

CHARACTERIZATION OF DYNAMIC BEHAVIOR OF Cd(II) AND Zn(II) UPTAKE FROM A BINARY SOLUTION ONTO THE FIXED ZEOLITE BED

Ivona Nuić, Kristina Sabljo, Marina Trgo, Nediljka Vukojević Medvidović, Marin Ugrina*

Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21 000 Split, Croatia

*E-mail: ivona@ktf-split.hr

ABSTRACT

Cd(II) and Zn(II) were successfully removed from the equimolar binary aqueous solution by the column process. Two experiments were conducted with the 80 mm fixed bed of natural zeolite, at the flow rate of 1 ml/min. The obtained S-shape breakthrough curves and regeneration curves almost completely overlap, indicating that the compactness of the zeolite layer, reproducibility and stationary conditions were achieved. The dynamic behaviour in the packed column reactor has been examined according to the Advection-Dispersion-Reaction (ADR) model and kinetic parameters have been estimated.

Keywords: packed column reactor, cadmium, zinc, binary solution, ADR model.

INTRODUCTION

The application of natural zeolites as ion exchangers represents an efficient and cost-effective method of heavy metal removal from wastewaters to below the permissible concentrations [1]. Ion exchange can be performed by batch or column process. The practical application of zeolites includes only performance in the column as it offers the possibility of treatment of a larger amount of wastewater. It also provides for the use of the same zeolite sample for many service cycles due to the possibility of its regeneration. In order to design the column process, the dynamic behavior of the system has to be characterized [2]. In this paper the Advection-Dispersion-Reaction (ADR) model [3,4], which takes into account the fluid dynamics, has been applied to experimental breakthrough curves for a binary system and kinetic parameters in the column have been estimated.

EXPERIMENTAL

The raw zeolite sample which originated from Vranjska Banja (Serbia) deposit consists of up to 80% of clinoptilolite. The zeolite was milled and sieved to the particle size of $d_p = 0.6-0.8$ mm, rinsed with ultrapure water and dried at 60°C. Two experiments were carried out in a glass column with the inner diameter of 12 mm and height of 500 mm. The column was filled with the zeolite sample up to $H = 80$ mm, which corresponds to the zeolite mass of 5.9 g and bed volume of 9.04 cm³, with bed porosity of $\varepsilon = 0.693$. The (Cd+Zn) feed solution was prepared by dissolving Cd(NO₃)₂ x 4 H₂O and Zn(NO₃)₂ x 6 H₂O in ultrapure water, without pH adjustment (the initial pH was 5.1). The initial concentration $c_0 = 1.026$ mmol/l contained the approximately equimolar amount of Cd and Zn, Cd/Zn = 1.04. Column experiments were conducted at ambient temperature using the down flow mode through the fixed bed at the constant volumetric flow rate of $Q = 0.06$ l/h, which corresponds to the interstitial velocity of $\bar{v} = 0.766$ m/h. For recovery of the exhausted zeolite bed and its reuse, the regeneration was performed with NaNO₃, $c = 176.5$ mmol/l, under the same experimental conditions as the

service cycle. In all experiments the samples were collected at the bottom of the column and analysed for Cd(II) and Zn(II) using the Methrom 761 Compact IC liquid chromatograph and Perkin Elmer AS 800 AAS.

RESULTS AND DISCUSSION

The experimental results for two service cycles are plotted in Figure 1 as the ratio of effluent and influent (Cd+Zn) concentrations versus time t .

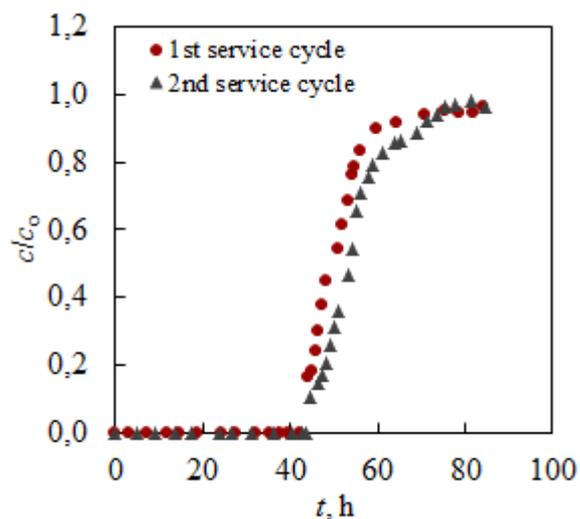


Figure 1. The breakthrough curves.

