

# 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  $11.19 \pm 5.53\%$ . 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  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that can be exchanged with other metal ions such as  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ .

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-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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  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 modelled. 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 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. Warchoń 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

$\text{Zn}^{2+}$  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  $\text{Pb}^{2+}$  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  $\text{Cu}^{2+}$  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  $\text{Ba}^{2+}$  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. Górká 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  $\text{Pb}^{2+}$  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<sup>2+</sup> 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, it 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.

**Table 1.** Summary of diffusion-based models and the derived solid-phase diffusion coefficients for batch and fixed bed systems at 20-25°C unless otherwise specified.

Type of model used	Ion(s) studied	Zeolite type	Solid-phase diffusion coefficients (D <sub>s</sub> , cm <sup>2</sup> /s)	Reference
<b>Fixed bed experiments</b>				

Heterogeneous pore and surface diffusion model (PSDM) by use of Fickian solid phase diffusion rate and external liquid phase diffusion with axial dispersion term  Langmuir isotherm	Pb <sup>2+</sup>	Clinoptilolite  Na-Clinoptilolite	2×10 <sup>-8</sup> cm <sup>2</sup> /s  2×10 <sup>-8</sup> cm <sup>2</sup> /s	[8]
HSDM model, solid phase diffusion described by LDF, single diffusion step, including axial dispersion term  Langmuir isotherm	Cu <sup>2+</sup>	Na-Clinoptilolite	0.66-2.28×10 <sup>-8</sup> cm <sup>2</sup> /s (22°C)  0.68-2.36×10 <sup>-8</sup> cm <sup>2</sup> /s (2°C)	[10]
HSDM model, solid phase diffusion described by Fick's law, single diffusion step, constant pattern and ideal flow conditions  Langmuir isotherm	Pb <sup>2+</sup>	Clinoptilolite	1.08-5.45×10 <sup>-8</sup> cm <sup>2</sup> /s	[9]
HSDM model, simplified analytical solution for LDF, single diffusion step, constant pattern and ideal flow conditions  Langmuir isotherm	Zn <sup>2+</sup> , Mn <sup>2+</sup>	Clinoptilolite  Vermiculite	6.2×10 <sup>-8</sup> cm <sup>2</sup> /s (Zn <sup>2+</sup> )  7.4×10 <sup>-9</sup> cm <sup>2</sup> /s (Zn <sup>2+</sup> ) 6.1×10 <sup>-9</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> )	[2]
Heterogeneous pore and surface diffusion model (PSDM), external liquid phase diffusion, plug flow conditions  Langmuir isotherm	Sr <sup>2+</sup>	Clinoptilolite	1-2×10 <sup>-10</sup> cm <sup>2</sup> /s	[33]
Boyd's model for infinite solution volume for isotopic exchange, shallow bed technique was used.	Cu <sup>2+</sup>	NH <sub>4</sub> -Clinoptilolite	1.5×10 <sup>-9</sup> cm <sup>2</sup> /s (25°C)  2.2×10 <sup>-9</sup> cm <sup>2</sup> /s (80°C)	[34]

Rigorous ion exchange equilibrium models.				
Diffusion model (Crank's equation) - through-diffusion method by use of diffusion cells was employed  Isotherm type not specified.	Se	Clinoptilolite-containing tuff	$3.4-8.8 \times 10^{-8} \text{ cm}^2/\text{s}$	[35]
TPHDM model, LDF for solid phase diffusion, plug flow and constant pattern conditions assumed  Isotherm type not specified.	Sr <sup>2+</sup>	Clinoptilolite	$5 \times 10^{-8} \text{ cm}^2/\text{s}$	[36]
		Chabazite	$5 \times 10^{-8} \text{ cm}^2/\text{s}$	
		Mordenite	$5 \times 10^{-8} \text{ cm}^2/\text{s}$	
TPHDM model, LDF approximation for both the liquid and solid phase diffusion, including axial dispersion term  Isotherm type not specified.	Ba <sup>2+</sup>	Na-enriched chabazite/phillipsite	$6 \times 10^{-9} \text{ cm}^2/\text{s}$	[31]
TPHDM model, LDF approximation for both the liquid and solid phase diffusion, including axial dispersion term  A heterogeneous pore and surface diffusion model (PSDM) was used to verify the results of a simplified TPHDM but the diffusion coefficient was determined by the later.  Rigorous ion exchange equilibrium models.	NH <sub>4</sub> <sup>+</sup>	Synthetic zeolite	$4.97 \times 10^{-8} \text{ cm}^2/\text{s}$	[32]
TPHDM model by use of Fickian solid phase diffusion rate and axial dispersion term	Pb <sup>2+</sup>	ETS-10 zeolite	$2.57 \times 10^{-6} \text{ cm}^2/\text{s}$	[5]
HSDM model, simplified analytical solution	Cu <sup>2+</sup> ,	Vermiculite	$5.4 \times 10^{-10} \text{ cm}^2/\text{s}$ (Cu <sup>2+</sup> )	[37]



