EVA CHMIELEWSKÁ[*]

BATCH TRIALS FOR DESCRIPTION OF
^{59}Fe TRANSPORT PROCESSES ONTO CLINOPTILOLITE

The paper deals with the fundamental transport processes of ^{59}Fe radionuclide from modelled aqueous solutions onto Slovakian zeolite and Chinese clinoptilolites as reference in order to determine external and internal diffusion parameters K, k_1, k_2, D.

A simplified adsorption model was applied. Classical equilibrium and kinetic experiments in batch operating mode at 3 various temperatures (20, 40, 50 °C) were used to compare behaviours of 4 types of zeolite samples – natural and Na-converted forms.

ABBREVIATIONS AND SYMBOLS

a — adsorption capacity of clinoptilolite with respect to Fe(III) ion species, mmol/g,

a_{max} — maximum adsorption capacity of clinoptilolite, mmol/g,

t — time, min,

c — concentration of Fe(III) ion species in solution, mmol/cm^3,

K — equilibrium distribution coefficient,

k_1, k_2 — external and internal rate constants, 1/s,

D — effective diffusion coefficient, cm^2/s,

r — radius of zeolite particles, cm,

α — angle of the slope represented by a graphical plot of a/a_{max} vs. $t^{1/2}$.

1. INTRODUCTION

Current procedures allowing abatement of pollution and remediation of environment are moderately centered on zeolite ion-exchange properties. Due to the selectivity of some cations, nuclear radiation resistance, low cost and ecological compatibility, natural zeolites are being applied not only in pollutant removal, but also in agricultural fertilizing, waste stabilization and the others.

[*] Comenius University, Faculty of Natural Sciences, Bratislava, Slovak Republic.

As is generally known, most industrial uses of ion exchange depend critically on the kinetics of this process. In a zeolite ion-exchange, the rate-controlling step is particle diffusion process, which means that the rate of the exchange depends upon the diffusion of cations, water molecules as well as cation–water complexes passing the zeolite framework.

Kinetic analyses of exchange rates can be performed via an appropriate solution of the Fickian diffusion laws [1], [2].

The application of kinetic analyses in heterogenic systems is less successful compared to an idealized, one-component system. Some progress is made to fit the kinetics of the zeolite ion-exchange to current theory [3].

Therefore the aim of this paper was to characterize the kinetics of adsorption of ionic Fe(III) species on local clinoptilolite and Chinese one as reference, modelled by pure water solutions with izotopic carrier and batch operating technique.

2. EXPERIMENTAL

The zeolitic tuffs employed in this project were local clinoptilolite obtained from the industrial deposit at Nižný Hrabovec and Chinese clinoptilolite as comparable natural ion exchanger from south-east Hubei.

The zeolite content of the samples, measured according to various techniques (e.g. X-ray diffraction, ion exchange, water-vapour desorption), for Slovakian tuff ranged between 65–70% and for Chinese tuff between 50–55%.

The samples were loaded up with Na following an ion exchange procedure analogous to that reported by many other authors [1], [2], [4]. The zeolite was machine ground and thereafter screened mechanically to make it ready for a pre-selected particle size distribution (0.250–0.315 mm), followed by agitation in 10% aqueous solution of NaCl at room temperature for 3 days. After equilibration, samples were filtered, once more washed with distilled water and oven-dried at 105 °C.

Weighed quantity of $FeCl_3 \cdot 6H_2O$ salt in deionized water enriched with the tracer Fe(59) of low activity and acidified to pH 2 simulated a polluted water.

Analyses of Fe(59) concentration were made by means of a spectrometric set combined with well-γ-scintillation detector NaI(Tl).

