ZINC UPTAKE IN A FIXED BED OF NATURAL ZEOLITE

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INTRODUCTION

Among the tertiary wastewater treatment processes, ion exchange on the natural zeolite is a very efficient one. Zeolites are hydrated alumosilicate minerals characterized by an outstanding capability of exchange of alkaline and earth-alkaline cations from their structure with heavy metal ions from aqueous solutions. Bearing in mind how widely spread natural zeolites are, and the simplicity and economic feasibility of their application, research into zeolites and their properties is of great scientific and practical interest [1-3]. This study has examined zinc uptake on natural zeolite in a column with a number of successive service and regeneration cycles.

EXPERIMENTAL

The natural zeolite sample originates from the Vranjska Banja (Serbia) deposit. The sample was milled, sieved to the particle size fraction of 0.6-0.8 mm, and pre-treated into the Na-form. The experiments were carried out in a glass column with the inner diameter of 12 mm and the height of 500 mm. The examination of Zn uptake on the zeolite was performed isothermally ($T = 23^oC$) at different zeolite bed depths (120, 80, and 40 mm), initial concentrations (c_o= 0.770 - 1.787 mmol Zn/l), and solution flows through the column (Q=1 - 3 ml/min), in the down-flow mode. At selected time intervals, the zinc concentration was determined in the effluent by complexometrical titration in an acid medium, using the highly selective indicator 3,3 dimetildinaftidin, and checked by ion chromatography (Methrom IC 761) [4]. The flow rate constancy was maintained by a vacuum pump. After the service cycle, regeneration was performed with the sodium sulphate solution $c_o(Na_2SO_4)$ = 105.60 mmol/l and the flow rate of Q = 1 ml/min, also using the down-flow mode. Table 1 shows the experimental conditions during the service cycle.

RESULTS AND DISCUSSION

The experimental results for zinc uptake on a fixed bed natural zeolite are represented by breakthrough curves plotted in Figures 1 - 5, and Table 1 shows the parameters calculated from the curves.

Table 1. Experimental conditions and the parameters calculated from breakthrough curves.

Cycle No.	Experimental conditions		V_B BV	t_B h	V_E BV	t_E h	q_B mmol /g	q_E mmol/g
	c_o mmol/l	Q ml/min						
zeolite bed depth H= 120 mm								
1st	1.067	1.0	293	69.12	469	110.53	0.451	0.547
2nd	1.067	1.0	340	76.83	540	122.00	0.528	0.650
3rd	1.067	1.0	395	89.33	524	118.50	0.604	0.692
4th	1.787	1.0	210	47.42	267	60.42	0.564	0.631
zeolite bed depth H= 80 mm								
5th	0.770	1.0	420	63.25	569	85.75	0.624	0.726
6th	1.083	1.0	348	52.50	473	71.33	0.578	0.786
zeolite bed depth H= 40 mm								
7th	1.083	1.0	353	26.58	482	36.33	0.593	0.703
8th	1.051	2.0	271	10.21	633	23.83	0.443	0.714
9th	1.054	3.0	294	7.39	649	16.31	0.482	0.759

Note: V_B, V_E, t_B, t_E - volume and time at the breakthrough and exhaustion points; BV- bed volume, q_B – capacity at the breakthrough point, q_E – capacity at the exhaustion point.

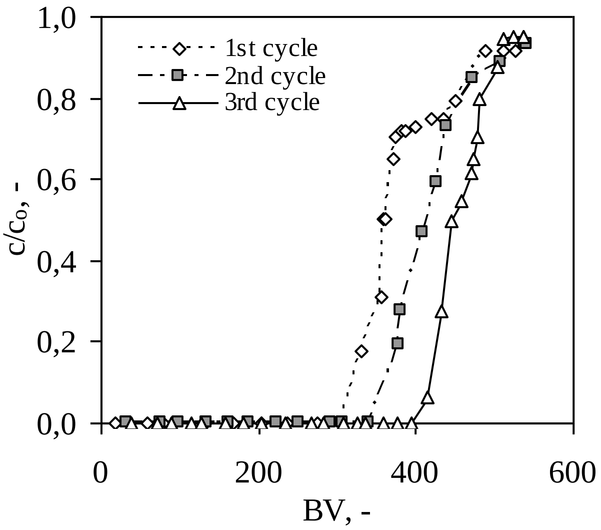

Figure 1. Breakthrough curves for the three first service cycles, at the constant solution concentration of 1.067 mmol Zn /l and the flow of 1.0 ml/min.