for quadratic driving force, single diffusion step, constant pattern and ideal flow conditions  Isotherm type not specified.	Ni <sup>2+</sup> , Zn <sup>2+</sup> , Cr <sup>3+</sup>		1.7×10 <sup>-9</sup> cm <sup>2</sup> /s (Ni <sup>2+</sup> ) 1.2×10 <sup>-9</sup> cm <sup>2</sup> /s (Zn <sup>2+</sup> ) 1.7×10 <sup>-9</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> )	
<b>Batch experiments</b>				
Finite solution volume diffusion model	Pb <sup>2+</sup> Na <sup>+</sup>	Na-Clinoptilolite	0.17-3.9×10 <sup>-10</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 25°C) 4.3-19.80×10 <sup>-10</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 35-45°C)	[38]
Paterson's model (finite solution volume diffusion model)	Pb <sup>2+</sup>	Clinoptilolite	7×10 <sup>-10</sup> cm <sup>2</sup> /s	[9]
Nernst-Planck's model	Cu <sup>2+</sup>	Na-Clinoptilolite	3×10 <sup>-9</sup> cm <sup>2</sup> /s (22°C) 3.1×10 <sup>-9</sup> cm <sup>2</sup> /s (2°C)	[10]
Paterson's model (finite solution volume diffusion model)	Pb <sup>2+</sup> , Cu <sup>2+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup>	Clinoptilolite	6.2-6.4×10 <sup>-10</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 27°C) 2.2×10 <sup>-9</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 50°C) 1.08×10 <sup>-9</sup> cm <sup>2</sup> /s (Cu <sup>2+</sup> , 27°C) 1.08-1.40×10 <sup>-9</sup> cm <sup>2</sup> /s (Cu <sup>2+</sup> , 50°C) 3.2×10 <sup>-10</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> , 27°C) 5.1×10 <sup>-10</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> , 50°C) 2-2.5×10 <sup>-10</sup> cm <sup>2</sup> /s (Fe <sup>3+</sup> , 27°C) 3.7×10 <sup>-10</sup> cm <sup>2</sup> /s (Fe <sup>3+</sup> , 50°C)	[39] [40]
		Na-Clinoptilolite	1.7×10 <sup>-9</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 27°C) 9×10 <sup>-9</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> , 50°C) 0.9×10 <sup>-9</sup> cm <sup>2</sup> /s (Cu <sup>2+</sup> , 27°C) 1.8×10 <sup>-9</sup> cm <sup>2</sup> /s (Cu <sup>2+</sup> , 50°C) 4×10 <sup>-10</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> , 27°C) 5.7×10 <sup>-10</sup> cm <sup>2</sup> /s (Cr <sup>3+</sup> , 50°C) 1.6×10 <sup>-10</sup> cm <sup>2</sup> /s (Fe <sup>3+</sup> , 27°C)	[40]

			$3 \times 10^{-10} \text{ cm}^2/\text{s}$ ( $\text{Fe}^{3+}$ , $50^\circ\text{C}$ )	
Vermeulen's, Paterson's, and Nernst-Plank's models	$\text{Pb}^{2+}$	Clinoptilolite	$3 \times 10^{-10} \text{ cm}^2/\text{s}$	[41]
		Na-clinoptilolites	$0.17-1.37 \times 10^{-8} \text{ cm}^2/\text{s}$	[42]
Paterson's and Nernst-Plank models	$\text{Pb}^{2+}$	Na-Clinoptilolite	$6.78-8.96 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $16^\circ\text{C}$ ) $6.3-16.8 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $35^\circ\text{C}$ )	[43]
Diffusion-base model and Boyd's model	$\text{Cu}^{2+}$	Na-Clinoptilolite	$0.7-1.2 \times 10^{-10} \text{ cm}^2/\text{s}$	[44]
Paterson's model (finite solution volume diffusion model)	Alkylammonium ions	Na-Clinoptilolite	$4.7-5.1 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{CH}_3\text{NH}_3^+$ , $45^\circ\text{C}$ ) $4.3-5 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $(\text{CH}_3)_2\text{NH}_2^+$ , $45^\circ\text{C}$ ) $2.6-3 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{C}_2\text{H}_5\text{NH}_3^+$ , $45^\circ\text{C}$ )  $8.7-10.5 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{CH}_3\text{NH}_3^+$ , $75^\circ\text{C}$ ) $7.9-9.1 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $(\text{CH}_3)_2\text{NH}_2^+$ , $75^\circ\text{C}$ ) $13-13.8 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $(\text{CH}_3)_3\text{NH}^+$ , $75^\circ\text{C}$ ) $5.6-6.3 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{C}_2\text{H}_5\text{NH}_3^+$ , $75^\circ\text{C}$ ) $1.8-3.5 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $n\text{-C}_3\text{H}_7\text{NH}_3^+$ , $75^\circ\text{C}$ ) $4-9.6 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{iso-C}_3\text{H}_7\text{NH}_3^+$ , $75^\circ\text{C}$ ) $7.4-12.3 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $n\text{-C}_4\text{H}_9\text{NH}_3^+$ , $75^\circ\text{C}$ )	[45]
Carman-Haul equation (finite solution volume diffusion model)	$\text{NH}_4^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	NH <sub>4</sub> -Clinoptilolite	$2.99 \times 10^{-7} \text{ cm}^2/\text{s}$ ( $\text{Na}^+$ ) $2.76 \times 10^{-7} \text{ cm}^2/\text{s}$ ( $\text{K}^+$ ) $1.26 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Ca}^{2+}$ ) $2.5 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Mg}^{2+}$ )	[46]
		Na-Clinoptilolite	$9 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{NH}_4^+$ ) $1.9 \times 10^{-7} \text{ cm}^2/\text{s}$ ( $\text{K}^+$ ) $3.4 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Ca}^{2+}$ )	
		K-Clinoptilolite	$1.01 \times 10^{-7} \text{ cm}^2/\text{s}$ ( $\text{Na}^+$ ) $2.72 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{NH}_4^+$ ) $1.6 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Ca}^{2+}$ )	

