Diffusion models for adsorption kinetics of Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ onto natural zeolite

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ABSTRACT

The kinetics of zinc, cadmium, and lead ions removal by natural zeolite-clinoptilolite has been investigated using an agitated batch adsorber. Batch experiments at constant temperature have been performed. The influence of agitation speed, initial heavy metals concentration and particle size of the sorbent on the removal efficiency of heavy metals from liquid phase have been studied. A decrease in the initial heavy metals concentration in aqueous solutions prolongs the time needed for equilibrium. Two kinetics models according to the Vermeulen’s approximation and the parabolic diffusion model have been tested with the experimental data for adsorption of heavy metals onto natural zeolite. For the systems examined, the fit of the proposed models with the experimental data was shown to be equally good using both models. The diffusion coefficients are calculated from kinetic models of heavy metal ions and they are of the order from $10^{-5}$ to $10^{-6}$ cm$^2$/min. The diffusion coefficients depend on initial concentration for both models.

Key words | heavy metal sorption, kinetic, natural zeolite, parabolic diffusion model, Vermeulen’s approximation

INTRODUCTION

Heavy metal bearing wastes are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even at tract concentrations. As a consequence, methods to remove metal species from wastewaters have been the subject of different researches, in order to improve the water quality (McKay 1996; Cooney 1998). A number of methods for metal ions removal from wastewaters have been used, but most of them have disadvantages, such as continuous input of chemicals, high cost and even incomplete metal removal (Brown et al. 2000).

Adsorption is a very effective process for a variety of applications, and now it is considered an economical and efficient method for metal ions removal from wastewaters. The most generally used solid adsorbent is activated carbon which is a very efficient solid adsorbent in many different applications (Cooney 1998). However, activated carbon is expensive and for effluents containing metal ions activated carbon requires chelating agents to enhance its performance, thus increasing the treatment cost. Therefore, the need of alternative low-cost adsorbents has encouraged the search for new and cheap sorption processes for aqueous effluent treatment, as these materials could reduce significantly the wastewater-treatment cost (Yavuz et al. 2003; Erdem et al. 2004; Meshko et al. 2006; Babu & Gupta 2008; Southichak et al. 2009).

Natural materials that are available in large quantities may have the potential as inexpensive adsorbents. A review of several alternative adsorbents is given by Bailey et al. (1999) and Babel & Kurniawan (2003). Zeolites are low-cost naturally occurring hydrated aluminosilicate minerals, with wide geographic distribution and large size of deposits.

doi: 10.2166/wst.2010.918
(Kurniawan et al. 2006). In the last decade, there has been an increasing interest in the use of natural zeolites as cation exchangers in the treatment of heavy metals containing effluents. In addition, the ion exchange capacity natural zeolites exhibit adsorption behaviour that is based on the theory of acid and basic sites in the framework structure. The sorption on zeolite particles is a complex process because of their porous structure, presence of exchangeable ions, the inner and outer changed surface, the mineralogical heterogeneity, the existence of crystal edges, the broken bonds, and other imperfections on the surface (Altin et al. 1998).

Among the natural zeolites, clinoptilolite is the most abundant and commonly used as an ion exchanger or adsorbent for inorganic or organic compounds. The specific structure of the clinoptilolite, consisting of a three-dimensional system of two types of channels (ten-member and eight-member rings) that are occupied by exchangeable Na, K, Ca and Mg ions, is responsible for its ion exchange and molecular sieve properties (Arcaya et al. 1996; Minceva et al. 2007, 2008a). These exchangeable ions are located in the frame channels, coordinated with the defined number of water molecules that affect their mobility within the structure. Several researchers have studied the removal performance and selectivity sequence of heavy metal ions by natural zeolites (Bectas & Kara 2004; Culfaz & Yagız 2004; Wingenfelder et al. 2005; Berber-Mendoza et al. 2006).

The study of sorption kinetics in wastewater treatment is important since it provides valuable insights into the reaction pathways and mechanism of the adsorption process. In addition, the kinetics describes the solute uptake rate and mass transfer resistance at the solid–solution interface. In the literature, the kinetic models with varying degrees of complexity have been developed for sorption in batch systems. Most of these models, which may include surface reaction kinetics (Chu 2002; Bectas & Kara 2004), as well as various steps of mass transfer resistance (Markovska et al. 2006; Trgo et al. 2006) were already discussed. The aim of this work is to evaluate the kinetic models that can be used to describe the rate of the heavy metal ions uptake within heterogeneous and porous zeolite particles. Vermeulen’s approximation and the parabolic diffusion model are used to describe kinetic of the heavy metals adsorption onto natural zeolite (ZEO).

