Experimental study of zeolitic diffusion by use of a concentration-dependent surface diffusion model

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A B S T R A C T

Surface diffusivity in adsorption and ion exchange processes is probably the most important property studied extensively in the literature but some aspects, especially its dependence on solid phase concentration, is still an open subject to discussion. In this study a new concentration-dependent surface diffusion model, equipped with a flexible double selectivity equilibrium relationship is applied on the removal of Pb\textsuperscript{2+}, Cr\textsuperscript{3+}, Fe\textsuperscript{3+} and Cu\textsuperscript{2+} from aqueous solutions using a natural zeolite. The model incorporates the Chen-Yang surface diffusivity correlation able to deal with positive and negative dependence with surface coverage. The double selectivity equilibrium relationship successfully represents the experimental equilibrium data, which follow Langmurian isotherm type for Pb\textsuperscript{2+}, sigmoidal for Cr\textsuperscript{3+} and Fe\textsuperscript{3+} and linear for Cu\textsuperscript{2+}. The concentration-dependent surface diffusion model was compared with the constant diffusivity surface diffusion model and found to be moderately more accurate but considerably more useful as it provides more insights into the diffusion mechanism. The application of the model resulted in an average deviation of 8.56 \pm 6.74\% from the experimental data and an average solid phase diffusion coefficients between 10^{-9} and 10^{-10} cm\textsuperscript{2}/s. The results showed that the diffusion of metal ions in the zeolite structure is unhindered following the surface diffusion mass transfer mechanism.

1. Introduction

Heavy metals are common constituents of wastewater and many of them are toxic to environment and, therefore, treatment is required prior to disposal or recycling. Heavy metals are non-biodegradable, tend to accumulate in the environment and eventually though the food chain threaten human health. There is a number of methods for the removal of heavy metals from wastewater, namely precipitation, adsorption, ion exchange and membrane separation. Sorption processes (adsorption and ion exchange) are dominant technologies utilized across different industries and they are especially important in water and wastewater sectors (Fu and Wang, 2011). Several materials are used for the removal of heavy metals from wastewater such as resins, carbons, zeolites and clays (Inglezakis et al., 2016, 2010; Stylianou et al., 2016). Zeolites are hydrated porous aluminosilicate minerals that offer good mechanical and thermal properties and surface area for sorption. The most popular zeolite studied is clinoptilolite (Gincotti et al., 2001; Inglezakis et al., 2003; Stylianou et al., 2015; Woinarski et al., 2006). Although literature on zeolites utilization for heavy metals removal is rich, there are only a few experimental data on solid phase diffusion coefficients and the application of appropriate mass transfer diffusion-based models is rare. The majority of models used are empirical pseudo-first or second order chemical reaction-like models, which ignore the diffusion steps always apparent in adsorption and ion exchange and thus from physical point of view are problematic (V.J. Inglezakis et al., 2018a,b; Sen Gupta and Bhattacharyya, 2011).

Sorption process is comprised of three steps: (1) mass transfer by diffusion from the bulk fluid phase to the solid's external surface (film diffusion), (2) mass transfer by diffusion into the solid phase (intra-particle diffusion) and (3) adsorption (physical or chemical) on the solid's surface. These steps are common in adsorption and ion exchange the difference being the the stoichiometric character of the later (Zagorodni, 2007). Nevertheless, in practical applications both processes are modeled by using the same equilibrium and kinetics equations. Adsorption in porous solids is typically controlled by the intra-particle diffusion step as film diffusion and adsorption steps are much faster processes (Schwaab et al., 2017). Similar is the situation in ion exchange although the overall rate can be controlled by a slow chemical reaction, if such a reaction...
follows diffusion (Zagorodni, 2007). Analytical solutions to the diffusion-based models are possible under certain conditions such as linear or rectangular isotherm and infinite solution volume (Suzuki, 1990). The analytical and approximate solutions are mostly based on the work of Crank (1975) and those of Boyd et al. (1947), Paterson (1947) and Helfferich (1962). A comprehensive review on the mechanisms and models used in adsorption and ion exchange is provided by Inglezakis et al. (2019) (Inglezakis et al., 2019).

This study presents and evaluates a new versatile diffusion-based adsorption model equipped with a mixed concentration dependence variable diffusivity correlation and an S-shaped equilibrium isotherm. The model is applied to the removal of heavy metals from aqueous solutions by a natural zeolite. In this kind of systems, there are only two studies employing constant-diffusivity HSDM models, i.e. these of Meshko et al. (2001) and Castillo-Araiza et al. (2015), and none a variable-diffusivity model. Thus, the combined model presented in this paper is for the first time applied in zeolite liquid-phase adsorption.