		Mg-Clinoptilolite	$0.5 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Na}^+$ ) $0.3 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{K}^+$ ) $3.7 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{NH}_4^+$ ) $0.9 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Ca}^{2+}$ )	
TPHDM model	Basic dyes	Clinoptilolite	$1.5 \cdot 33.33 \times 10^{-10} \text{ cm}^2/\text{s}$ $0.15 \text{--} 31.6 \times 10^{-10} \text{ cm}^2/\text{s}$	[47]
TPHDM model	Dye	Clinoptilolite	$0.39 \text{--} 1.19 \times 10^{-10} \text{ cm}^2/\text{s}$	[48]
Diffusion-based model	$\text{NH}_4^+$	Na-Clinoptilolite	$3.8 \text{--} 4.4 \times 10^{-8} \text{ cm}^2/\text{s}$	[49]
Modified Vermeulen's model (infinite solution volume diffusion model)	$\text{NH}_4^+$ , $\text{Na}^+$	Na-Clinoptilolite	$4.2 \text{--} 6.8 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{NH}_4^+$ )	[50]
		$\text{NH}_4$ -Clinoptilolite	$5.7 \text{--} 9 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Na}^+$ )	
Vermeulen's model (infinite solution volume diffusion model)	$\text{Pb}^{2+}$ , $\text{Zn}^{2+}$	Na-Clinoptilolite	$0.8 \text{--} 1.7 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Pb}^{2+}$ ) $3.1 \text{--} 6.2 \times 10^{-10} \text{ cm}^2/\text{s}$ ( $\text{Zn}^{2+}$ )	[51]
Boyd's model (infinite solution volume diffusion model)	$\text{Cu}^{2+}$	Clinoptilolite	$0.051 \text{--} 11.83 \times 10^{-9} \text{ cm}^2/\text{s}$	[52]
		Synthetic calcium hydroxyapatite	$0.32 \text{--} 1.36 \times 10^{-9} \text{ cm}^2/\text{s}$	
Not reported	$\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	Na-Clinoptilolite	$0.2 \text{--} 21 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Pb}^{2+}$ , $25^\circ\text{C}$ ) $0.4 \text{--} 39 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Pb}^{2+}$ , $50^\circ\text{C}$ ) $0.2 \text{--} 17 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ , $25^\circ\text{C}$ ) $0.4 \text{--} 35 \times 10^{-9} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ , $50^\circ\text{C}$ )	[53]
Not reported	$\text{Cu}^{2+}$	Ca/Na-Clinoptilolite	$0.3 \text{--} 2.5 \times 10^{-9} \text{ cm}^2/\text{s}$	[54]
		Zeolite X	$3.52 \times 10^{-10} \text{ cm}^2/\text{s}$	
Isotopic, infinite solution volume model	$\text{Gd}^{3+}$	Clinoptilolite	$3.4 \text{--} 5.2 \times 10^{-8} \text{ cm}^2/\text{s}$	[55]
Fick's law	$\text{Cd}^{2+}$ , $\text{Tl}^{2+}$	Clinoptilolite	$2.1 \text{--} 2.9 \times 10^{-6} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ ) $1.5 \text{--} 1.9 \times 10^{-6} \text{ cm}^2/\text{s}$ ( $\text{Tl}^{2+}$ )	[56]

Vermeulen's model (infinite solution volume diffusion model)	Zn <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	Clinoptilolite	1.3-5.6×10 <sup>-9</sup> cm <sup>2</sup> /s (Zn <sup>2+</sup> ) 1.25-8.5×10 <sup>-8</sup> cm <sup>2</sup> /s (Cd <sup>2+</sup> ) 1.28-3.3×10 <sup>-7</sup> cm <sup>2</sup> /s (Pb <sup>2+</sup> )	[57]
Simplified phenomenological model	Ni <sup>2+</sup>	Clinoptilolite	2.5×10 <sup>-9</sup> cm <sup>2</sup> /s	[58]
Nernst-Planck and Vermeulen's model (both infinite solution volume diffusion models)	Cu <sup>2+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup> and Fe <sup>3+</sup>	Clinoptilolite	2.7×10 <sup>-7</sup> cm <sup>2</sup> /s (Cu <sup>2+</sup> ) 1.64×10 <sup>-7</sup> cm <sup>2</sup> /s (Mn <sup>2+</sup> ) 1.77×10 <sup>-7</sup> cm <sup>2</sup> /s (Zn <sup>2+</sup> ) 1.05×10 <sup>-7</sup> cm <sup>2</sup> /s (Fe <sup>3+</sup> )	[59]
Vermeulen's model (infinite solution volume diffusion model)	NH <sub>4</sub> <sup>+</sup>	Na- Clinoptilolite	3.21-3.49×10 <sup>-8</sup> cm <sup>2</sup> /s	[60]
Vermeulen's model (infinite solution volume diffusion model)	NH <sub>4</sub> <sup>+</sup>	Sepiolite	1.5×10 <sup>-6</sup> cm <sup>2</sup> /s	[61]
Boyd's model (infinite solution volume diffusion model)	Cs <sup>+</sup>	Na-Clinoptilolite  Na-Erionite	1.66×10 <sup>-7</sup> cm <sup>2</sup> /s (25°C) 3.07×10 <sup>-7</sup> cm <sup>2</sup> /s (50°C)  1.55×10 <sup>-7</sup> cm <sup>2</sup> /s (25°C) 2.06×10 <sup>-7</sup> cm <sup>2</sup> /s (50°C)	[62]
Not specified	Ce <sup>3+</sup>	Mordenite	3.8- 4.3×10 <sup>-8</sup> cm <sup>2</sup> /s	[63]
Barrer-Barri- Klinowski equation (analytical approximate model)	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup>	Synthetic analcime	10 <sup>-13</sup> cm <sup>2</sup> /s	[64]
Boyd's model (infinite solution volume diffusion model)	Zn <sup>2+</sup>	NaA zeolite  NaX zeolite	0.96×10 <sup>-11</sup> cm <sup>2</sup> /s  0.65×10 <sup>-11</sup> cm <sup>2</sup> /s	[65]
Boyd's model (infinite solution volume diffusion model)	Cs <sup>+</sup> , Sr <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	Zeolite A	6.45×10 <sup>-8</sup> cm <sup>2</sup> /s (Cs <sup>+</sup> , 25°C) 7.21×10 <sup>-8</sup> cm <sup>2</sup> /s (Cs <sup>+</sup> , 40°C) 9.44×10 <sup>-8</sup> cm <sup>2</sup> /s (Cs <sup>+</sup> , 60°C)  6.50×10 <sup>-8</sup> cm <sup>2</sup> /s (Sr <sup>2+</sup> , 25°C) 8.13×10 <sup>-8</sup> cm <sup>2</sup> /s (Sr <sup>2+</sup> , 40°C) 11.21×10 <sup>-8</sup> cm <sup>2</sup> /s (Sr <sup>2+</sup> , 60°C)	[66]