The breakthrough curves in Figure 1 assume the typical S-shape. After the first service cycle, the breakthrough curves shift slightly to the right, towards higher BV values and capacity. This may be attributed to the establishment of stable exchange conditions, better contact of the solid and liquid phases, and activation of exchangeable places in the zeolite-clinoptilolite structure during regeneration cycles.

Figure 2 shows the behaviour of breakthrough curves for zinc uptake for three different bed depths at the constant initial concentration and flow rate of the zinc solution (comparison of 3rd, 6th and 7th cycle).

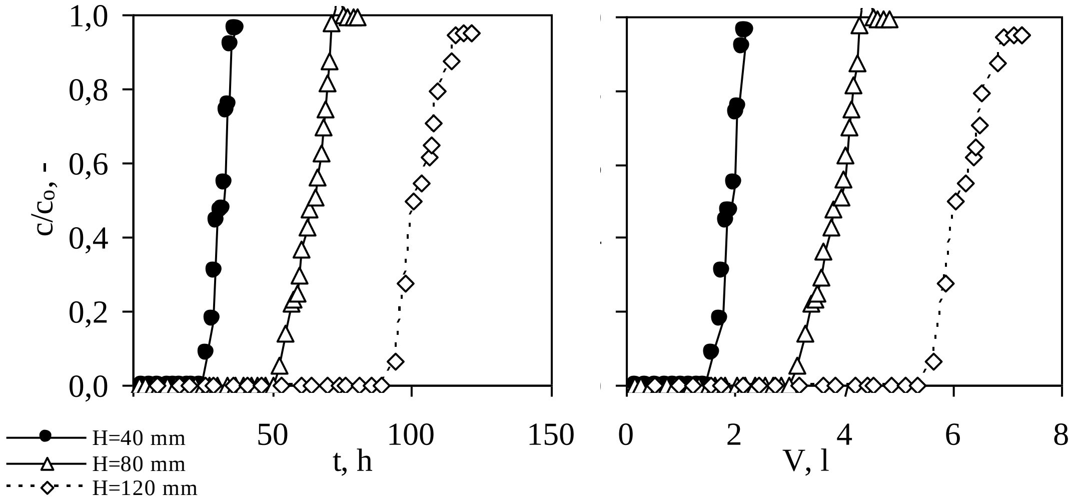

Figure 2. Breakthrough curves for zinc uptake for three different bed depths: (left) c/c_o vs. t, (right) c/c_o vs. V.

The effect of bed depth is clearly seen both on time and volume in the breakthrough and exhaustion points. With the decrease of bed depth, the breakthrough and exhaustion points shift towards lower values of time and volume. The results shown in Table 1 indicate that with increased bed depth, BV values at the breakthrough slightly increase (353, 384 and 395 respectively). Thereafter, the difference between the capacity at the breakthrough and exhaustion points for three different bed depths is negligible.

The effect of the initial zinc concentration on the breakthrough curve has been examined on the zeolite bed depths of 120 and 80 mm, with the flow of 1.0 ml/min (Figure 3).