2. Background

Experimental papers on liquid phase adsorption using batch reactors complete diffusion-based models are summarised in Table 1. Although

| Solid Adsorbate | Model1,2 | Isotherm3 | Reactor | Film mass transfer coefficient4 (cm/ s) | Surface diffusion coefficient (cm²/s) | Reference |
|-----------------|---------|-----------|---------|----------------------------------------|---------------------------------------|-----------|
| Activated carbon | R6G (dye) | TP-HSDM | Freundlich | Batch with stirring | 1.0 × 10⁻⁶ (MOD) | 1.3 × 10⁻¹⁰ | (Traeger and Suidan, 1989) |
| Activated Carbon | Pesticides | HSDM | Freundlich | Differential column batch reactor | - | 6.5 × 10⁻¹¹⁻¹.1 × 10⁻¹⁰ | (Baupp et al., 2000) |
| Activated carbon | Basic dyes | TP-HSDM | Freundlich | Batch with stirring (50-600 rpm) | 5.8×6.7×10⁻³ (MOD) | 1.5×10⁻¹¹⁻3.3×10⁻²⁹ | (Meshko et al., 2001) |
| Activated carbons | Pesticides | TP-HSDM | Freundlich | Differential column batch reactor | - | 2.1×10⁻¹¹⁻1.5×10⁻¹⁰ | (Baupp et al., 2002) |
| Anion resin | Bovine serum albumin | PSDM* | Langmuir | Batch with stirring | 3.4×10⁻¹³ | 1.6×10⁻¹⁰ | (Chen et al., 2003) |
| Activated carbon | Acid dyes | TP-HSDM | Freundlich | Batch with stirring | 3.5×10⁻⁶ (MOD) | 4.7×10⁻¹¹⁻3.1×10⁻¹⁰ | (Choy et al., 2004) |
| Granular ferric hydroxide | Arsenate | TP-HSDM | Freundlich | Differential column batch reactor | - | 3.1×10⁻¹³⁻6.4×10⁻¹¹ | (Badruzzaman et al., 2004) |
| Bone char | Cd, Cu, Zn | TP-b-HSDM | Sips# | Batch with stirring (400 rpm) | 1.3×2.1×10⁻³ (MOD) | 3.8×2×10⁻⁹ | (Ko et al., 2005) |
| Polymeric adsorbents | Lervulicin acid | TP-PSDM* | Sips# | Batch with stirring (500-800 rpm) | 4.3×8.9×10⁻³ (MW/COR) | 8×10⁻¹⁰⁻2.6×10⁻⁸ | (Li et al., 2006) |
| Activated carbon | Geosmin | b-HSDM | Freundlich | Batch with stirring | - | 5.4×10⁻⁸ | (Masui et al., 2009) |
| Activated carbon | Pyridine | TP-PSDM* | Freundlich | Rotating basket batch adsorber (100-200 rpm) | 0.3×1.2×10⁻² (MW) | 4.6×10⁻⁸⁻3.8×10⁻⁷ | (Ocampo-Pérez et al., 2010) |
| Organobentonite | Phenol | TP-HSDM* | Langmuir | Batch with stirring (300-500 rpm) | 0.6×2.4×10⁻² (MW) | 4.1×5.8×10⁻⁸ | (Ocampo-Pérez et al., 2011) |
| Activated carbon | Lanfill leachate micropolutants | TP-PSDM | Prausnitz-Radke | Batch with agitation (135 rpm) | 0.7×10⁻⁴ | 2.8×8.7×10⁻¹¹ | (Rad Ocampo-Pérez et al., 2012a,b) |
| Activated carbon | Tetracycline | TP-PSDM | Langmuir | Batch with agitation | - | 9.7×10⁻¹¹ | (R. Ocampo-Pérez et al., 2012a,b) |
| Activated carbon cloth | Several organics | TP-PDM* | Prausnitz-Radke | Differential column batch reactor | - | - | (Leva-Ramos et al., 2012) |
| Chitosan films | Food dyes | TP-HSDM | Redlich-Peterson | Batch with stirring (80-200 rpm) | 1.3×2.2×10⁻² (MW) | 4.1×10⁻¹¹⁻2.3×10⁻⁹ | (Dottu et al., 2014) |
| Zeolitic (clinoptilolite) | Rhodamine B (dye) | k-PSDM | Langmuir | Rotating basket batch adsorber | - | 3.9×10⁻¹¹⁻1.2×10⁻¹⁰ | (Castillo-Araiza et al., 2015) |
| Activated carbons pellets | Tetracyclines | TP-PSDM | Langmuir | Batch with stirring | 1.9×3.2×10⁻² (MW) | 2.6×10⁻⁸⁻1.1×10⁻¹⁰ | (Ocampo-Pérez et al., 2015) |
| Activated carbon | Acetaminophen | TP-PSDM | Langmuir | Rotating basket batch adsorber (200 rpm) | 0.9×2.3×10⁻² (MW) | 0.6×1.4×10⁻⁸ | (Ocampo-Pérez et al., 2017) |
| Activated carbon | Acid Orange 10 (dye) | TP-HSDM | Freundlich | Batch with stirring (400 rpm) | 8.2×10⁻³ (COR) | 2.2×10⁻¹¹ | (Muthukkumaran and Aravamudan, 2017) |
| Activated carbon | Ph, Gd, Ni | TP-PSDM | Langmuir | Batch with stirring (150-330 rpm) | 0.9×2×10⁻³ (MOD) | 3.4×7.5×10⁻¹¹ | (Kavand et al., 2017) |
| Bentonite | Dye | TP-PSDM | Redlich-Peterson | Batch with shaking (150 rpm) | 2.2×9×10⁻³ (MW) | 0.7×1.2×10⁻⁹ | (Souza et al., 2017) |
| Activated carbon fabric | Ibuprofen | TP-PSDM | Langmuir-Freundlich | Rotating basket batch adsorber (250 rpm) | 7.9×10⁻⁶ | - | (Ondarts et al., 2018) |
| Activated carbons | Ibuprofen | TP-PSDM | Freundlich | Batch with shaking (125 rpm) | 9.1×10⁻³ | 3.7×10⁻⁶⁻1.8×10⁻⁹ | (Frollich et al., 2018) |
| Activated carbon | Metronidazole | TP-PSDM | Prausnitz-Radke | Rotating basket batch adsorber | 0.5×2.8×10⁻² (MW) | 2.7×10⁻⁸⁻2.1×10⁻¹⁰ | (Díaz-Blancas et al., 2019) |