			$1.83 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Zn}^{2+}$ , 25°C) $2.64 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Zn}^{2+}$ , 40°C) $3.05 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Zn}^{2+}$ , 60°C)  $3.35 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ , 25°C) $4.18 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ , 40°C) $5 \times 10^{-8} \text{ cm}^2/\text{s}$ ( $\text{Cd}^{2+}$ , 60°C)	
Thin-film boundary condition of Fick's law	$\text{Na}^+$	K-Vermiculite	$3.5\text{-}25.2 \times 10^{-8} \text{ cm}^2/\text{s}$	[67]

### **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 chemicals used were analytical grade reagents and high-purity deionized water. pH was initially adjusted to avoid precipitation during all ion exchange experiments, at pH=4 using HNO<sub>3</sub>. The samples were analyzed for heavy metal cations by atomic absorption spectrometry. All experiments were performed at least in duplicate and the average standard deviation was 5%.

#### **3.2 Fixed bed experiments**

Heavy metals solutions were passed through the fixed column packed with zeolite particles of size of 0.135-3.5 mm, at a relative volumetric flow rate between 5 and 15.36 BV/h (where BV is a volume of liquid equal to the volume of the empty bed), under a total normality of 0.01N (eq/L), initial pH of 4 and ambient temperature (25°C). For all metal solutions, nitrate salts were used. The experimental runs' operational variables are presented in Table 3.

The process was conducted in 20-70 cm long plexiglass columns of 2 cm internal diameter. The solution was introduced at a constant volumetric flow rate ( $Q$ ) and concentration ( $C$ ), using a peristaltic pump in up-flow mode in order to assure complete wetting of the mineral particles (Figure 1). Liquid samples were withdrawn at the exit of the bed at specific time intervals, acidified with HNO<sub>3</sub> at pH=2 and

analyzed for heavy metal cations. By plotting the exit metal concentration versus time, the breakthrough curves were obtained. Given the very long duration of the experiments, a sufficient number of them were performed in duplicate and the resulting average standard deviation was 5%. The operating capacity in (mg/g) is determined by use of the following equation [68]:

$$q_{max} = \frac{C_o \cdot V_T - \int_0^t C \cdot dV}{\rho_b \cdot V_o}$$

where ( $V_T$ ) is the total effluent volume at time ( $t$ ), when the exit concentration is equal to the inlet concentration.

**Figure 1.**

### 3.3 Equilibrium models

Of particular interest for zeolite adsorption and ion exchange systems are the inhomogeneous models, which are used to describe multisite (heterogeneous) solid phases behaving differently towards the same component. A simple approach to this problem is to assume that the solid is composed of two distinct regions with no interaction between them. In this way, equilibrium equations can be applied to each region separately and the overall isotherm is obtained by the summation of the two equations [69, 70]. Bricio et al. [71] and later Pepe et al. [72] developed the double-selectivity model (DSM) for heterogeneous ion exchangers using the concept of multisite adsorption. In the case of the exchange of monovalent ions the derived equation is:

$$Y = p \cdot \frac{K_1 \cdot X}{1 + (K_1 - 1) \cdot X} + (1 - p) \cdot \frac{K_2 \cdot X}{1 + (K_2 - 1) \cdot X}$$

where ( $K$ ) are the equilibrium constants and ( $p$ ) is the proportion of sites on the solid surface, all positive numbers. This approach is particularly useful as it gives both Type-II and Type-V isotherms. Similar models have been developed by Lee et al. [73] and Zhu and Gu [74].

Although this equation is derived for monovalent exchange, this isotherm is used in the present paper due to its simplicity and flexibility as is able to model Langmurian as well as S-Shaped experimental isotherms. The model can be viewed as two-sites Langmurian with  $La=1/K$ :

$$Y = p \cdot \frac{X}{\left(\frac{1}{K_1}\right) + \frac{(K_1 - 1)}{K_1} \cdot X} + (1 - p) \cdot \frac{X}{\left(\frac{1}{K_2}\right) + \frac{(K_2 - 1)}{K_2} \cdot X}$$

The residual sum of squares (RSS) is used as a measure of the discrepancy between the experimental data and the model prediction. For the regression analysis Excel's Solver was used with RSS as the objective function to be minimized:

$$RSS = \sum_{i=1}^n (Y_{EXP,i} - Y_{MOD,i})^2$$

### 3.4 Fixed bed model

Isotherm defines the characteristic shape of the breakthrough curve and analytical fixed beds model solutions have been derived decades ago for rectangular, linear and favorable isotherms [69, 75, 76]. Both favorable and unfavorable isotherms give long-time asymptotic solutions, namely constant pattern and proportionate pattern [77]. The constant pattern approximation is a classic approach and provides analytical solutions when combined with a LDF or other simplified mass transfer equations [75, 78, 79]. Proportionate pattern, is equivalent to the local equilibrium theory (infinite mass transfer rate), also called equilibrium-limited model, and gives simple analytical solutions as well. Although the isotherm shape determines the general shape of the breakthrough curve, kinetics and axial dispersion become important in systems away from the asymptotic limits.

