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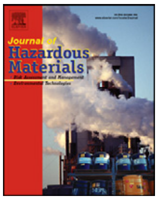

Novel kinetic model of the removal of divalent heavy metal ions from aqueous solutions by natural clinoptilolite

Mina Jovanovic[a], Nevenka Rajic[b], Bojana Obradovic[b,*]

[a] Innovation Center of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia
[b] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

HIGHLIGHTS

- A novel kinetic model for heavy metal removal by natural clinoptilolite.
- Two-step reaction in zeolite lattice: release of Na^+ followed by M^{2+} bonding.
- Kinetics of Cu(II), Mn(II), Zn(II) and Pb(II) removal from aqueous solutions.
- Kinetic constant of Na^+ release is not influenced by different metals.
- Kinetics prediction requires only one experimentally determined parameter.

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ABSTRACT

Removal of heavy metal ions from aqueous solutions using zeolites is widely described by pseudo-second order kinetics although this model may not be valid under all conditions. In this work, we have extended approaches used for derivation of this model in order to develop a novel kinetic model that is related to the ion exchange mechanism underlying sorption of metal ions in zeolites. The novel model assumed two reversible steps, *i.e.* release of sodium ions from the zeolite lattice followed by bonding of the metal ion. The model was applied to experimental results of Cu(II) sorption by natural clinoptilolite-rich zeolitic tuff at different initial concentrations and temperatures and then validated by predictions of ion exchange kinetics of other divalent heavy metal ions (*i.e.* Mn(II), Zn(II) and Pb(II)). Model predictions were in excellent agreements with experimental data for all investigated systems. In regard to the proposed mechanism, modeling results implied that the sodium ion release rate was constant for all investigated metals while the overall rate was mainly determined by the rate of heavy metal ion bonding to the lattice. In addition, prediction capabilities of the novel model were demonstrated requiring one experimentally determined parameter, only.

1. Introduction

Natural zeolites are attractive sorbents for applications in water treatment processes due to their abundance, low cost and excellent selectivity for a number of toxic metal cations. Numerous studies investigated sorption of different cations such as Cu(II) (*e.g.* [1–6]), Mn(II) (*e.g.* [7–11]), Zn(II) (*e.g.* [12–16]), Pb(II) (*e.g.* [2,4,10,13,17]), Ni(II) (*e.g.* [1,2,12,18,19]), Cr(III) (*e.g.* [10]) and Cd(II) (*e.g.* [1,2,12]). Recently, we have found that natural clinoptilolite-rich zeolitic tuff from the region of Vranjska Banja (Serbia) exhibits a good efficiency in removal of different heavy metal ions such as Mn(II), Ni(II), Cu(II) and Zn(II) [20–23].

Design and scale-up of sorption-based processes largely depends on the knowledge and understanding of the sorption kinetics and mechanism [24]. In this regard, various adsorption systems have been investigated and compared, as reviewed previously [25]. Kinetic models that have been proposed include reversible and irreversible first and second order kinetics, pseudo-first and pseudo-second order kinetics, Elovich's equation, and Ritchie's equation. Table 1 shows the most frequently used models for the sorption by zeolites.

It is evident that the pseudo-second order kinetics has been reported to provide the best results in most cases (Table 1). However, this model is widely used for different systems without any presumptions or specifications of process conditions while it can be derived based on different sorption mechanisms [31].

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* Corresponding author at: Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia. Tel.: +381 113370414; fax: +381 113370503.
E-mail addresses: mjovanovic@tmf.bg.ac.rs (M. Jovanovic), nena@tmf.bg.ac.rs (N. Rajic), bojana@tmf.bg.ac.rs (B. Obradovic).

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Table 1
Literature review of kinetic models used for sorption of various metal cations from aqueous solutions in zeolites.