**MODEL EQUATIONS**

The solute uptake by microporous solid has been examined previously for lead onto clinoptilolite (Inglezakis & Grigoropoulou 2001), copper onto chitosan (Chu 2002) zinc and lead onto clinoptilolite (Trgo et al. 2006). The authors suggested three time-dependent steps for diffusive transport of solutes into microporous zeolite: (1) mass transfer of solute from the bulk solution to the particle surface across the boundary layer, also termed external diffusion, (2) intraparticle diffusion, and (3) adsorption at the interior sites, with either 1 or usually 2 being the rate-limiting steps.

External diffusion is the diffusion through the boundary layer from the solution to the surface of the solid that affects the length of time for the solute to reach the external surface of a solid. Within the boundary layer, the diffusive mass transfer dominates over the turbulent actions of the surrounding fluid. For a given sorbent and solvent, the boundary layer resistance is determined by the hydrodynamics of the system. In some cases, usually associated with high agitation rates, the external diffusion is not the rate-limiting step and does not affect the overall uptake rate. In other cases the external diffusion rate is sufficiently diminished across the boundary layer to retard the initial uptake, creating a boundary layer resistance (Ruthven 1984; Crank 1975). In this study, it is assumed that the external diffusion is not the rate-limiting step (the external mass transfer is an insignificant result of good mixing) and that the interparticle diffusion affects the overall uptake rate.

**The diffusion model according to Vermeulen’s approximation**

Considering the particle diffusion as a controlling step, the balance equation in radial coordinates is:

\[
\frac{\partial C}{\partial t} = D_r \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right)
\]

where \( r \) is the radial distance, \( t \) is the time, \( C \) is the concentration of the dissolved metal inside the microporous
zeolite, \( D \) is the diffusion coefficient. Crank (1975) gives an exact solution to Equation (1) for the case where the sphere is initially free of the solute and the concentration of the solute at the surface remains constant. The constant surface concentration also requires that the external film resistance is negligible. For the average concentration in the solid at any given time, \( q_t \), relative to the average concentration in the solid at infinite time, \( q_e \), (equilibrium concentration in solid phase) the Equation (1) can be expressed as:

\[
F = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp \left( -\frac{D t \pi^2 i^2}{r^2} \right)
\]

where \( F = q_t / q_e \) is the fractional attainment of equilibrium in the sorption at time \( t \). \( i \) is an integer that defines the infinite series solution (Ruthven 1984). For the criterion of “infinite solution volume” Equation (2) can be simplified in the form:

\[
F = 1 - \exp \left( -\frac{D t \pi^2}{r^2} \right)
\]

Vermeulen’s approximation (Equation (2)) is widely applied in the related literature, in case of the sorption onto various materials (Inglezakis & Grigoropoulou 2001; Mohan & Singh 2002; Trgo et al. 2006).

The parabolic diffusion model

The assumption that macropore and micropore diffusion occurs in series that leads to a model containing coupled partial differential equations, involving time and spatial variables. Researchers (Inglezakis & Grigoropoulou 2001; Trgo et al. 2006) often simplify the mathematics by assuming that concentration profiles in zeolite crystals have parabolic shape. This model assumes that the quantity of metal bound throughout the spherical particle is uniform and can be expressed as:

\[
F = \frac{4}{\pi^{1/2}} \left( \frac{D t}{r^2} \right)^{1/2} - \frac{1}{3} \pi \left( \frac{D t}{r^2} \right)^{3/2}
\]

For small values of time \( t \) the third term may be ignored, and from the slope of the linear relationship \( F/t \) versus \( 1/t^{1/2} \), the diffusion coefficient may be calculated. In this model \( F \) is again the fractional approach to equilibrium.

MATERIALS AND METHODS

Chemicals

The Pb\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) ion water solutions were prepared by dissolving respective amount of metal nitric salts, Pb(NO\(_3\))\(_2\) (Merk, Germany), Zn(NO\(_3\))\(_2\)-6H\(_2\)O (Fluka, Germany) and Cd(NO\(_3\))\(_2\)-4H\(_2\)O (Fluka, Germany), respectively, in distilled water. All chemicals used were analytical grade. The NO\(_3\)\(^-\) anions do not influence the ion-exchange process, since they do not form any metal-anion complexes and do not hydrolyze in water solution. The initial metal ion concentration used in the adsorption kinetics experiments was in the range between 50 mg dm\(^{-3}\) and 1,400 mg dm\(^{-3}\). The concentration of metal ions was measured by atomic absorption spectrophotometer (ARL, Ecublens, Switzerland).