Mass transfer is divided into two steps, interface diffusion between fluid phase and the exterior of the solid phase, and intraparticle mass transfer involving pore diffusion and surface diffusion. There are several fixed bed models, such as the two-phase (liquid/solid) homogeneous diffusion model (TPHDM),



single phase (solid) homogeneous surface diffusion model (HSDM), and heterogeneous pore and surface diffusion model (PSDM) [13, 76]. However, only limited studies are using these reliable diffusion-based models for the description of solid phase mass transfer while for the vast majority of the published papers the fixed bed models used are based on phenomenological chemical reaction-based models (kinetics-based models) [7]. The use of such outdated models is widespread despite the advent of modern software and computing power able to cope with diffusion-based models. Taking into account that adsorption and ion exchange are not chemical reactions but diffusion-driven and controlled processes, render the extrapolation quality and the physical significance of the derived parameters of kinetic-based models problematic. Surprisingly, papers dealing with this subject are rare and one example is the excellent paper published by Rodrigues and Silva [18] where the authors compare a common used kinetics-based model (Lagergreen model) with the classic diffusion-based LDF model (Glueckauf model). The authors conclude that although the kinetic-based model is simple, at the same time is theoretically inconsistent and it is recommended to use first principles models instead of the short-cut approach of pseudo-first order equations. Concerning diffusion-based models, a review of the literature reveals that the development of simplifying assumptions on the mass transfer rates is mainly based on the use of a single mass transfer controlling mechanism, either fluid or solid diffusion step, and the representation of mass transfer rate within the adsorbent particles is modeled using a LDF instead of the Fickian diffusion equation [6, 80, 81]. Apart from the oversimplifications, another issue of the related literature is that the models and their solutions are dimensional, limiting their usefulness to the specific systems. Solution of the dimensional form is the solution of a particular problem, while the dimensionless approach typically generalizes the problem and can describe many dimensional solutions. Furthermore, the use of a limited set of dimensionless parameters eases the numerical solution of the models.

The details of the model used in the present paper are provided in a previous publication and are not repeated here [7]. In this section the core non-dimensional model is presented without discussion on its derivation. The pertinent assumptions are incompressible flow and dilute solutions (trace systems),

isobaric and isothermal process, perfect radial mixing, spherical particles, single component (adsorption) or binary system (ion exchange) and single mass transfer controlling mechanism with a constant effective diffusion coefficient in the solid phase and local equilibrium is established at the fluid-liquid interface.

The dimensionless averaged fluid and solid concentrations are:

$$\bar{X} = \frac{\bar{C}}{C_o} \quad \text{and} \quad \bar{Y} = \frac{\bar{q}}{q_{\max}}$$

The partition ratio ( $\Lambda$ ), residence time ( $\tau$ ) and stoichiometric time are defined as [82]:

$$\Lambda = \frac{\rho_b \cdot \bar{q}_{\max}}{C_o}, \quad \tau = \frac{V_o}{Q} \quad \text{and} \quad t_s = \Lambda \cdot \tau$$

Where ( $q_{\max}$ ) is the solid phase capacity, ( $C_o$ ) the fluid phase initial concentration, ( $V_o$ ) the empty fixed bed volume and ( $Q$ ) the volumetric fluid flow rate. Then, the dimensionless time ( $T$ ), or throughput parameter, is defined [82]:

$$T = \frac{t - \varepsilon \cdot \tau}{t_s}$$

The bed Peclet number is:

$$Pe = \frac{u_s \cdot L}{D_{ax} \cdot \varepsilon}$$

where ( $L$ ) is the bed length. Finally, the fluid ( $N_f$ ) and solid phase ( $N_s$ ) mass transfer units are defined as follows [78]:

$$N_f = (k_f \cdot a_u) \cdot \tau = K_f \cdot \tau$$

$$N_s = \left( \frac{15 \cdot D_s}{r_p^2} \right) \cdot \Lambda \cdot \tau = K_s \cdot \Lambda \cdot \tau$$

The dimensionless distance from the solid's center is  $R=r/r_p$  and the dimensionless distance from the bed inlet  $Z=z/L$ .

By using the equations and dimensionless parameters presented above the dimensionless fixed bed material balance is derived:

$$\frac{1}{Pe} \cdot \frac{\partial^2 \bar{X}}{\partial Z^2} - \frac{\partial \bar{X}}{\partial Z} - \frac{\partial \bar{Y}}{\partial T} = \frac{\varepsilon}{\Lambda} \cdot \frac{\partial \bar{X}}{\partial T}$$

The fluid and solid phase mass transfer rates in dimensionless form are:

$$\frac{\partial \bar{Y}}{\partial T} = N_f \cdot (\bar{X} - X_{R=1})$$

$$\frac{\partial Y}{\partial T} = \frac{N_s}{15 \cdot R^2} \cdot \frac{\partial}{\partial R} \left( R^2 \cdot \frac{\partial Y}{\partial R} \right) = \frac{N_s}{15} \cdot \left( \frac{\partial^2 Y}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial Y}{\partial R} \right)$$

The same equations are presented in LeVan [77]. However, in the later the product (N·T) instead of (T) is used as independent variable and thus, the numerical solution procedure followed is somewhat different. In order to get the solid phase average concentration the following equation is used [78]:

$$\bar{Y} = 3 \cdot \int_0^1 Y \cdot R^2 dR$$

By multiplying both terms of the solid mass transfer rate dimensionless equation by  $(3 \cdot R^2)$  and integrating the following equation is derived:

$$\frac{\partial \bar{Y}}{\partial T} = \frac{N_s}{5} \cdot \left( \frac{\partial Y}{\partial R} \right)_{R=1}$$

This equation in dimensional form is also given by Hall et al. [75]. The initial and final conditions are:

$$T = 0 \rightarrow \bar{Y} = \bar{X} = 0$$

$$T = \infty \rightarrow \bar{Y} = \bar{X} = 1$$

The boundary conditions at  $Z=0$  and  $Z=1$  for the fixed bed material balance are:

$$\frac{1}{Pe} \cdot \left( \frac{\partial \bar{X}}{\partial Z} \right)_{Z=0} = \bar{X} - 1$$

$$\left( \frac{\partial X}{\partial Z} \right)_{Z=1} = 0$$

The boundary condition at the bed inlet with somewhat different notation is used by LeVan [77] as well.