1 HSDM: homogeneous diffusion model, b-HSDM: branched pore kinetic model, PSDM: heterogeneous pore and surface diffusion model, k-PSDM: PSDM coupled to a chemical reaction, PDM: pore diffusion model. Models with TP prefix include fluid phase resistance (two-phase models).
2 Studies marked by asterisc (*) perform an analysis of the surface diffusion variability but the correlation is not included in the model.
3 Isotherms marked with hashtag (#) are S-shaped.
4 COR: film mass transfer correlation (dimensional approach), MW: initial slope method (Mathews and Weber method), MOD: diffusion model application.
this is not an exhaustive list, is evident that studies are mostly limited to activated carbons and systems that obey monotonic, aka non-sigmoidal isotherms. A review on fixed beds modeling is presented elsewhere and the main conclusions are the same (V.J. Inglezakis et al., 2018a,b). Also, there are only few experimental studies employing concentration-dependent diffusion-based models as shown in Table 2. This is due to the complexity of the models as non-linear variable diffusivity correlations and equilibrium isotherms are required.

Some studies investigate the variability of surface diffusivity but the analysis is performed on the results of a constant diffusivity model. The constant diffusivity values are correlated with the equilibrium solid phase loading or initial fluid phase concentration, as for example in Hu et al. (2001), Ko et al. (2005) and Ocampo-Perez et al. (2011, 2010). However, the solid phase loading is increasing from zero to the equilibrium value and the surface diffusivity changes during the transient conditions. Therefore the variable diffusivity correlations must be incorporated into the model equations. Also, it should be noted that in pore diffusion models (PDM and PSDM) the overall (effective) solid phase diffusivity is variable but this is not due to the variability of surface diffusivity, see for example the study of Kavand et al. (2017).

Recently, Marban et al. (Marbán et al., 2018) claimed that the diffusion coefficient dependence on the surface coverage has not been considered in published adsorption kinetic models onto porous solids which is not accurate as according to Table 2 such models have been solved since 1991; however, it is true that no batch adsorption model incorporating a surface diffusivity correlation able to deal with positive and negative dependence with surface coverage has been published. As discussed in paragraph 3.1 surface diffusivity may have positive, negative or mixed concentration dependence with surface coverage, however the inverse concentration dependence has been rarely reported in batch reactor modeling (Liu et al., 2006). This is evident from Table 2 where with the exception of the work of Marban et al. (Marbán et al., 2018) all other studies employ simple variable diffusivity correlations with a positive dependence with surface coverage. While Marban et al. (Marbán et al., 2018) use an empirical correlation, Chen-Yang correlation used in the present study has a sound theoretical basis and from this point of view is superior.