3. RESULTS AND DISCUSSION

Film theory, penetration theory, boundary layer theory and the other have been provided to explain mass transfer in the region separating a turbulent bulk solution and a solid surface [2], [3].
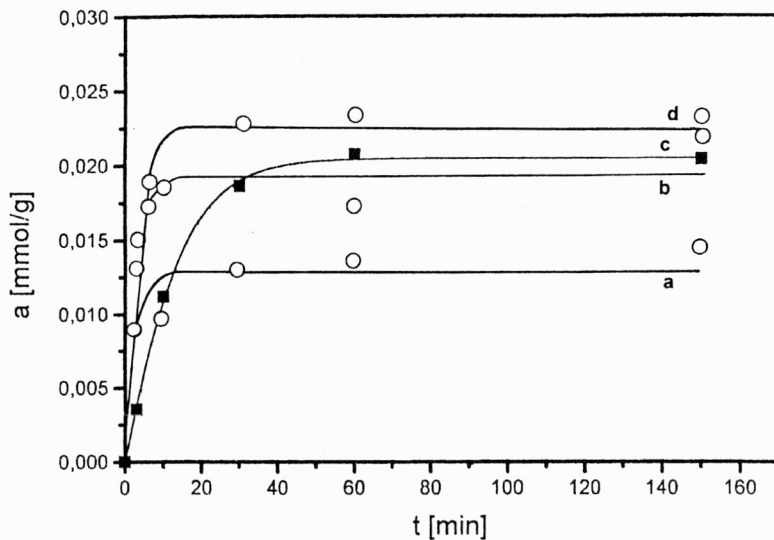
Fig. 1. Kinetic plot: time vs. adsorption capacity of zeolite
with respect to Fe(III) species at a system temperature of 20 °C for:
a) Chinese natural clinoptilolite, b) Chinese Na-modified clinoptilolite,
c) Slovakian natural clinoptilolite, d) Slovakian Na-modified clinoptilolite

Fig. 2. Kinetic plot: time vs. adsorption capacity of zeolite
with respect to Fe(III) species at a system temperature of 40 °C for:
a) Chinese natural clinoptilolite, b) Chinese Na-modified clinoptilolite,
c) Slovakian natural clinoptilolite, d) Slovakian Na-modified clinoptilolite
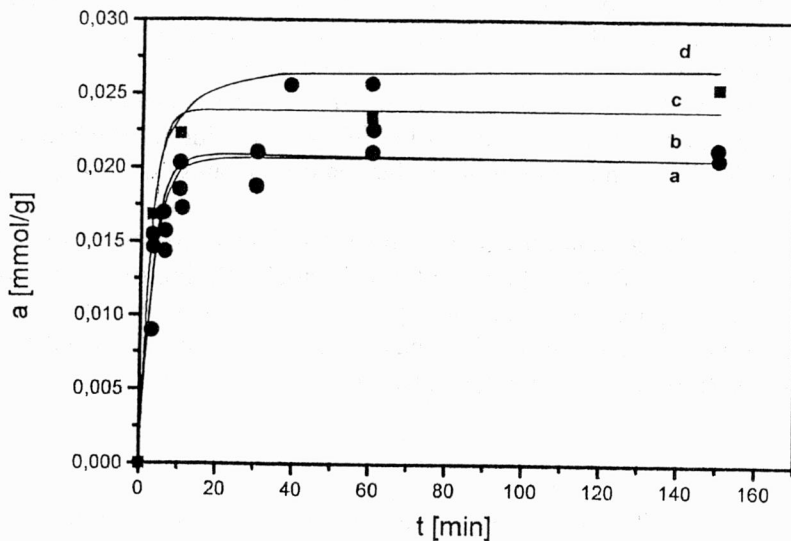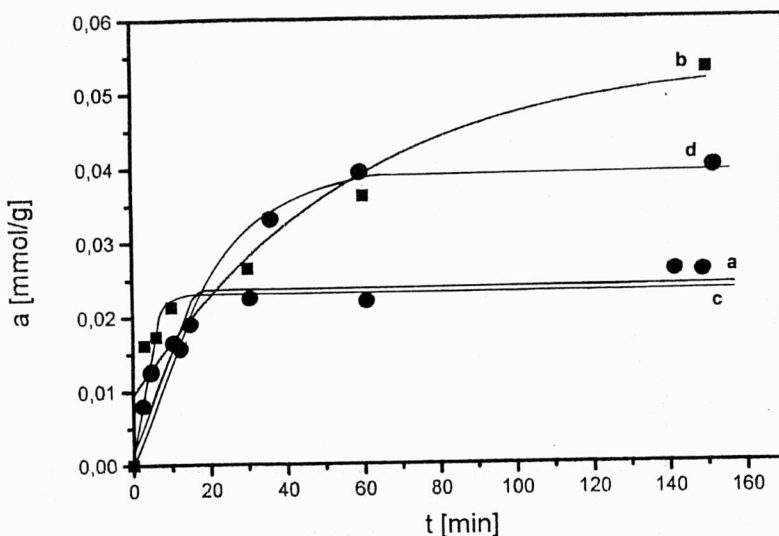
Fig. 3. Kinetic plot: time vs. adsorption capacity of zeolite
with respect to Fe(III) species at a system temperature of 50 °C for:
a) Chinese natural clinoptilolite, b) Chinese Na-modified clinoptilolite,
c) Slovakian natural clinoptilolite, d) Slovakian Na-modified clinoptilolite