Note that in the case of plug flow the boundary condition at  $Z=0$  becomes:

$$Pe \rightarrow \infty \Rightarrow \bar{X} = 1$$

The boundary condition for the solid phase at  $R=0$  is [75, 78]:

$$\left( \frac{\partial Y}{\partial R} \right)_{R=0} = 0$$

At the solid-liquid interface ( $R=1$ ) local equilibrium is assumed to take place and the dimensionless general equilibrium equation is:

$$Y_{R=1} = f(X_{R=1})$$

The above equation is always true but the boundary condition at  $R=1$  also depends on the controlling steps. Note that in the general case at  $R=1$ :

$$X_{R=1} \neq \bar{X}$$

$$Y_{R=1} \neq \bar{Y}$$

For combined solid and fluid phase mass transfer resistances at R=1:

$$X_{R=1} = \bar{X} - \frac{\gamma}{5} \cdot \left( \frac{\partial Y}{\partial R} \right)_{R=1} \Leftrightarrow \left( \frac{\partial Y}{\partial R} \right)_{R=1} = \frac{5}{\gamma} \cdot (\bar{X} - X_{R=1})$$

where  $\gamma = N_s/N_f$ . The left-hand equation, in a somewhat different form is also given by Fleck et al. [78], adopted for constant pattern condition.

The numerical methods employed are described elsewhere [7]. In summary, the partial differential equations are transformed to a system of first-order ordinary differential equations in time, by discretizing the spatial derivatives using central differences. For the time derivatives forward differences are used, and in particular the modified-Euler scheme. This allows for an explicit calculation of the concentration field, sequentially in time, which is straightforward to implement numerically. Because explicit schemes are conditionally stable, a small-time step has to be used, which is computationally intensive for long integration times. However, because highly accurate solutions are sought, a small time step would have been inevitable even if implicit numerical schemes had been used.

Two convergence criteria are used, one for the numerical convergence and another for estimating the distance between the experimental and model results. Concerning numerical convergence, the overall material balance is used. The classic relationship used in the related literature to position the stoichiometric center of the transition and normalize the time scale, satisfying the overall material balance in the bed [75, 78, 80, 82]:

$$I = \int_{T=0}^{X=1} (1 - \bar{X}) \cdot dT = \int_{X=0}^{X=1} T \cdot d\bar{X} = 1 + \frac{\varepsilon}{\Lambda}$$

In order to compare the experimental and the numerical results, the area difference between the experimental and the numerical breakthrough curves was calculated. The calculation is limited within the timeframe of the experimental data. By employing the trapezoidal rule, the area under each of the experimental and the numerical curves is approximated by trapezoids of very small length/step. After

experimentation a value of  $dT=0.001$  is used. At each time-step the value of the concentrations, both experimental and numerical, are estimated using linear interpolation. Hence, the area of the two curves is easily calculated using the trapezoidal rule, along with the difference: (a) the area of each curve is easily calculated by adding the sum of all the trapezoids. (b) Their difference is calculated by calculating the difference of the two trapezoids, i.e. experimental and numerical, at each time-step and finally adding the sum of the absolute values.

### 3.5 Fixed bed model parameters

#### External mass transfer coefficient

Liquid mass transfer coefficient (or convection coefficient) is a flow dependent parameter, which can be evaluated from several correlations found in the related literature. Excellent reviews on external mass transfer coefficients correlations are provided by Dwivedi and Upadhyay [83] and Chowdiah et al. [84]. There is not any universal correlation used with liquid-solid fixed beds and thus a short review is conducted below in order to conclude on the most suitable one for the system studied in the present paper. The correlation by Chern and Chien [85] is popular in water treatment processes:

$$Sh = \left(2 + 0.644 \cdot Re_p^{1/2} \cdot Sc^{1/3}\right) \cdot [1 + 1.5 \cdot (1 - \varepsilon)]$$

Kataoka correlation has been used in liquid phase adsorption systems and  $Re_p < 40$  [4]:

$$Sh = 1.85 \cdot (Re_p \cdot Sc)^{1/3} \cdot \left(\frac{1 - \varepsilon}{\varepsilon}\right)^{1/3}$$

For  $0.0015 < Re_p < 55$ , the Wilson-Geankoplis correlation has been used in adsorption from liquid phase [4, 86, 87]:

$$Sh = \frac{1.09}{\varepsilon} \cdot Sc^{1/3} \cdot Re_p^{1/3}$$

Finally, Dwivedi and Upadhyay correlation has been also used for liquid-phase adsorption systems for the whole range of  $Re_p$  [83, 84]:

$$Sh = \frac{Sc^{1/3} \cdot Re_p}{\varepsilon} \cdot \left( \frac{0.765}{Re_p^{0.82}} + \frac{0.365}{Re_p^{0.386}} \right)$$

A comparison of the above correlations is shown in Figure 2. Although there is no consensus in the related literature on the most suitable correlation, Dwivedi and Upadhyay correlation is selected in the present work as seems to be best suited for predicting ion exchange mass-transfer coefficients at low solute concentrations [84].

**Figure 2.**

### **Peclet number**

Plug flow is the situation where axial mixing between the several cross sections of the bed is minimal, whereas radial mixing in each section is maximal. Ideal flow is studied and represented using the dispersed plug flow model of [88]. The main parameter in this model characterizing the quality of the flow is the axial dispersion coefficient ( $D_L$ ). Then, based on this parameter the particle Peclet number is defined:

$$Pe_p = \frac{u \cdot d_p}{D_L}$$

where ( $d_p$ ) is the solid particle diameter, ( $D_L$ ) the axial dispersion coefficient and ( $u$ ) the interstitial fluid velocity. Multiplying this number with the term ( $Z/d_p$ ), where ( $Z$ ) is the fixed bed length, the vessel Peclet number is obtained. High vessel Peclet number means better flow quality, closer thus to ideal flow. Typically, if this number is higher than about 100 the flow is considered to be ideal (plug flow).