3. Theory

3.1. Variable surface diffusivity correlations

Mass transport in porous solids occurs in macropores (>50 nm), where pore characteristics are not contributing much, in mesopores (2–50 nm), where surface and capillary forces are important and in micropores (<2 nm) where surface forces are dominant (Choi et al., 2001; Valiullin et al., 2004). In surface diffusion, the transport occurs on the surface of the solid involving jumps between adsorption sites and is an activated process (Ruthven, 1984). In adsorption modeling literature the transport in macropores and mesopores is called pore diffusion, i.e. diffusion in the pore’s fluid. In micropores, the diffusion is called configurational or intra-crystalline and shares common characteristics with the surface diffusion (Choi et al., 2001).

For a monolayer surface diffusion, such as molecular diffusion in zeolites without significant pore restriction, the surface diffusivity...
normally increases and in some systems decreases with the increase of surface coverage (Chen and Yang, 1998, 1991). At low surface coverage, adsorption occurs on high energy sites where binding of the adsorbed molecules is strong and thus exhibits low mobility (Fig. 1). As the surface coverage increases more lower than high energy sites are available and, because of the weaker binding, molecules diffuse at a faster rate (Do, 1998).

Mass transfer in microporous materials is called configurational or intra-crystalline diffusion and occurs when the pore diameter is close to that of the adsorbate, a typical situation in zeolites. Intra-crystalline diffusion is closer to solid solution than adsorption and is influenced by the molecular size (stereic effects) while surface diffusion is a result of thermal motion of the adsorbed molecules (Do, 1998). Thus, strictly speaking, surface and intra-crystalline diffusion are different, but as they share similar features the same mechanism can be used for modeling (Choi et al., 2001). This kind of diffusion is called hindered or zeolitic diffusion.

In the present paper we focus on zeolite ion exchange systems and thus only correlations relevant to monolayer movement of adsorbates are discussed. Of the several models published since 1950’s this of Chen and Yang (1991) is the most useful as it has theoretical basis and covers both increasing and decreasing trends of the surface diffusion coefficient. The equation is:

\[
g(\theta) = \frac{D_s(\theta)}{D_m} = 1 - 0 + \frac{3}{2} \theta \cdot (2 - \theta) + H[1 - \lambda] \cdot (1 - \lambda) \cdot \frac{3}{2} \cdot \theta^2 \]

where \(\theta\) is the surface coverage (\(q/\rho_0\)), \(Q_M\) the saturation capacity of the solid, \(\lambda\) is the blockage parameter and \(H[1-\lambda]\) is the Heaviside step function; if \(\lambda \geq 1\) then \(H[1-\lambda] = 0\) and if \(\lambda < 1\) then \(H[1-\lambda] = 1\). The surface coverage is \(\theta = \frac{f_i}{f_i^{\text{MEL}}}\), where \(f_i = q_0/Q_M^\text{MEL}\) and \(q_0\) a reference solid phase concentration (see paragraph 4.1). In the experiments performed in the present study \(q_0 = Q_M^{\text{MEL}}\) (maximum exchange level) and thus \(\theta = 1\). Eq. (1) as a function of \((Y)\) becomes:

\[
g(Y) = 1 - (Y_1 \cdot Y) + \frac{3}{2} Y_1 \cdot Y_1 \cdot (2 - Y_1 \cdot Y) + H[1 - \lambda] \cdot (1 - \lambda) \cdot \frac{3}{2} \cdot (Y_1 \cdot Y)^2 \]

(2)

The blockage parameter expresses the degree of pores blocking by the adsorbate. If \(\lambda > 0\) hindered diffusion is dominant, as is common in zeolites and if \(\lambda = 0\) unhindered surface diffusion drives the mass transfer (Chen and Yang, 1991). Also, the surface diffusion coefficient is increasing for \(\lambda < 1\), has a mixed trend at \(\lambda > 1\), and practically decreases with solid loading at \(\lambda > 5\) (Fig. 2). Note that Chen-Yang model does not take into account the equilibrium and there is no \(\lambda\) that gives \(g(\theta) = 1\).

A review of available correlations is provided by Do (1998) and Choi et al. (2001). Chen-Yang variable diffusivity correlation was chosen for modeling in this work as, in contrast to previously published studies, it covers both positive and negative surface coverage dependence.