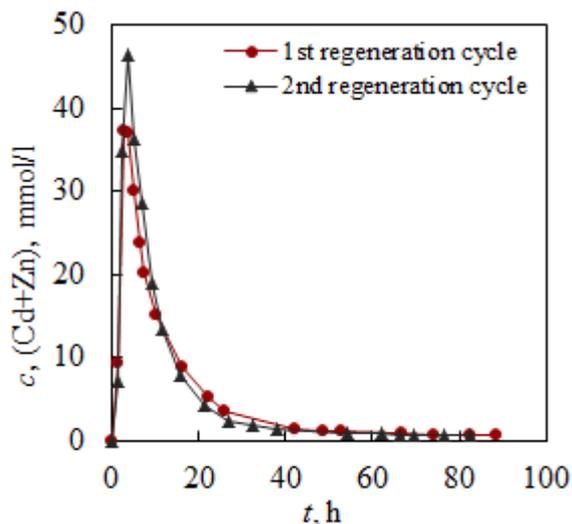


Figure 2. The regeneration curves.

It can be observed that the obtained S-shape breakthrough curves almost completely overlap. This indicates that the compactness of the layer and stationary conditions were achieved. Based on the Michael's method [5], the capacities in the breakthrough q_B and exhaustion q_E , as well as the total quantity n_R of Cd and Zn eluted from the zeolite bed during the regeneration cycle have been calculated and presented in Table 1. The breakthrough point t_B for both service cycles occurred after ≈ 44 hours, when $V_B \approx 2.6$ l of the binary solution was treated. The values of q_B are very close for both service cycles. The exhaustion point t_E for the 2nd service cycle was obtained a little later then for the first one, which made the curve of the 2nd cycle flatter and thus capacity q_E a bit higher.

Table 1. Parameters of the breakthrough and regeneration curves at $H = 8$ cm for the equimolar (Cd+Zn) solution.

Cycle	V_B , l	t_B , h	$q_B(\text{Cd+Zn})$, mmol/g	V_E , l	t_E , h	$q_E(\text{Cd+Zn})$, mmol/g	V_R , l	t_R , h	$n_R(\text{Cd+Zn})$, mmol/g	α , -
1st	2.64	44.00	0.442	3.87	64.50	0.514	0.48	8.00	0.633	1.23
2nd	2.67	44.50	0.437	4.40	73.33	0.547	0.49	8.17	0.658	1.20

Regeneration curves obtained after each service cycle are presented in Figure 2. Complete regeneration of the zeolite layer was finished after $t_R \approx 8$ hours with the consumption of NaNO_3 solution V_R less than 0.5 l. Regeneration is a very fast process that results in the 8-9 times smaller volume of the (Cd+Zn) solution compared to the volume treated in the service cycle. A

greater amount of ions was eluted in the 2nd regeneration cycle confirming that the layer was trained and more active sites in the zeolite structure were available for ion exchange. The regeneration coefficients $\alpha > 1$ indicate that ion exchange has continued even after the exhaustion point.

Although the column process is very useful for practical application, it is difficult to describe the dynamic behaviour of heavy metal removal in the column reactor because the process does not take place in steady state [2]. Since mass transfer from the liquid phase may be limited by the axial dispersion of the solution, an attempt was made to apply the ADR model to describe the breakthrough curve dynamics. The ADR model is based on the basic mathematical form of the material balance for fixed bed column reactors, and the axial dispersion coefficient D_L is used as a key parameter of the model [3,4]. The ADR model is given by Eq. (1):

$$\frac{c}{c_0} = \frac{1}{2} \cdot \left\{ 1 + \operatorname{erf} \left[\left(\frac{\bar{v} \cdot H}{4 \cdot D_L} \right) \cdot \frac{V_i - V_{\min}}{(V_i \cdot V_{\min})^{1/2}} \right] \right\} \quad (1)$$

where V_i is the total volume of the solution at the cross-sectional surface of zeolite bed, $V_i = \bar{v} \cdot \varepsilon \cdot t$, m^3/m^2 ; V_{\min} is the minimal volume of the solution required to saturate the zeolite bed at the cross-sectional surface, $V_{\min} = \bar{v} \cdot \varepsilon \cdot t_{\min}$, m^3/m^2 ; t_{\min} is the minimal time needed to saturate the zeolite bed at the cross-sectional surface, h. The parameters of the ADR model, D_L , V_{\min} and t_{\min} (Table 2) have been calculated by the nonlinear regression analysis in the MathCAD professional program including the experimental data t or V and c/c_0 of the 2nd service cycle in the derived form of Eq. (1).

