THE DERIVED FORM OF BREAKTHROUGH CURVES FOR MATHEMATICAL DESCRIPTION OF THE COLUMN PROCESS

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ABSTRACT

Mass transfer between the liquid and the solid phase in the column reactor has been analysed from the derived form of the model breakthrough curves obtained for the binary (Pb+Zn) solution at different flow rates. Up to the inflection area on breakthrough curves, mass transfer through the liquid phase governed the rate due to a higher number of available active sites in zeolite. After the inflection area, the active sites were occupied and competition between Pb and Zn occurred. Thus the particle kinetics became more significant and controlled the overall rate of the (Pb+Zn) uptake onto zeolite particles.

Keywords: mass transfer, zeolite fixed bed, binary solution, derived curve, Thomas model.

INTRODUCTION

The results of the column process are usually expressed by a breakthrough curve which has a typical S-shape. In order to define the mass transfer process and to characterize the dynamic behaviour of the system, the derivation of the model breakthrough curve has been made and its common form is shown in Figure 1. In the first part of the derived model curve the process rate increases, equals zero in the maximum, and then decreases. This approach has been successfully applied to Zn removal from a single solution [1,2]. This paper is the first attempt to apply this approach to the binary (Pb+Zn) solution at different flow rates.

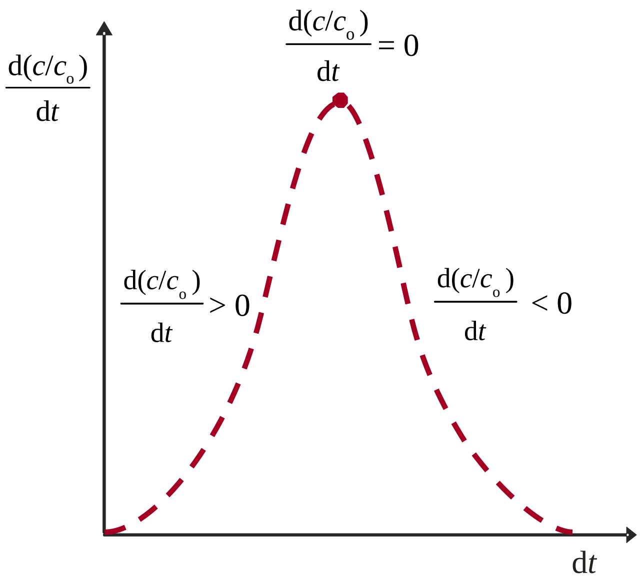

Figure 1. The derived form of breakthrough curve.

EXPERIMENTAL

The raw zeolite sample from the Zlatokop deposit in Vranjska Banja (Serbia) contains up to 80% of clinoptilolite. The zeolite was milled and sieved to the particle size of 0.6-0.8 mm, rinsed with ultrapure water and dried at 60°C. The equimolar (Pb+Zn) binary solution was prepared by dissolving $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ in ultrapure water, without pH adjustment (the initial pH was ~ 4.5). The total concentration of the binary solution was constant and equaled $c_o \approx 1$ mmol/l, with the Pb and Zn concentration ratio $c_o(Pb)/c_o(Zn) = 1.04$. A series of experiments was carried out at ambient temperature, in a glass column with the inner diameter of 12 mm and height of 500 mm. The column was filled with natural zeolite up to 80 mm, which corresponds to the mass of 5.9 g and bed volume of 9.04 cm^3. The inlet (Pb+Zn) solution was passed down through the bed at the constant flow rate of Q = 1, 2, 3 or 4 ml/min, with the aid of a vacuum pump. After each service cycle, the exhausted zeolite bed was prepared for reuse by regeneration with the $NaNO_3$ solution c = 176.5 mmol/l, at the flow rate of 1 ml/min, under the same operating conditions. In all experiments, the effluent samples were collected periodically and analyzed for Pb and Zn concentrations using the Methrom 761 Compact IC liquid chromatograph and Perkin Elmer AS 800 AAS.

RESULTS AND DISCUSSION

Total breakthrough curves (gray symbols in Figure 2) of Pb and Zn removal from the binary aqueous solution, at flow rates of 1, 2, 3 and 4 ml/min have been tested by the Thomas empirical kinetic model [3-5]. The obtained model breakthrough curves have been plotted (full blue lines in Figure 2) and compared with experimental points.