3.2. Concentration-dependent surface diffusion model

Before introducing the model equations the dimensionless variables are presented. The average dimensionless fluid and solid concentrations at any time \((t)\) are \(X = \frac{C_0}{C_s}\) and \(Y = \frac{C_f}{C_s}\), where \(C_s\) is the initial fluid phase concentration at \(t = 0\) and \(C_f\) is the solid phase concentration in equilibrium with \(C_s\). I should be noted that any equilibrium point can be used for the normalization of the model, replacing \(C_f\) and \(C_s\) in all equations and adapting the initial condition at \(t = 0\) accordingly. The partition ratio \((\Lambda)\) is (Worch, 2012):

\[
\Lambda = \frac{M \cdot C_f}{V_L \cdot C_s}
\]

where \(M\) is the solids mass and \(V_L\) the liquid volume. The dimensionless time \((T)\) is:

\[
T = \frac{D_m^{-1}}{r_p^2}
\]

where \(r_p\) is the particles radius. The Biot number is defined as follows (Worch, 2012):

\[
Bi = \frac{k_f}{D_m} \cdot \frac{C_s}{\rho_p \cdot C_f}
\]

where \(k_f\) is the liquid film mass transfer coefficient and \(\rho_p\) the density of the solid. The material balance is:

\[
\bar{Y} = \frac{1}{\Lambda} \cdot (1 - \bar{X})
\]

where \(\bar{Y}\) is the solid phase average concentration (eq. 8). The fluid phase mass transfer is:
\[
\frac{\partial Y}{\partial T} = 3 \cdot \text{Bi} \cdot (\mathbf{X} - \mathbf{X}_{R=1}) \\
\frac{\partial Y}{\partial T} = -3 \cdot \Lambda \cdot \text{Bi} \cdot (\mathbf{X} - \mathbf{X}_{R=1})
\]

By using the material balance we get:

\[
\frac{\partial Y}{\partial T} = -3 \cdot \Lambda \cdot \text{Bi} \cdot (\mathbf{X} - \mathbf{X}_{R=1})
\]

The solid phase mass transfer equation is:

\[
\frac{\partial Y}{\partial T} = \frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 \cdot g(Y) \cdot \frac{\partial Y}{\partial R} \right]
\]

where \(R = \tau / \tau_f\) and \(\tau\) the distance from the solid's center. By expanding Eq. (9):

\[
\frac{\partial Y}{\partial T} = g(Y) \frac{\partial^2 Y}{\partial R^2} + \frac{\partial g(Y)}{\partial R} \frac{\partial Y}{\partial R} + \frac{2}{R} g(Y) \frac{\partial Y}{\partial R}
\]

If surface diffusion coefficient is constant then \(D_s(Y) = \text{constant}\) then \(D_s(Y)\) can be considered but for zeolite adsorption and ion exchange systems

By multiplying both terms of the solid mass transfer rate dimensionless Eq. (11) by \(3 \cdot R^2\) and integrating by use of Eq. (17), the following equation is derived:

\[
\mathbf{Y} = 3 \cdot \int_0^{\tau_f} Y \cdot R^2 \, dR
\]

\[
= \frac{2^{1/3} \cdot \left(-a_1^2 + 3a_1 \cdot a_0\right)}{3a_0 \left(-2a_1^3 + 9a_1 \cdot a_2 \cdot a_3 + 27 \cdot a_2^3 + \sqrt{4(-a_1^2 + 3a_1 \cdot a_0)^3 + (-2a_1^3 + 9a_1 \cdot a_2 \cdot a_3 + 27 \cdot a_2^3)^2}\right)^{1/3}}
\]

\[
\frac{\partial Y}{\partial R} \bigg|_{R=1} = \frac{\partial Y}{\partial R} \bigg|_{R=0} = 0
\]

The initial conditions for \(T = 0\) are \(\mathbf{X}_{R=0} = 1\) and \(\mathbf{Y}_{R=0} = 0\). The boundary condition at the center of the solid \((R = 0)\) is:

\[
\mathbf{Y}_{R=1} = f(\mathbf{X}_{R=1}) \cdot \mathbf{X}_{R=1} = f^{-1}(\mathbf{Y}_{R=1})
\]

Also, for combined solid and fluid phase mass transfer resistances:

\[
\sum_{i=1}^{3} \frac{a_i}{(3 - K_i - K_3) \cdot \mathbf{X} + K_1 \cdot \mathbf{X} \cdot \mathbf{p} + K_2 \cdot \mathbf{w} \cdot \mathbf{p}}
\]

where:

\[
a_i = (3 - K_i - K_3) \cdot \mathbf{X} + K_1 \cdot \mathbf{X} \cdot \mathbf{p} + K_2 \cdot \mathbf{w} \cdot \mathbf{p}
\]

\[
a_2 = (3 - 2 \cdot K_1 + 2 \cdot K_2 - K_1 \cdot K_2 - K_3 \cdot \mathbf{X} + K_1 \cdot K_2 \cdot \mathbf{X} - K_1 \cdot \mathbf{X} \cdot \mathbf{p} + K_2 \cdot \mathbf{w} \cdot \mathbf{p})
\]

\[
a_3 = (1 - K_1 - K_2 + K_1 \cdot K_2)
\]