In the processes of adsorption and ion exchange, the rate of intraparticle transport frequently governs the overall rate of removal of solute from solution. According to the above theory, the research is focused on model, fundamental transport processes of Fe(59) radiotracer onto zeolite ion-exchanger and therefore maximum effort is devoted to the use of Fe(59) radionuclide in order to identify the transport mechanisms and to determine the scale and rates of Fe(III) species' adsorption onto zeolite [3].

Classical equilibrium and kinetic experiments in batch operating mode, at 3 various temperatures (20, 40, 50 °C) and with initial stock solution of 2 mmol/dm³ FeCl₃ were applied to compare behaviours of 4 types of zeolite samples (figures 1, 2, 3). In this paper, the rate constant of the film mass transfer (k_1) was estimated from the kinetic plot (a vs. t) using the following equation [4]:

$$k_1 = \frac{da/dt}{cK} \tag{1}$$

where K is the equilibrium distribution coefficient, c denotes the concentration of Fe(III) ions in the solution (in mmol/cm³) and da/dt represents adsorption rate (with the surface diffusion as limiting factor).

Since intraparticle diffusion is the rate-controlling step, determination of the diffusion coefficient (D) is essential and can be obtained from the following equation [4]:

$$\frac{a}{a_{max}} = \frac{6}{r}\left(\frac{Dt}{\pi}\right)^{1/2}.$$ (2)

The effective diffusion coefficient was evaluated on the basis of the graphical plot a/a_{max} vs. $t^{1/2}$ using the following equation [4]:

$$D = \frac{\pi r^2}{36}\tan^2\alpha,$$ (3)

whereas the rate constant (k_2) of the internal mass transfer can be approximated from the equation [4]:

$$k_2 = \frac{\pi^2 D}{r^2},$$ (4)

r is the radius of zeolite particle (in cm).

In addition to the above, it can be stated that the transport mechanism of an adsorbate within the adsorbent particle is simplified by the model which accepts spherical adsorbents' particles with an identical radius and uniform concentration of adsorbates in the batch adsorber.