By substituting the calculated model parameters into Eq. (1), for selected values of volume V_i , values c/c_0 have been calculated and model breakthrough curve plotted and compared in Figure 3 with experimental points.

A good agreement ($R^2 = 0.992$) of experimental points and the model curve has been obtained with slight deviations after the exhaustion point.

The axial dispersion coefficient D_L has been used for calculation of the mass transfer coefficient k_f through the diffusion boundary layer (Table 2) using Eq. (2) [6]:

$$\frac{c}{c_0} = \exp \left[\frac{Pe}{2} - \sqrt{\frac{Pe^2}{4} + \frac{(1-\varepsilon) \cdot k_f \cdot a \cdot H^2}{\varepsilon \cdot D_L}} \right] \quad (2)$$

where k_f is the mass transfer coefficient through the diffusion boundary layer of the zeolite particle (m/h), Pe is the Peclet number (-) which is calculated from $Pe = (\bar{v} \cdot H)/D_L$, and a is the

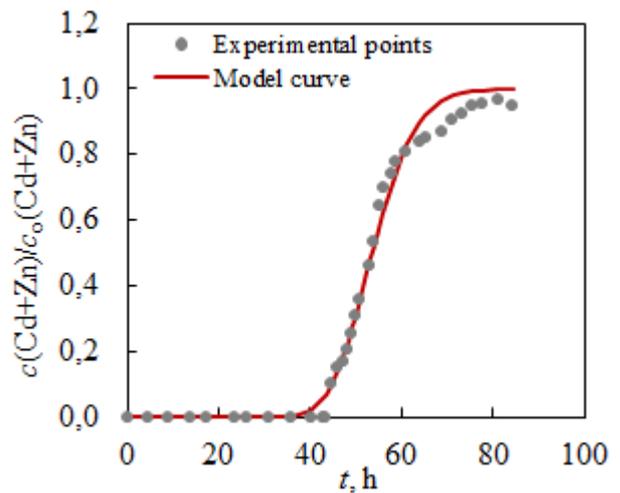


Figure 3. Comparison of experimental points and the obtained model breakthrough curve.

external surface of the zeolite particle per unit volume of the particle (m^{-1}) which equals $a = [6 \cdot (1 - \varepsilon)]/d_p$.

Table 2. The parameters of the ADR model and the mass transfer coefficient through the diffusion boundary layer.

Service cycle	$D_L \cdot 10^4$, m^2/h	V_{\min} , m^3/m^2	t_{\min} , h	R^2	$k_f \cdot 10^2$, m/h	
					$(k_f)_B$	$(k_f)_E$
2nd	6.07	28.47	53.63	0.992	1.918	0.066

The highest value of k_f is obtained in the breakthrough point $(k_f)_B$ and then decreases to the exhaustion $(k_f)_E$. Calculated values of k_f indicate a change in the mass transfer mechanism which has an impact on the overall process rate.

CONCLUSION

Cd(II) and Zn(II) have been successfully removed from the binary solution by the column process. The ADR model can be used for describing the dynamic behaviour of (Cd+Zn) uptake onto the fixed bed of natural zeolite. Continued binding even after the exhaustion point caused a significant increase of the ion concentration in the boundary layer of the zeolite particle. This increased the mass transfer resistance which finally resulted in reduction of k_f and had an impact on the overall process rate. The overall rate of the mass transfer process is influenced by the creation of the diffusion boundary layer around the zeolite particle and mass transfer by diffusion through the particle.

ACKNOWLEDGEMENT

We express our thanks to the Croatian Science Foundation which has fully supported this work under the project NAZELLT (IP-11-2013-4981).

REFERENCES

- [1] M.A. Barakat, *Arabian J. Chem.*, 2011, **4**, 361-377.
- [2] V.J. Inglezakis, *J. Eng. Stud. Res.*, 2010, **16**, No. 3, 29-41.
- [3] A. Hatzikioseyan, M. Tsezos and F. Mavituna, *Hydrometallurgy*, 2001, **59**, 395-406.
- [4] A. Kogej, B. Likozar and A. Pavko, *Food Technol. Biotechnol.*, 2010, **48**, 344-351.
- [5] I. Nuić, M. Trgo, J. Perić, and N. Vukojević Medvidović, *Microp. Mesop. Mater.*, 2013, **167**, 55-61.
- [6] Y.A. Alhamed, *J. Hazard. Mater.*, 2009, **170**, 763-770.