The fractional attainment of equilibrium for a solid phase free of solute at \(t = 0\) is defined as follows (Helfferich, 1962):

\[
U(T) = \frac{\mathbf{Y}_{R=0}}{\mathbf{Y}_{R=1}} = \frac{\mathbf{X}_0 - \mathbf{C}_T}{\mathbf{C}_0 - \mathbf{C}_\infty} = \frac{1 - \left(\frac{\mathbf{X}_R}{\mathbf{X}_{R=1}}\right)}{1 - \left(\frac{\mathbf{X}_R}{\mathbf{X}_{R=0}}\right)}
\]

Besides the diffusion equations presented above an equilibrium relationship is needed to solve the model. There are several models that can be considered but for zeolite adsorption and ion exchange systems
the inhomogeneous models are of particular importance as they are able to describe multisite (heterogeneous) solid phases. In its simple form, the solid is assumed to be composed of two distinct regions with no interaction between them. The derived model is called double-selectivity model (DSM) (Bricio et al., 1997; Inglezakis et al., 2018a, b; Pepe et al., 2003):

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

where \((K)\) are the equilibrium constants and \((p)\) is the proportion of sites on the solid surface, all positive numbers. This equation was derived for monovalent ions exchange but can represent multi-site adsorption, is simple and flexible and able to represent S-Shaped isotherms. The model can be viewed as two-sites Langmurian (Inglezakis et al., 2018a, b):

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

The numerical model was solved on MATLAB by using central differences to spatially discretize the partial differential equations and the modified Euler method to numerically solve the system of ordinary differential equations. The numerical model was validated by comparing its predictions with available analytical solutions found in Crank (1975). To estimate the deviation (error) between the numerical solution and the experimental data the area between the curves was used as the error, which does not depend on the orientation of the curves. A detailed description of the numerical methods is provided elsewhere (Inglezakis et al., 2019).

The application of the models were done by using \(D_0\) and \(k_f\) and \(D_0, k_f\) and \(\lambda\) as fitting variables for the constant and variable diffusivity models,

| Run | Particle size (mm) | Solid mass (g) |
|-----|--------------------|----------------|
| Cr  | 20                 |                |
| Cr_1| 10                 |                |
| Cu  | 20                 |                |
| Cu_1| 10                 |                |
| Fe  | 1.18–1.4           |                |
| Fe_1| 10                 |                |
| Pb  | 20                 |                |
| Pb_1| 10                 |                |
| Pb_2| 0.8–1              | 3.33           |

The experimental conditions for the kinetics experiments are shown in Table 3.

Fig. 3. Isotherms and DSM model fitting: Pb (upper left), Cr (upper right), Fe (lower left) and Cu (lower right).
respectively. The relative error (%) of the model fit on the experimental data was calculated as follows:

$$\text{error} = 100 \times \frac{\text{ABS}\left[U(T)_{\text{exp}} - U(T)_{\text{mod}}\right]}{U(T)_{\text{exp}}}$$

(26)

where $U(T)_{\text{exp}}$ and $U(T)_{\text{mod}}$ are the experimental and model $U(T)$ values, respectively. The residual sum of squares (RSS) is used for fitting the DSM model on the experimental equilibrium data:

$$\text{RSS} = \sum_{i=1}^{n} \left( Y_{\text{exp},i} - Y_{\text{mod},i} \right)^2$$

(27)

where $Y_{\text{exp}}$ and $Y_{\text{mod}}$ are the experimental and model solid phase equilibrium concentration values for the same liquid phase equilibrium concentration, respectively. Microsoft’s Excel’s Solver was used with RSS as the objective function to be minimized.

### 4. Experimental

The natural zeolite used in this study is clinoptilolite of particles size of 0.8–1.4 mm. The characterization of the material is presented elsewhere (Inglezakis et al., 2002). Equilibrium studies were conducted in 200mL flasks without agitation at 25 °C. Measured quantities of clinoptilolite (0.1–14 g) were mixed with 100 mL metals solutions of 0.01 N

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**Table 4**

DSM model parameters.

|   | r   | K1   | K2   | RSS  |
|---|-----|------|------|------|
| Pb| 0.6326 | 12.045 | 121.33 | 0.004 |
| Cr| 0.38  | 0.058 | 47.53 | 0.080 |
| Fe| 0.553 | 0.145 | 36   | 0.026 |
| Cu| 0.409 | 0.041 | 1.596 | 0.015 |

**Table 5**

Minimum values of $k_f$ (cm/s).