In the related literature, there are correlations for the evaluation of particle Peclet number ( $Pe_d$ ) for materials that are frequently used in adsorption and ion exchange systems, such as zeolites and similar

particles of irregular shape. For a detailed review on this subject see the review of Inglezakis [89]. For zeolites in particular the following equation can be used [90]:

$$Pe_p = L \cdot Re_p^k$$

where (L) is 0.523 for upflow and 0.050 for downflow, (k) is  $-0.645$  for upflow and  $0.475$  for downflow. This correlation was derived for  $0.6 < Re_p < 8.5$  where ( $Re_p$ ) is based on superficial velocity.

## 4. Results and discussion

### 4.1 Batch experimental results and equilibrium modeling

In Figure 3 the quality of the model fit is presented which, with the exception of a couple of outliers, demonstrates the successful implementation of the DSM model in all studied systems.

#### Figure 3.

The derived DSM parameters and the RSS values are provided in Table 2. The result is more than satisfactory taking into account that the equilibrium curves for  $Cu^{2+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  are sigmoidal and thus difficult to be modeled. The rest of metals showed favorable to linear-types of isotherms. Some characteristic examples of the model fit on a sigmoidal isotherm are provided in Figure 4.

**Table 2.** Derived DSM model parameters and the RSS values (Notation: Sample\_Metal).

System	RSS	r	K <sub>1</sub>	K <sub>2</sub>
V_Pb	0.02282	0.633	12.05	121.33
M_Pb	0.00430	0.263	0.44	42.37
M_Zn	0.02677	0.926	1.46	200.00
M_Mn	0.01505	1.754	1.72	2.20



M_Cr	0.02304	0.749	0.09	40.97
V_Cr	0.08000	0.380	0.06	47.53
V_Fe	0.02622	0.553	0.15	36.00
V_Cu	0.01493	0.409	0.04	1.60
M_Cu	0.03440	1.000	1.22	0.00

**Figure 4.**

### 3.2 Fixed bed experimental results and modeling

The experimental breakthrough curves are provided in Figures 5 and 6 in logarithmic scale so that the curves can be easily distinguished. As the purpose of this paper is to examine fixed beds modeling, deeper analysis on the breakthrough curves, selectivity series and operational capacities is not provided in this paper; instead see Inglezakis [39], Stylianou et al. [91], Stylianou et al. [92] and Stylianou et al. [11].

**Figure 5.**

**Figure 6.**

The results of the model application on experimental data are presented in Table 3 along with the numerical and model errors. Some characteristic dimensionless breakthrough curves and model predictions are presented in Figure 7. The application of the model resulted in average numerical and model errors (%) of  $3.25 \pm 1.95$  and  $11.19 \pm 5.53$ , respectively. Out of the 25 runs modeling failed in only 3 cases for no clear reason (M\_Mn at 12.47 BV/h, M\_Cr at 10 BV/h and M\_Cr at 12.47 BV/h). Taking into account the large number of parameters assumed for the model that were measured by separate experiments (isotherm constants, operating capacity, bed voidage) and are correlation-derived (external

mass transfer coefficients, Peclet number), the validity of the model is considered as satisfactory. Also, the model is successfully used in the cases of  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  which follow sigmoidal isotherms. To the best to our knowledge, diffusion coefficients of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  derived by applying fixed bed models on clinoptilolite are presented for the first time.

**Table 3.** Fixed bed operational variables and model results (Notation: Sample\_Metal).

Run	Flow rate	Particle size	$q_{\max}$				$D_s$ (cm <sup>2</sup> /s)	Numerical	Model
	(BV/h)	(mm)	(mg/g)	$N_r$	$N_s$	$\gamma$		error (%)	error (%)
V_Pb	5.25	1.29	59.27	21.6	0.4	0.02	$2.40 \times 10^{-9}$	5.07	15.77
	10.5	1.29	30.79	13.29	0.45	0.03	$1.04 \times 10^{-8}$	3.16	10.74
	15.36	1.29	22.52	10.35	0.8	0.08	$3.30 \times 10^{-8}$	2.47	10.6
M_Pb	5	1.7	134.62	16.81	3	0.23	$1.99 \times 10^{-8}$	2.24	4.89
	5.01	3.5	142.71	5.15	2.49	0.48	$5.17 \times 10^{-8}$	0.7	5.19
	10.02	1.7	128.74	10.8	1.76	0.16	$1.91 \times 10^{-8}$	1.41	9.88
M_Zn	10.02	0.625	8.63	45.98	4.21	0.09	$2.91 \times 10^{-8}$	4.85	8.67
	10.02	1.7	8.78	8.87	1.17	0.13	$5.89 \times 10^{-8}$	1.45	8.98
	12.48	0.135	7.81	308	3.5	0.01	$1.76 \times 10^{-9}$	8.52	9.9
M_Mn	10.02	0.625	7.84	46.38	1.1	0.02	$7.04 \times 10^{-9}$	1.21	10.07
	10.02	1.7	5.64	8.94	1.2	0.13	$7.91 \times 10^{-8}$	1.46	3.97
	12.48	0.135	7.08	311	3	0.01	$1.40 \times 10^{-9}$	8.5	22.85
M_Cr	10.02	0.625	4.02	41.14	80	1.94	$6.25 \times 10^{-7}$	2.5	25.65
	10.02	1.7	2.76	7.93	8	1.01	$6.75 \times 10^{-7}$	1.12	13.31
	12.48	0.135	2.87	311	150	0.48	$1.08 \times 10^{-7}$	17	27.4
V_Cr	5.25	1.29	2.94	15.87	2.2	0.14	$4.42 \times 10^{-8}$	2.6	18.44
	10.05	1.29	1.57	9.77	1.2	0.12	$8.81 \times 10^{-8}$	3.32	13.59
	15.36	1.29	1.76	7.6	1.3	0.17	$1.22 \times 10^{-7}$	2.54	14.13

