metals many of which are toxic to humans and the environment and, therefore, treatment is required prior to disposal or recycling. Heavy metals contamination is of major concern as they are not biodegradable and tend to accumulate in living organisms and, through food chain, they present a threat to the environment and human life. Several established methods are available for the removal of metal ions from aqueous solutions, such as precipitation, membrane separations, adsorption and ion exchange. Adsorption and ion exchange processes are prevailing technologies utilized across different industries and they are of particular importance in water and wastewater treatment [1]. This is especially true for heavy metals removal using natural minerals such as zeolites and clays [2,3]. Zeolites are hydrated aluminosilicate minerals with interconnected pores with a cage-like structure that offers a large surface area for sorption. Clinoptilolite is the most abundant natural zeolite with open structure and easy access, formed by open channels of 8–10 membered rings. These channels are occupied by ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} that can be exchanged with other metal ions such as Mn^{2+}, Cr^{3+} and Zn^{2+}.

Most ion exchange and adsorption processes, both at the laboratory and plant scale, are performed in fixed beds. A solution is continuously passing through a bed of solid material and the composition of the effluent depends on the properties of the solid, the composition of the feed and the operating conditions. The exit concentration versus time (or effluent volume) is called breakthrough curve and is used to study the process [4]. Fixed bed experiments are time consuming and can be costly, and thus modeling and simulation are frequently used as alternatives for predicting the dynamic behavior of fixed bed systems and to optimize the design [5]. The simulation of adsorption and ion exchange processes is challenging. Adsorption in a fixed-bed is an unsteady-state process evaluated by examining the breakthrough curve. Several mathematical models have been developed to describe fixed bed processes that require solving a system of coupled partial differential equations (PDEs) representing material, energy, and momentum balances supplemented by mass transfer rate equations, equilibrium isotherms and the appropriate initial and boundary conditions. The solution of such a complicated system is difficult and the use of simplified models, capable of satisfactorily predicting fixed bed behavior, is an attractive alternative [6]. However, these simplified models are rough approximations that describe the derived experimental data only mechanistically and under very specific operating conditions, while they fail to provide useful insights into the mechanisms involved [7].

Concerning modeling of heavy metals removal from aqueous solutions using zeolite fixed beds, the most popular zeolite studied is clinoptilolite [8–11]. Several types of fixed bed models have been applied on clinoptilolite fixed beds but only few are using reliable diffusion-

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based models. The majority of fixed bed models used in adsorption and ion exchange studies on several materials, including zeolites, make use of phenomenological pseudo-first or second order chemical reaction-like models, which from a physical point of view are problematic as ion exchange and adsorption are not chemical reactions but diffusion-driven processes. Furthermore, in order to interpret and model fixed beds equilibrium data derived by use of batch reactors are needed, a fact that in a number of publications is overlooked.

In the present study, both batch and fixed bed experiments were conducted by use of clinoptilolite for the removal of Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+} and Cr^{3+} from aqueous solutions. Then, the batch and fixed bed experimental data are fed to a two-phase homogeneous solid diffusion model (TPHDM) equipped with an axial dispersion term for the estimation of the diffusion coefficient of heavy metals in the solid phase. The model used is non-dimensional, built using a universal double-selectivity equilibrium model (DSM). In overall, six metals and two different clinoptilolite samples were studied providing 25 experimental breakthrough curves which were subsequently modeled. To the best of authors' knowledge such comprehensive study on zeolite fixed beds modeling is rare in the related literature and especially the zeolites fixed bed modeling of systems obeying S-shaped isotherms is presented here for the first time. Furthermore, an extended literature review on solid phase diffusion coefficients is provided.

2. Literature review and analysis

Surprisingly, the vast majority of adsorption kinetics studies, associated with liquid phase adsorption and ion exchange, are based on phenomenological kinetic models or oversimplified intra-particle/liquid film diffusion [12]. Taking into account that most adsorbents are porous, obviously these models disregard the diffusion into the porous structure of the materials, which in many occasions is proven to be the controlling step of the sorption process. Widely used fixed bed chemical reaction-based models (kinetics-based models) are those of Adams-Bohart, Clark, Yoon-Nelson and Thomas/Bed Depth Service Time (BDST) models [13–18]. Another group of models are based on the unused bed zone (UBZ) and are purely empirical [19].