| Run   | Constant diffusivity model ($B_{\text{min}} = 2000$) | Variable diffusivity model ($B_{\text{min}} = 200$) |
|-------|---------------------------------------------------|--------------------------------------------------|
| Cr    | $1.41 \times 10^{-2}$                             | $7.10 \times 10^{-4}$                           |
| Cr_1  | $1.00 \times 10^{-2}$                             | $4.44 \times 10^{-4}$                           |
| Cu    | $2.77 \times 10^{-2}$                             | $1.71 \times 10^{-2}$ (B_{\text{min}} = 2000)$ |
| Cu_1  | $1.85 \times 10^{-2}$                             | $1.00 \times 10^{-2}$                           |
| Fe    | $4.94 \times 10^{-4}$ (B_{\text{opt}} = 196)$    | $4.28 \times 10^{-4}$ (B_{\text{opt}} = 200)$  |
| Fe_1  | $4.40 \times 10^{-3}$                             | $8.26 \times 10^{-4}$ (B_{\text{opt}} = 1000)$ |
| Pb    | $7.22 \times 10^{-3}$                             | $4.82 \times 10^{-4}$ (B_{\text{opt}} = 1000)$ |
| Pb_1  | $8.53 \times 10^{-3}$                             | $6.19 \times 10^{-4}$ (B_{\text{opt}} = 1000)$ |
| Pb_2  | $6.26 \times 10^{-2}$                             | $2.23 \times 10^{-4}$ (B_{\text{opt}} = 500)$  |

*$B_{\text{min}}$ and $B_{\text{opt}}$ is the minimum and optimum Biot number, respectively.

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**Fig. 4.** Error minimization for the constant diffusivity (left) and variable diffusivity (right) model (Pb).

**Fig. 5.** Characteristic $U(T)$-$T$ curves for Pb experiment of the constant (left) and variable (right) diffusivity models. The dimensionless time in x-axis is different in the two models.
and initial pH of 4. Every couple of weeks the solution concentration was measured until no further metals removal was observed. Total sampling volume was kept up to 2% of the total solution volume. All experiments were performed at least in duplicate and the average standard deviation was 5%. Kinetic runs were conducted in batch mode where a quantity of zeolite was added in a vessel, containing 500 ml of metal solutions at 0.01 N under rigorous agitation (650 rpm) at 25 °C. Liquid samples were withdrawn at several time intervals and the total sampling volume was kept lower than 1.5% of the total solution volume. pH was initially adjusted to avoid precipitation during all ion exchange experiments, at 4 for Pb²⁺ and Cu²⁺, 2 for Fe³⁺, and 3 for Cr³⁺, using HNO₃. The samples were analyzed for metal ions by AAS, using a Perkin–Elmer Model 350B spectrophotometer. The mean standard deviation of concentration measurements was 1.5 ± 1%. Table 3 presents the experimental runs for the kinetics experiments where two particle sizes of the zeolite were used, namely 0.8–1 and 1.18–1.4 mm. Two runs for each metal were performed by using 3.33, 10 or 20 g of the zeolite.

5. Results and discussion

The DSM application on the experimental equilibrium results is shown in Fig. 3 and Table 4. As is evident, the model is highly flexible and represents the experimental data well.

Although film diffusion is typically much faster than intra-particle diffusion, the film mass transfer coefficient is a key model parameter which influences the overall mass transfer rate. Experimental values of mass transfer coefficients lower than 10⁻³ cm/s can be generally explained by a combination of incomplete mixing and low solid density. However, as is shown in Tables 1 and 2, values in the order of magnitude of 10⁻⁴ cm/s are frequently reported. Many of these mass transfer coefficients were estimated by the Mathews-Weber method which is suffering from the arbitrary selection of the time where the initial slope is taken which is theoretically at t = 0 but practically is calculated for times between 0 and 10 min. In fact in the classic paper of Furusawa and Smith (1973) the authors highlighted the uncertainty associated with the Mathews-Weber method and propose a more general one based on the assumptions of a linear isotherm and absence of intra-particle diffusion at the beginning of the adsorption. In the case of adsorption uptake data, a more accurate method is the application of a complete diffusion model where typically the mass transfer coefficient and the solid phase diffusion coefficient are the fitting variables.

The application of the proposed model showed that the optimum Biot number was always much higher than 100 for both constant and variable diffusivity models demonstrating that the solid phase diffusion is the mass transfer controlling mechanism. Biot numbers up to 2000 and 200 for the constant and variable diffusivity models were tested, respectively, beyond which the computational time was long and the application of a two-phase model becomes meaningless (see Table 5). These minimum Biot numbers correspond to minimum liquid phase mass transfer coefficients discussed above. Thus, the optimization was made by varying the Ds in the constant diffusivity model and the Ds and λ in the variable diffusivity model (Fig. 4).