Table

Kinetics of ^{59}Fe removal from aqueous solution on zeolite

Clinoptilolite type	Ambient temperature	da/dt	$K = a_{eq}/c_{eq}$	k_1	D	k_2
		mmol/g/s		1/s	cm^2/s	1/s
a – Chinese natural	20 °C	$1.6333 \cdot 10^{-5}$	7.9331	$1.0820 \cdot 10^{-3}$	$1.1500 \cdot 10^{-9}$	$5.7846 \cdot 10^{-5}$
b – Chinese Na-form		$3.0716 \cdot 10^{-5}$	13.1862	$1.2830 \cdot 10^{-3}$	$9.9000 \cdot 10^{-10}$	$4.9797 \cdot 10^{-5}$
c – Slovak natural		$1.8238 \cdot 10^{-5}$	11.3585	$8.5055 \cdot 10^{-4}$	$1.8775 \cdot 10^{-9}$	$9.4440 \cdot 10^{-5}$
d – Slovak Na-form		$3.3333 \cdot 10^{-5}$	12.4227	$1.4906 \cdot 10^{-3}$	$1.0674 \cdot 10^{-9}$	$5.3692 \cdot 10^{-5}$
a – Chinese natural	40 °C	$3.0816 \cdot 10^{-5}$	11.5200	$1.4779 \cdot 10^{-3}$	$1.1734 \cdot 10^{-9}$	$5.9023 \cdot 10^{-5}$
b – Chinese Na-form		$3.0483 \cdot 10^{-5}$	11.9890	$1.3992 \cdot 10^{-3}$	$1.0593 \cdot 10^{-9}$	$5.3285 \cdot 10^{-5}$
c – Slovak natural		$3.7100 \cdot 10^{-5}$	14.5475	$1.4247 \cdot 10^{-3}$	$1.0732 \cdot 10^{-9}$	$5.3983 \cdot 10^{-5}$
d – Slovak Na-form		$3.3683 \cdot 10^{-5}$	19.6172	$9.5501 \cdot 10^{-4}$	$1.5159 \cdot 10^{-9}$	$7.6251 \cdot 10^{-5}$
a – Chinese natural	50 °C	$3.1666 \cdot 10^{-5}$	14.6723	$1.2193 \cdot 10^{-3}$	$1.2415 \cdot 10^{-9}$	$6.2448 \cdot 10^{-5}$
b – Chinese Na-form		$3.5555 \cdot 10^{-5}$	36.0925	$5.5135 \cdot 10^{-4}$	$1.3005 \cdot 10^{-9}$	$6.5416 \cdot 10^{-5}$
c – Slovak natural		$3.3166 \cdot 10^{-5}$	14.4885	$1.2717 \cdot 10^{-3}$	$1.4741 \cdot 10^{-9}$	$7.4148 \cdot 10^{-5}$
d – Slovak Na-form		$3.1916 \cdot 10^{-5}$	23.8313	$7.4053 \cdot 10^{-4}$	$1.5095 \cdot 10^{-9}$	$7.5929 \cdot 10^{-5}$

The table summarizes the data computed. From the table it can be seen that the surface diffusion is dominant, however an adsorption rate, comparable to other published data dealing with kinetics of ion exchange on natural zeolites, is generally very low [4]. There is some tendency to increase the values of effective diffusion coef-

ficients D and the rate constants of internal mass transfer k_2 with the rise of ambient temperature. The same concerns the equilibrium distribution coefficients. This phenomenon correlates with the increase in mass fraction of the tested radionuclide in zeolite.

The rate constants of the film mass transfer k_1 cannot be defined strictly with the temperature rise.

Probably adsorption capacity of the Slovakian Na-modified clinoptilolite (tested under extremal laboratory conditions) with respect to Fe(III) ion species was predominantly due to the higher clinoptilolite content in zeolite tuff of domestic origin compared to the Chinese clinoptilolite tuff and due to the monoionic nature of exchangeable cations.

The temperature rise up to 50 °C apparently increased the adsorption capacity data. This phenomenon may occur due to the increased total number of ions involved in the ion exchange and adsorption process, the removal of cation's water shells causing the accessibility to active sites. In a steady-state equilibrium, only slight differences in favour of natural forms of zeolites were observed.

4. CONCLUSIONS

As the method of removal of ^{59}Fe radionuclide dissolved in aqueous solution, batch adsorption experiment were carried out using local and Chinese clinoptilolites in natural and Na-modified forms.

The results show that the radionuclide–zeolite systems are highly heterogeneous basing on the adsorbate–adsorbent interaction as well as on the pore structure.

In the majority of the systems selected, the equilibrium steady-state was set up after approximately 10 minutes. Only Na-converted zeolites at ambient temperature of 50 °C exhibited a retarded steady-state process attainment.

External and internal parameters of zeolite diffusion were determined from experimental concentration histories.

ACKNOWLEDGEMENT

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SERIA PRÓB ZMIERZAJĄCYCH DO OPISU TRANSPORTU ^{59}Fe NA KLINOPTILOLICIE

Opisano zasady transportu radionuklidu ^{59}Fe z modelowych roztworów wodnych na słowacki zeolit i chiński klinoptilolit, który stanowi wzorzec. Celem artykułu było ustalenie parametrów dyfuzji, tj. K, k_1, k_2 i D.

Zastosowano uproszczony model adsorpcji. Przeprowadzono klasyczne doświadczenia równowagowe i kinetyczne polegające na serii prób w trzech temperaturach: 20, 40 i 50 °C. Posłużyły one do porównania czterech rodzajów próbek zeolitu zarówno naturalnego, jak i w formie zmodyfikowanej.