As far as clinoptilolite is concerned, some examples that use kinetics-based models are these of Cortés-Martínez et al. [20] for the sorption of cesium, Nuić et al. [21] for the removal of lead and zinc, Gutiérrez-Segura et al. [22] for the sorption of a dye, Shavandi et al. [23] for metal and residual oil removal from palm oil mill effluent, Malovanyy et al. [24] for the concentration of ammonium from municipal wastewater, Trgo et al. [25] and Medvidović et al. [26] for the removal of lead. Away from this kinetics-based of models, another type of models are diffusion-based, which they either use overall mass transfer coefficients or lumped variables. The problem with this kind of models is not the physical significance but rather the absence of the solid phase diffusion coefficient which is a fundamental variable in diffusion-driven processes. Warchoł and Petrus [27] studied the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} in clinoptilolite fixed beds, however they use of an equilibrium-dispersive and a lumped-kinetic model and thus no solid phase diffusion coefficients are reported. Nuić et al. [28] studied the removal of Pb^{2+} and Zn^{2+} in clinoptilolite fixed beds and used a so-called Advection–Dispersion-Reaction (ADR) model, which however again does not give a solid phase diffusion coefficient. Pepe et al. [29] used a TPHDM model, linear driving force (LDF) approximation for both the liquid and solid phase diffusion and an axial dispersion term. The system studied was Pb^{2+} ion exchange on phillipsite, however only a mass transfer coefficient is given, and not a solid phase diffusion coefficient. Similar approach is followed by Taamneh and Dwairi [30] who used a simplified analytical solution for studying the removal of heavy metals by use of a natural zeolite, under the assumptions of negligible axial dispersion LDF mass-transfer.

Another set of models are purely diffusion-based, and mainly, the simplifications made concern the form of the solid phase diffusion coefficient, the type of equilibrium and the plug flow assumption. Woinarski et al. [10] used clinoptilolite to remove Cu^{2+} from aqueous solutions and employed a simplified model assuming particle diffusion control and LDF, including a dispersion term to account for the non-ideal flow. Notably, the particle diffusion coefficients were found to be dependent on flow rate and were between 2.2 and 7.6 times greater than the value determined from batch kinetic tests, a result in agreement with the findings of Inglezakis and Grigoropoulou [9]. Pepe et al. [31] studied a phillipsite/chabazite-rich tuff for Ba^{2+} removal in fixed beds. They used a diffusional model, based on the LDF approximation for both the liquid and solid phase diffusion, including a dispersion term. Górka et al. [32] studied ammonia removal from wastewaters by ion exchange on a commercial synthetic zeolite. An advanced generalized heterogeneous model is discussed, i.e. a model including liquid and two distinct solid phase mass transfer resistances (pore and solid diffusion) as well as a dispersion term to account for non-ideal flow. However, the generalized model was used only to verify the results of a simplified dynamic model based on the equation of LDF. Inglezakis and Grigoropoulou [9] examined ion exchange of Pb^{2+} by use of a homogeneous solid phase diffusion model (HSDM) under constant pattern and plug flow conditions. The study showed that the solid-phase diffusion coefficient depends on the volumetric flow rate in fixed bed experiments and is much higher than those deduced from batch-type experiments, which indicates that the batch-type equilibrium behavior is different from that in fixed beds, probably because of the effect of partial equilibration in fixed beds [9]. More recently, Inglezakis et al. [2] studied the sorption of several heavy metals by use of clinoptilolite and vermiculite and employed a simplified analytical solution to a HSDM model, with single diffusion step under constant pattern and ideal flow conditions. The most advanced models used on clinoptilolite are those of Lv et al. [5] and Cincotti et al. [8]. Lv et al. [5] used a TPHDM model, i.e. combined liquid and solid phase resistances including a dispersion term. The model was successfully used to describe and predict breakthrough curves for the fixed-bed sorption of lead ions onto microporous ETS-10 zeolite. The same model was used by Cincotti et al. [8] for the removal of Pb^2 in fixed beds of clinoptilolite.

The summary of the models and derived solid diffusion coefficients is provided in Table 1. Notably, the models are used mainly with simple isotherms, such as Langmuir, and to the best of the authors' knowledge no sigmoidal isotherms have been studied in heavy metals-clinoptilolite systems. Moreover, most of the available few studies that utilize diffusion-based models use simplifications such as single controlling step, LDF approximation for solid phase mass transfer, constant pattern and ideal plug flow conditions. However, is well known that the effects of the mass transfer controlling step and axial dispersion become significant especially away from the asymptotic limits (constant and proportionate patterns). A comprehensive literature review on fixed bed models is presented elsewhere [7]. The discussion on the solid phase diffusion coefficients is presented in Results and Discussion section.

3. Materials and methods

3.1. Batch equilibrium experiments

Two different natural zeolite samples were used in this study, both of the clinoptilolite type denoted as (V) and (M) samples. The samples were crushed and separated in different particle sizes between 0.09 and 5 mm. The characterization of the materials is presented elsewhere [11,39]. Equilibrium studies were conducted in batch mode without agitation. Measured quantities of clinoptilolite (0.1–14 g) were added to vessels containing measured volume of metals solutions (100 mL) of 0.01 N (eq/L) and initial pH of 4. For all metal solutions, nitrate salts were used. Every 10 days the solution was analyzed for metal concentrations until no further uptake from the minerals was observed. Total sampling volume was 2% of the total solution volume. The temperature was kept constant during the batch reaction time at 25 °C. All