Adsorbent	Kinetic models investigated	Heavy metal	Reference
Natural clinoptilolite	Reversible first order Lagergren pseudo-first order Pseudo-second order[a]	Cu(II), Cd(II), Ni(II)	[1]
Natural zeolite	Lagergren pseudo-first-order	Cu(II), Pb(II), Ni(II), Cd(II)	[12]
Clinoptilolite-chitosan	Lagergren pseudo-first order Pseudo-second order[a]	Cu(II), Co(II), Ni(II)	[26]
Clinoptilolite	Lagergren pseudo-first order Pseudo-second order[a]	Pb(II), Cu(II), Ni(II)	[2]
Natural clinoptilolite	Reversible first order Lagergren pseudo-first order Pseudo-second order[a]	Pb(II)	[17]
Natural zeolite	Irreversible first order Reversible first order Irreversible second order Elovich's equation[a]	Cu(II)	[27]
Synthetic zeolite NaX	Lagergren pseudo-first order Pseudo-second order Ritchie's equation[a]	Cu(II)	[28]
Zeolite A	Reversible first order Pseudo-second order Reversible second order[a]	Cu(II), Cd(II), Ni(II)	[29]
Zeolites: NaA and NaX	Lagergren pseudo-first order Pseudo-second order[a]	Zn(II)	[30]
Natural zeolite	Lagergren pseudo-first order Pseudo-second order[a]	Mn(II)	[11]
Clinoptilolite	Lagergren pseudo-first order Pseudo-second order[a]	Mn(II), Fe(III)	[9]
Manganese oxide coated zeolite	Lagergren pseudo-first order Pseudo-second order[a]	Mn(II)	[7]

[a] The best kinetic model selected by the authors.

The pseudo-second order kinetic model is described by the equation:

$$\frac{dx}{dt} = k_{II}(x_e - x)^2 \qquad (1)$$

where x and x_e are the concentrations of sorbed metal ions at time t and at equilibrium, respectively, and k_{II} is the rate constant. Integration of Eq. (1) from the starting time $t = 0$ and $x = 0$ to the time t and x, leads to:

$$x = \frac{k_{II} x_e^2 t}{1 + k_{II} x_e t} \qquad (2)$$

Eq. (2) can be rearranged to obtain a linearized form suitable for experimental data fitting:

$$\frac{t}{x} = \frac{1}{k_{II} x_e^2} + \frac{1}{x_e} t \qquad (3)$$

Several sorption mechanisms were considered to lead to this kinetic model.

Blanchard et al. [32] assumed that $NH_4{}^+$-modified zeolite reacts with divalent metal ions in the solution by an irreversible reaction:

$$M^{2+} + Z_{(2NH_4^+)} \rightarrow Z_{(M^{2+})} + 2NH_4^+ \qquad (4)$$

where Z presents the site in zeolite occupied either by two $NH_4{}^+$ ions, $Z_{(2NH_4^+)}$, or by a divalent metal ion, $Z_{(M^{2+})}$. The reaction rate was then assumed to be second order with respect to the number of available sites for the exchange at any given time t, which is further proportional to the difference in the amounts of metal ions exchanged at equilibrium and at the time t. Furthermore, the concentration of the M^{2+} in solution was assumed to be approximately constant leading to Eq. (1).

Ho and McKay [25] included chemisorption into the analysis and assumed that Cu(II) sorption on peat can be represented in two ways:

$$2P^- + Cu^{2+} \leftrightarrow CuP_2 \qquad (5)$$

and

$$2HP + Cu^{2+} \leftrightarrow CuP_2 + 2H^+ \qquad (6)$$

where P^- and HP are polar sites on the peat surface. It was assumed that the process may be second-order and that the reaction rate may depend on the amount of M^{2+} on the surface of the peat and the amount of M^{2+} adsorbed at equilibrium so that Eqs. ((1)–(3)) are derived.

Finally, Azizian [31] derived the model described by Eq. (2) by means of a different approach based on a general sorption mechanism:

$$A +^{*} \leftrightarrow A_{*} \qquad (7)$$

where the symbol * represents the vacant site on a sorbent and A is the adsorbate. The overall kinetic rate is assumed to be equal to the difference of the adsorption and desorption rates. The former was further assumed to be proportional to the concentration of the adsorbate A and the concentration of vacant sites while the latter was assumed to be proportional to the amount of sorbed A. Thus, the overall rate can be expressed as:

$$\frac{d\theta}{dt} = k_a C(1 - \theta) - k_d \theta \qquad (8)$$

where θ represents the coverage fraction, C is the concentration of adsorbate A in the solution and k_a and k_d are the kinetic rate constants of adsorption and desorption, respectively. Then the concentration C is expressed in terms of the initial adsorbate concentration and the amount sorbed that is proportional to the coverage fraction. Finally, by a rather complicated integration of Eq. (8), the pseudo-second order model can be derived for cases when the initial adsorbate concentration in solution is not too high [31].

It should be noted that only the mechanism described by Eq. (4) [32] is directly related to the ion exchange process taking place in zeolite lattice. However, it is assumed that the process is irreversible and that the metal ion concentration in the solution is