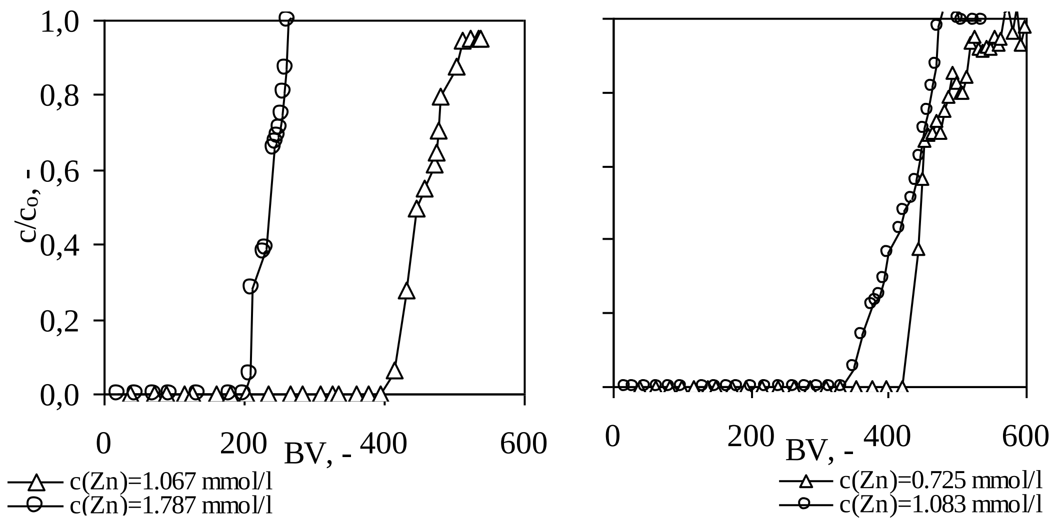

Figure 3. The effect of the initial zinc concentration on the breakthrough curve: (left) at a bed depth of 120 mm, (right) at a bed depth of 80 mm.

The comparison of these curves shows that when the initial Zn concentration increases, the breakthrough is reached earlier, and the zeolite becomes exhausted earlier.

Figure 4 shows the breakthrough curves for zinc uptake at three different flows, obtained at a zeolite bed depth of 40 mm and at a constant concentration (comparison of 7th, 8th and 9th cycle).

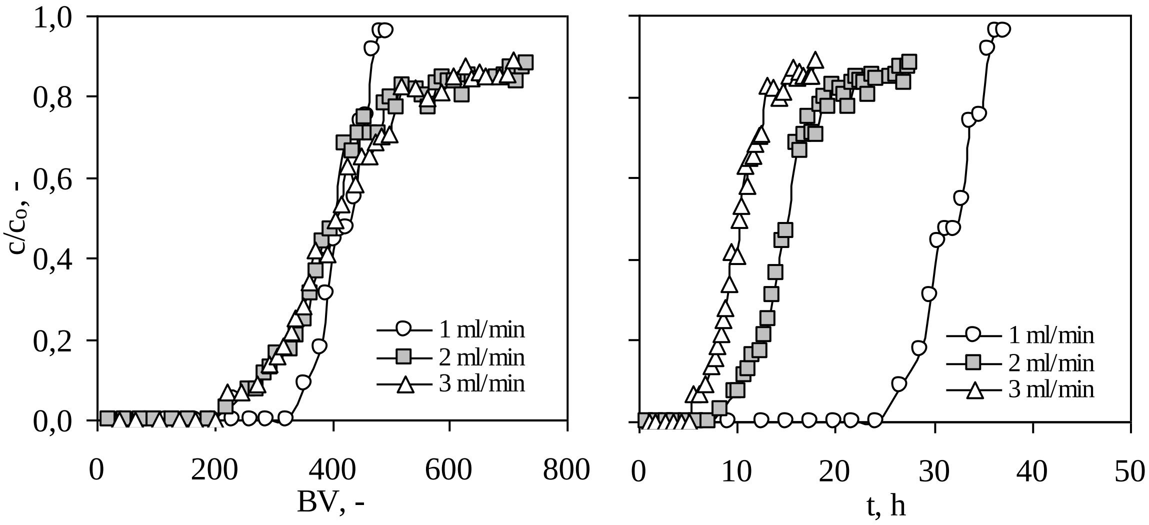

Figure 4. Breakthrough curves for zinc uptake at three different flows: (left) c/c_o vs. BV, (right) c/c_o vs. t.

The breakthrough point is reached earlier and the exhaustion point is delayed at higher flows through the column. This is due to the effect of axial dispersion in the zeolite bed, and the reduced contact time between the zeolite and the solution.

The time needed to reach the breakthrough point and the exhaustion point is shorter at the flow of 3.0 ml/min. Therefore, the same volume of a zinc solution can be treated in a much shorter period.

CONCLUSION

Zinc can be removed from aqueous solutions very successfully by means of the column method on natural zeolite-clinoptilolite, with several successive service and regeneration cycles. The symmetry and "S" shape of curves, and high values of breakthrough and exhaustion capacities for Zn during nine subsequent service cycles indicate a high efficiency of the column performance of a fixed bed of natural zeolite for zinc removal from aqueous solutions.

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