Some characteristic examples of the model results are shown in Figs. 5 and 6 and the quality of the fit is shown in Fig. 7. The average relative error was 12.54 ± 9.44% and 8.56 ± 6.74% for the constant and variable diffusivity models, respectively. As is evident, although the differences are moderate the variable diffusivity model owing to its flexibility provides better predictions. However, its major advantage is the insights it provides into the diffusion process, as discussed below.

The diffusion coefficients derived from the constant diffusivity model are in general agreement with the published data (Table 6). A comprehensive summary on diffusion coefficients in clinoptilolite is provided by Inglezakis et al., (2018 a,b) and for untreated clinoptilolite, diffusion coefficients are generally in the range of 10⁻⁹–10⁻¹⁰ cm²/s. The available surface diffusivities at zero loading values for liquid phase adsorption on zeolites are rare; values between 1.18–4.20×10⁻⁹ cm²/s have been reported for dyes adsorption on clinoptilolite (Meshko et al., 2001), 0.18–0.9×10⁻⁹ cm²/s and 3.00–6.40×10⁻⁹ cm²/s for Sr, Cs, Ca and Mg ion exchange on two different types of chabazite (Robinson et al., 1994) and 10⁻¹⁵–10⁻¹⁴ cm²/s for xylenes adsorption on felspite (Minceva and Rodrigues, 2004). All diffusion coefficients (Dₛ, Dₛ, Dₛ) are following the order Cu > Cr > Fe > Pb. As is evident, especially in the case of Pb, the difference between the Dₛ given by the constant diffusivity model and Dₛ given by the variable diffusivity model is considerable and thus the diffusion coefficient derived by use of the former provides a very rough approximation of the actual average diffusion coefficient. The blockage parameter (λ) shows some variation for the same metal but it is insignificant as is close to zero indicating the surface diffusion as the controlling intra-particle mass transfer mechanism. An exception is Fe where a value of 0.26 is observed but the overall conclusion is not altered. Moreover, Chen-Yang correlation predicts that for the same Dₛ and unhindered diffusion Dₛ increases with the increase of the surface coverage, which is observed for Pb but not for the other metals probably due to differences in the Dₛ and/or the experimental and model application errors. More data are needed in order to investigate the possible effect of surface coverage on Dₛ.
Table 6

Results summary.

|        | Cr   | Cr_1 | Cu  | Cu_1 | Fe  | Fe_1 | Pb   | Pb_1 | Pb_2 |
|--------|------|------|-----|------|-----|------|------|------|------|
| \(\text{Ds} \times 10^{-9} \text{ (cm}^2\text{/s)}\) | 6.00 | 4.00 | 11.00 | 7.89 | 4.00 | 2.75 | 1.10 | 1.30 | 5.06 |
| \(Y_{oo} \text{ (mod)}\) | 0.56 | 0.63 | 0.34 | 0.45 | 0.50 | 0.58 | 0.23 | 0.46 | 0.86 |
| \(\text{D}_{avg} \times 10^{-9} \text{ (cm}^2\text{/s)}\) | 4.20 | 2.83 | 7.72 | 4.95 | 3.40 | 1.32 | 0.17 | 0.24 | 1.64 |
| \(\lambda \) | 4.00 \times 10^{-4} | 9.00 \times 10^{-3} | 10^{-3} | 6.00 \times 10^{-5} | 0.26 | 4.00 \times 10^{-3} | 0.03 | 0.01 | 6.00 \times 10^{-6} |

Fig. 7. Model quality: constant diffusivity model (upper) and variable diffusivity model (lower).
6. Conclusions

A highly flexible homogeneous diffusion model was applied on the kinetics of Pb2+, Zn2+, Cr3+, Fe3+ and Cu2+ adsorption on clinoptilolite. The model incorporates the Chen-Yang surface diffusivity correlation and the double selectivity equilibrium equation. The studied systems follow Langmuir isotherm type for Pb2+, Zn2+ for Cr3+ and Fe3+ and linear for Cu2+. The concentration-dependent surface diffusion model was compared with the constant diffusivity surface diffusion model and found to be moderately more accurate. The concentration-dependent surface diffusion model average deviation from the experimental data is 8.56 ± 6.74% and the average solid phase diffusion coefficients between 10−9 and 10−11 cm2/s. All diffusion coefficients (Da, Dso, Davr) are following the order Cu > Cr > Fe > Pb. The application of the model showed that the uptake rate is controlled by the intra-particle diffusion with a very low blockage parameter, which indicates unhindered surface diffusion mechanism. Further experiments are needed to investigate the apparent variability of the blockage parameter and surface diffusion coefficient at zero loading.

Declarations

Author contribution statement

V.J. Inglezakis: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
M. M. Fyrillas: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Additional information

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