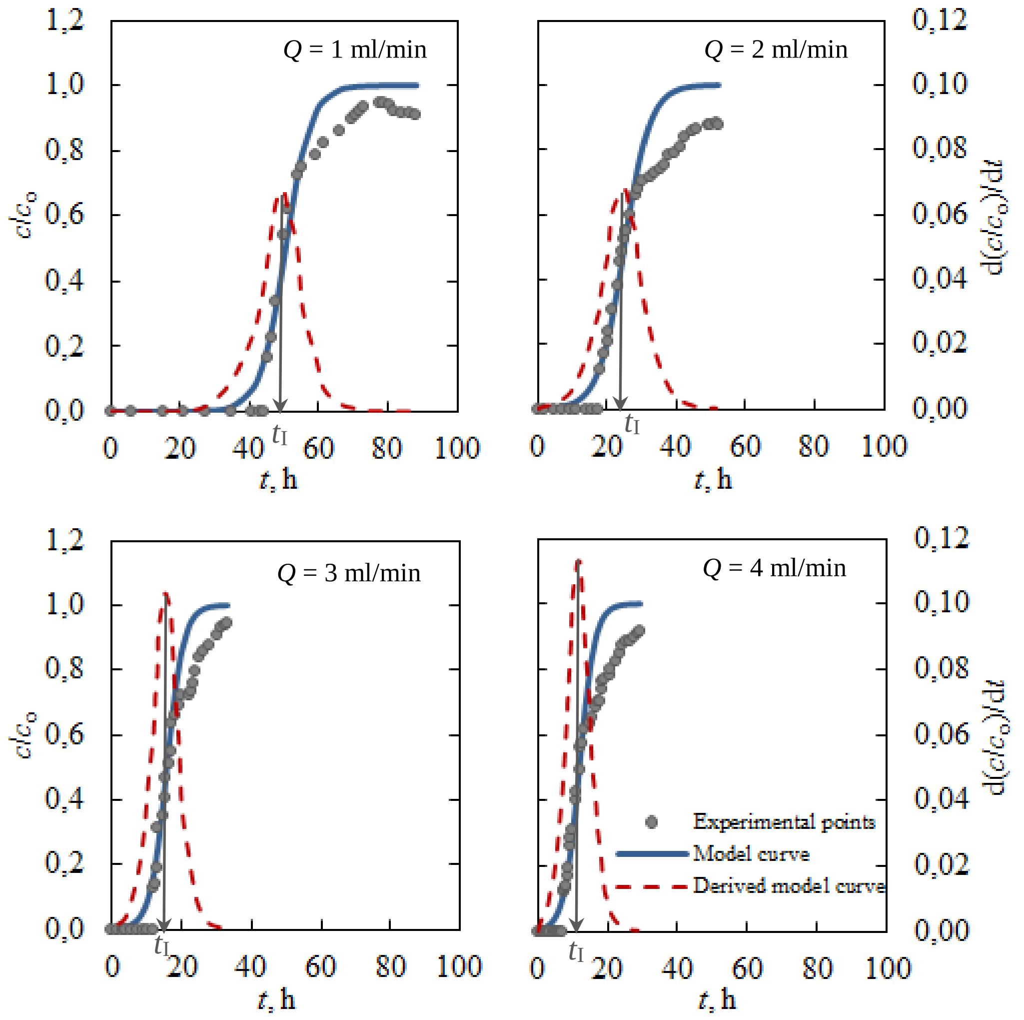

Figure 2. Comparison of experimental points and breakthrough curves obtained by the Thomas model and their derived form, for equimolar (Pb+Zn) solution at H = 80 mm for different flow rates.

A good agreement of experimental points and model curves can be observed, which indicates that the Thomas model can be used to obtain the derived form of the model curves. The obtained derived model curves (dashed red lines) plotted in Figure 2 have the form of a peak. With increasing flow rate, the derived curves are less extended and their maximum is higher. The maximum of each derived model curve occurs at an inflection point t_I of the model curve, indicating the change in mass transfer. Time t_I to achieve the inflection point is reduced with increased flow rate. A significant contribution to the interpretation of this change is given by the analyses of the quantity of Pb and Zn ions bound onto zeolite (Figure 3).