Sorbent

The adsorbent was characterized by: X-ray diffraction (XRD) using Philips X’pert X-ray diffractometer; scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using Philips XL 30 CP Scanning Electron Microscope; and Fourier transform infrared spectroscopy (FTIR) techniques using Nicolet Impact 400 FTIR spectrometer. The ZEO specific surface area, total pore volume and real density were measured using multy-point-N2-BET method, using Quantachrome NovaWin2 system. The particle density was determined using Hg picnometry analysis. According to the supplier of the zeolite tuff, the ZEO consists mainly of clinoptilolite (more than 80%), heulandite and mordenite, also quartz, sanidine, and biotite are present in very small quantities. Prior to the experiments the ZEO was washed with distilled water in order to remove the surface dust and possible impurities and dried at 350°C for 48 h. After the treatment, the material was stored in well closed glass bottles. The results of the natural zeolite characterization and its properties are given in our previous work (Minceva et al. 2008a).
Equilibrium and kinetics experiments

The influence of the initial metal concentration and the adsorbent particle size on the rate of uptake of Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ was determined by carrying out contact time experiments using batch agitated reactor. The range of varying the initial metal concentration was 50–250 mg dm$^{-3}$ for Pb$^{2+}$, Zn$^{2+}$ and 900–1,400 mg dm$^{-3}$ for Cd$^{2+}$. The range of average particle size was 700–1,400 μm. The range of agitation speed was 150–190 rpm. Batch kinetic studies were performed in order to investigate the applicability of the simplified models on natural zeolite. A certain quantity of zeolite (1 g) was added a vessel containing a known volume of metal solutions (200 ml), in the 5–7 pH range at 25°C for 1 to 4 days, a period checked to be adequate for equilibrium attainment. Equilibrium capacities of natural zeolite for investigated heavy metals were reported in our previous work (Minceva et al. 2008a). Samples were withdrawn at several time intervals and analyses of heavy metals remaining in the solution were performed. All the experiments were repeated three times. The concentrations of adsorbed Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ on the natural zeolite were calculated according to the equation of material balance (Equation (5)):

\[ q_t = \frac{V}{m}(C_0 - C_t) \]  

(5)

where V is solution volume, m is sorbent mass, C$_0$ initial heavy metal concentration, C$_t$ heavy metal concentration at time t.

RESULTS AND DISCUSSION

Series of experiments were undertaken to study the influence of the agitation speed, the particle size of the adsorbent, and the initial metal concentration for the three investigated systems heavy metal–natural zeolite. The results of contact time studies are plots of $q_t$ versus time.

Effect of agitation speed

The rate of the heavy metals removal was not significantly influenced by the degree of agitation. These results show that the mass transfer through the external film is not affecting the sorption rate, and therefore is not rate controlling step of the entire sorption process. McKay et al. (1982) and later Meshko et al. (2001) found that the variation of the external mass transfer coefficient with the agitation was more significant if very low agitation speeds were used (rpm < 50). Within this investigation the agitation speed of 190 rpm has been used in order to eliminate the effect of liquid film resistance.

Effects of particle size

The influence of the particle size on the Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ sorption kinetics have been studied. The sorption of Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ on natural zeolite is slightly increased by decreasing the average particle size from 1,400 to 700 μm. The relatively higher sorption with smaller sorbent particles may be a result of the fact that smaller particles yield a large surface area. There is a tendency that smaller particles produce shorter time to equilibration (Minceva et al. 2008b).

Effects of initial concentration

The initial Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ concentrations of an effluent are important since a certain mass of sorbent can only adsorb a fixed amount of heavy metal. Therefore, the more concentrated the effluent, the smaller the volume of effluent that a fixed mass of zeolite can purify.