V_Fe	5	1.29	2.17	16.83	1.7	0.1	$4.70 \times 10^{-8}$	5.18	30.67
	10.5	1.29	1.44	9.86	1.2	0.12	$9.23 \times 10^{-8}$	5.24	9.78
	15	1.29	1.06	7.87	1.92	0.24	$2.87 \times 10^{-7}$	3.99	10.93
V_Cu	5.17	1.29	4.87	18.18	2	0.11	$4.23 \times 10^{-8}$	5.11	11.03
	10	1.29	2.9	11.58	2	0.17	$1.44 \times 10^{-7}$	5.13	9.82
	15.31	1.29	2.79	8.54	2	0.23	$2.06 \times 10^{-7}$	3.36	8.66
M_Cu	10.02	1.7	17.54	8.96	1.2	0.13	$2.94 \times 10^{-8}$	1.44	7.25

The resulting solid phase diffusion coefficients are between  $10^{-7}$  and  $10^{-9}$  cm<sup>2</sup>/s depending on the metal, flow rate and particle size. These values are in general agreement with the reported ones (Table 1). The diffusion coefficients are decreasing in the order: Cu>Fe, Cr>Zn, Pb>Mn. Moreover, the higher the flow rate and the larger the particle size the higher is the solid phase diffusion coefficient. Both trends have been reported in the literature (Inglezakis et al., 1999; Inglezakis and Grigoropoulou, 2003; Malliou et al., 1994; Neveu et al., 1985; Woinarski et al., 2006). These results were interpreted by assuming partial equilibration (flow rate) and pore clogging (particle size) and require further investigation. Concerning the controlling mechanism the values of ( $\gamma$ ) are between 0.01 and 1.94, which indicates that liquid film diffusion may pose significant resistance to diffusion. Nevertheless, for most systems ( $\gamma$ ) is much lower than 1, which indicates solid diffusion-controlled process. With the exception of few runs, the flow can be considered as ideal as the Peclet number is much higher than 100. However, there are some runs where the Peclet number is as low as 44 indicating moderate axial dispersion.

### Figure 7.

In Table 1, for comparison, we present results of the same materials that use constant pattern models [2, 9]. For (V) sample the solid phase diffusion coefficient for Pb<sup>2+</sup> is between  $1.1$ - $5.4 \times 10^{-8}$  cm<sup>2</sup>/s compared to  $0.24$ - $3.3 \times 10^{-8}$  estimated in the present paper. For (M) sample the values for Zn<sup>2+</sup> and Mn<sup>2+</sup> are  $6.2 \times 10^{-8}$

and  $4.1 \times 10^{-8}$  cm<sup>2</sup>/s, compared to  $3.6 \times 10^{-8}$  and  $7.7 \times 10^{-8}$  cm<sup>2</sup>/s, respectively estimated in the present paper. This indicates that constant pattern models, if used under the right experimental conditions, can provide a good estimation of the solid phase diffusion coefficient. However, they can model only systems following favorable isotherms.

Concerning the solid phase diffusion coefficient, it should be emphasized that what is of interest is mostly the order of magnitude as it is difficult to compare natural minerals of different purities, as is the case of natural zeolites as clinoptilolite. Other factors that affect the value of the diffusion coefficients is the pre-treatment/modification of natural minerals applied in some studies, the composition of the liquid phase (competitive cations, complexing co-ions etc) and temperature. There are studies reported that even the particle size plays significant role, and smaller particle sizes give smaller diffusion coefficients, possibly due to structural damage and/or pore clogging [43, 50, 53]. In fixed beds, apart from the ones mentioned above, flow rate has been shown to indirectly affect the solid phase diffusion coefficient due to partial equilibration [9, 10]. Partial equilibration effectively means lower surface coverage and it is connected to the fact that solid phase diffusion coefficients have been found to be concentration-dependent [47]. Also, as expected, diffusion coefficients measured in single crystals (intra-crystalline diffusion) are much smaller than those measured in zeolite grains (inter-crystalline diffusion). Furthermore, isotopic exchange measurements provide self-diffusion coefficients of cations, which maybe different than those measured when different cations are exchanged [46, 93]. Having these in mind, in order to ease the analysis of data in Table 1, inter-crystalline diffusion (measured by use of single crystals) and isotopic exchange measurements (by use of cations isotopes) are excluded. On the other hand, for comparison, data on some other zeolites substances other than heavy metals are also provided. Last but not least, simplified models are occasionally used without considering their inherent limitations and assumptions, leading thus to erroneous results. For example Vermeulen's and Nernst-Planck's models used in batch systems are both derived for infinite solution volume condition, which is not always met in the experimental set ups used in several studies. Despite these limitations, some general conclusions can be drawn. Solid phase diffusion coefficients depend greatly on the zeolite type and it is quite clear that the Na-forms of

clinoptilolite give greater diffusion coefficients than the untreated material. Also, for untreated clinoptilolite, diffusion coefficients measured in batch systems by reliable models and experimental techniques are generally smaller ( $10^{-9}$ - $10^{-10}$  cm<sup>2</sup>/s) than those measured in fixed beds ( $10^{-8}$ - $10^{-9}$  cm<sup>2</sup>/s).

## 5. Conclusions

A two-phase homogeneous diffusion model equipped with a dispersion term and a universal isotherm was successfully applied on 25 experimental breakthrough curves of Pb<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> removal by use of clinoptilolite. The double-selectivity equilibrium model represented well the experimental equilibrium isotherms, including S-shaped isotherms that are difficult to be modeled. The resulting solid phase diffusion coefficients are between  $10^{-7}$  and  $10^{-9}$  cm<sup>2</sup>/s depending on the metal, flow rate and particle size in the decreasing order of Cu>Fe, Cr>Zn, Pb>Mn. The effect of flow rate and particle size on the solid phase diffusion coefficients was reconfirmed and requires further investigation. Also it was demonstrated that constant pattern simplified models, when applied on systems that follow favorable isotherms, can result in similar solid phase diffusion coefficients if used under the right experimental conditions fulfilling the required assumptions.

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