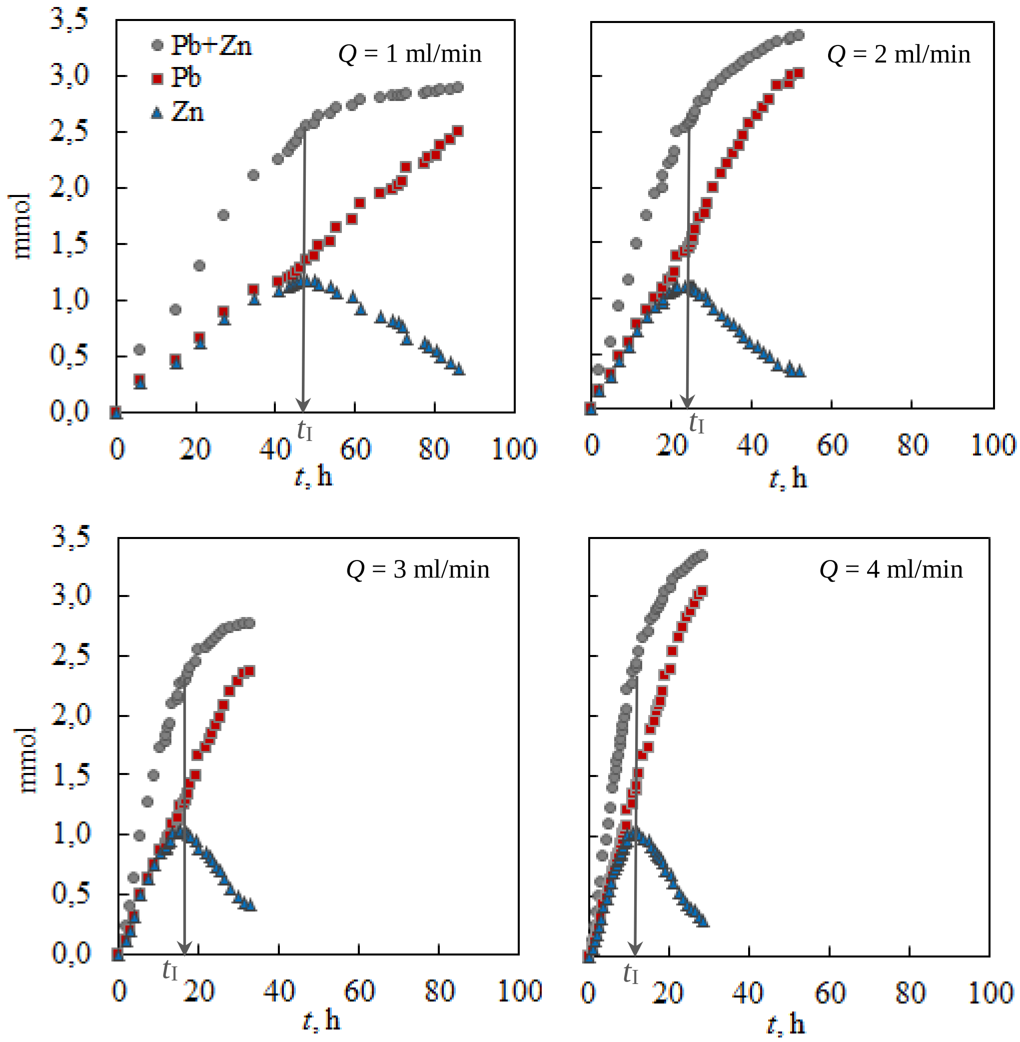

Figure 3. The quantity of Pb and Zn ions bound onto zeolite for the equimolar (Pb+Zn) solution at H = 80 mm for different flow rates. Note: t_I is the time which corresponds to the inflection point.

It can be noticed that for all examined flow rates the quantity of (Pb+Zn) ions increases linearly from the beginning of the experiment to t_I, after which it becomes slower, and thus parabolic. The change from linear to parabolic growth in quantity indicates a change in the mechanism of mass transfer and thus a change in the rate that controls the overall process. Up to the inflection area the overall process rate is controlled by mass transfer in the liquid phase. This is due to a higher number of available active sites in the zeolite structure, so Pb and Zn ions which come from the solution to zeolite are bound simultaneously. As the process progresses, active sites in the zeolite structure are increasingly occupied, so that all ions which come to zeolite will not be bound. Consequently, the competition between Pb and Zn ions for remaining active sites occurs [5]. This is the reason for deviations after the inflection on the breakthrough curve. Namely, after the inflection area, high concentrations of ions which participate in the ion exchange process accumulate around the zeolite particle, which affects the rate of mass transfer through the boundary layer. From the curves for single ions in Figure 3 it can be seen that after the inflection point, the quantity of Pb ions continues to increase, while the quantity of Zn ions rapidly decreases. This confirms the displacement of Zn by Pb, and thus higher affinity of Pb compared to Zn, as well as greater selectivity of zeolite towards Pb. Therefore, after inflection, particle kinetics i.e. mass transfer by diffusion through the boundary layer of the zeolite particle controls the overall process rate.

CONCLUSION

The maximum of the derived model curve, marked with time t_I, overlaps with the change from linear to parabolic growth of the quantity of Pb and Zn ions onto zeolite. This confirms that the derived form of the breakthrough curve can be used as a simple tool for the mathematical description of mass transfer mechanism through the zeolite fixed bed in the column reactor for the binary (Pb+Zn) solution.

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