The effect of initial concentrations on the sorption was investigated by varying the initial heavy metals concentration at constant agitation speed of 190 rpm and the particle size of $d_p = 1,100$ μm, sorbent dosage of 1 g, and temperature of 25°C. Initial uptakes for lead and cadmium are very rapid for all investigated initial concentration, then gradually decreased toward the equilibrium concentration. At a lower initial lead concentration, the equilibrium is established at 100 min, while at higher concentrations it is achieved within 250 min. The adsorption of zinc shown in Figure 1 is slower for all investigated concentrations than the adsorption of lead and cadmium. At a lower initial concentrations the equilibrium is established for 3,000 min, while at a higher concentration it is achieved within 7,000 min. The equilibrium of cadmium for all investigated concentrations is established within 700 min (Figure 2).
Sorption kinetics modelling

In order to evaluate the effectiveness of the kinetic models used, investigations are deliberately made with a kinetic viewpoint. The kinetic studies involve the effect of some major parameters, initial concentration in the aqueous solution, and particle size on the uptake of Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ on the natural zeolite. In this study two kinetic models have been used to describe kinetics of sorption of Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ onto natural zeolite: the diffusion model according to Vermeulen's approximation and the parabolic diffusion model. The models used take into consideration that the intraparticle diffusion is a slow and controlling step.

Intraparticle diffusivities have been estimated by matching the predictions of the two models to the results of the batch reactor data shown in Figures 1 and 2. The simulation studies have been performed using MatLab software for different values of the diffusion coefficients. The simulation studies were stopped when the fitting of experimental data with both models examined has shown good correlation expressed by the values of the correlation coefficient. The values of $R^2$ are between 0.8–0.95 for all investigated systems. High values of $R^2$ show an agreement of experimental data with both the theoretical models proposed. Both models give good correlation between the theoretical models and experimental data for the system lead–natural zeolite. For the system zinc-natural zeolite (Figure 1) both models also have good correlation between the experimental data and the theoretical curves. For the system cadmium-natural zeolite (Figure 2) Vermeulen’s approximation model shows better correlation between experimental data and theoretical curves than the parabolic model. It can also be seen that the parabolic model gives higher values of the diffusion coefficients for all investigated

![Figure 1](https://iwaponline.com/wst/article-pdf/62/5/1136/446608/1136.pdf)

**Figure 1** | Application of two models to the experimental results for zinc.

![Figure 2](https://iwaponline.com/wst/article-pdf/62/5/1136/446608/1136.pdf)

**Figure 2** | Application of two models to the experimental results for cadmium.
concentrations than Vermeulen’s approximation model. The experimental results have shown a dependence of the diffusion coefficients on the initial heavy metals concentration (Table 1). The further investigation will be focused on obtaining the initial concentration dependence of diffusion coefficients for all the investigated systems. The diffusion coefficients of Pb²⁺ and Zn²⁺ calculated in this work have been compared with those calculated by other authors who examined adsorption and ion exchange of heavy metals on natural zeolite. Inglezakis & Grigoropoulos (2001) reported diffusion coefficients for lead calculated by using Vermeulen’s approximation and are of order 10⁻² cm²/min. These values are in the different order of magnitude comparing with the values obtained in our work. According to Trgo et al. (2006) the calculated diffusion coefficients for lead using Vermeulen’s approximation and the parabolic model are of order 10⁻⁶ cm²/min. Comparing these values with the values obtained in our work has shown that the order of magnitude is the same. However, the order of diffusion coefficient for zinc and Vermeulen’s approximation is 10⁻⁸ cm²/min which defers, as in our investigation the order is 10⁻⁶ cm²/min. The more detailed explanations for the differences of the diffusion coefficient order of the magnitude should be performed on the base of ions-exchange capacity for the metals ions. Data for diffusion coefficients of Cd²⁺ sorption on zeolites could not be found in the literature. In general, the simplified mathematical models lead to efficient and fast determining of the model parameters. For more rigorous estimations and more accurate model parameters values, the more complex models for approximation of the real situation should be used (Markovska et al. 2006). The values of the diffusion coefficients obtained in this investigation could be used for simulation studies based on the mathematical models presented by partial differential equations.

The results obtained within this study together with the adsorption capacities of the natural zeolite for the metal ions removal (Minceva et al. 2007, 2008) could be used for utilization of this adsorbent for the treatment of wastewater containing heavy metals. The natural zeolite is plentiful, inexpensive and readily available and gains attention as a simple effective and economical means of wastewater treatment.

### CONCLUSIONS

Experimental kinetic studies have been performed in a batch reactor to determine the mass-transfer mechanisms which significantly affect heavy metal sorption onto natural zeolite. Simplified solution of the partial differential equation which describes mass transfer mechanism in the particle, meaning Vermulen’s approximation and parabolic model, have been used for the determination of diffusion coefficients. Vermeulen’s approximation model shows better correlation between experimental data and theoretical curves than the parabolic model. The parabolic model gives higher values of diffusion coefficients for all investigated concentrations than Vermeulen’s approximation model. The experimental results have shown a dependence of the diffusion coefficients on the initial heavy metals concentration.

### REFERENCES


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