Use of natural zeolites from Maramures county (Romania) in removal of Cu^{2+}, Pb^{2+}, Zn^{2+} ions from industrial wastewaters

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Abstract. The use of natural zeolites in wastewaters cleaning is a highly appreciated method especially due to the natural zeolites high ion exchange capacity correlated to their relative low-cost exploitation. In order to study the influence of the solution flow with heavy metals on the adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+} ions by natural zeolite tuff an installation was performed assuring the solution passing through the zeolite tuff bed. In accordance with the analyses data, the used zeolite tuff contains a high ratio of clinoptilolite, which renders the high quality of the studied tuff. The influence of the three flows (8 BV/h, 10 BV/h and 12 BV/h) on the adsorption process was pursued and it was observed that the highest heavy metal ions retention was registered at lower solution flow. It was also noticed that the natural zeolite tuff used in the experiment had the best affinity for Pb^{2+} ions.
Key Words: natural zeolite tuff, wastewater, adsorption, ion exchange.

Rezumat. Utilizarea zeoliţilor naturali în epurarea apelor uzate este o metodă foarte apreciată, în special datorită capacităţii foarte ridicate de schimb ionic a acestora corelată cu costurile reduse de exploatare. Pentru a studia influenţa debitului soluţiei cu metale grele asupra adsorbţiei ionilor de Cu^{2+}, Pb^{2+}, Zn^{2+} de către tuful zeolitic natual a fost montată o instalaţie care să asigure trecerea soluţiei prin patul de tuf. În conformitate cu rezultatele analizelor, tuful zeolitic conţine clinoptilolit în proporţie mare ceea ce îi conferă tufului studiat o calitate ridicată. S-a urmărit influenţa celor trei debite (8 BV/h, 10 BV/h şi 12 BV/h) asupra procesului de adsorbţie şi s-a observat că cea mai mare reţinere de metale grele s-a înregistrat la debite mai mici. De asemenea, s-a mai observat că tuful zeolitic natural utilizat în experiment prezenta cea mai mare afinitate pentru ionul de Pb^{2+}.
Cuvinte cheie: tuf natural zeolitic, apă uzată, adsorbţie, schimb ionic.

Introduction. The highest heavy metal concentrations in environment and especially in waters are caused by uncontrolled wastewater discharges originated from different kind of industries, like: electroplating, ferrous and non-ferrous metallurgy (Cu^{2+}, Zn^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}), mining, refinery, cellulose production, pigments production, fertilizers production (Cr^{3+}, Cu^{2+}, Pb^{2+}), so on (Alvarez-Ayuso et al 2003; Chojnacki et al 2004).

The traditional methods used in heavy metals removal from wastewaters, like: chemical precipitation, coagulation, sorption, ion exchange and membranes usage, are either expensive or they do not allow a massive reduction of the heavy metals concentration in order to respect the regulation limits. Thus, the natural zeolites usage and especially the clinoptilolite appears like an efficient alternative for wastewater cleaning due to firstly the high efficiency of zeolites in retaining the impurities and heavy metal ions and not in the end due to the low exploitation costs of zeolite tuffs (Inglezakis et al 2004; Stylianou et al 2007; Almaraz et al 2003; Alvarez-Ayuso et al 2003; Chojnacki et al 2004; Bailey et al 1999; Kesraoui-Ouki et al 1994).

Unlike the organic resins, natural zeolites present a higher cationic selectivity, a better resistance to high temperatures and an excellent compatibility with the environment (Inglezakis et al 2004; Stylianou et al 2007; Almaraz et al 2003; Maliou et al 1992; Pansini 1996; Lee & Moon 2001; Nicula et al 2010; Smical et al 2010).

Beside their ion exchange capacity, zeolites also have the sorption capacity (Alvarez-Ayuso et al 2003).

The advantage of using the zeolite tuffs in wastewater cleaning is given by the regeneration capacity of this material for several times until its physical properties are by approximately 50% affected (Cesbron 1999).

Material and Method. The zeolitic tuff (Figure 1) used in the experiment is sampled from the Bârsana village area (Maramureş County).

Figure 1. Sample of Bârsana zeolite tuff.

The tuff sample was ground at approximately 1-3 cm, followed by grinding with bar mill, and the dried ground classifying was made using a sieving machine Retsch A220 basic (Germany). The samples were processed in several cycles. After every cycle, the fraction – 2.5 mm was removed using a dried sieve in order to prevent the over-grinding.

Several analyses were made for tuff sample in order to observe the mineralogical constituents of the studied zeolite tuff.

Measurements for adsorption and transmittance in IR (FTIR - Fourier-Transform Infrared) were made using the equipment Bruker Tensor-27 (setting source: multiple internal reflection, beam splitter: KBr; aperture setting: 5mm; scanner velocity: 10 KHz). The pellets were made from a mixed 1 mg sample with 200 mg KBr (ratio: 1/100).
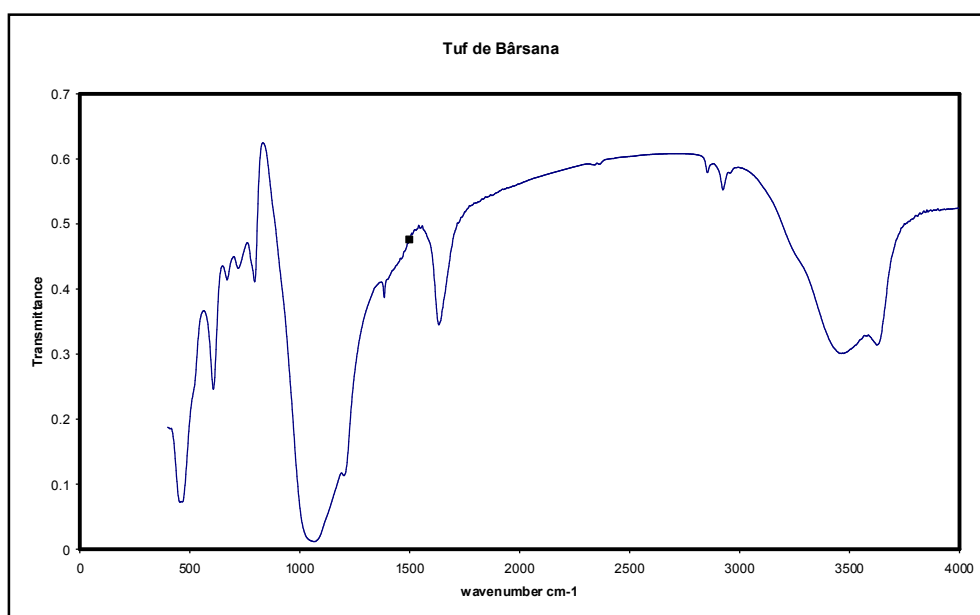

Figure 2. FTIR analysis of the Bârsana zeolite tuff.

The spectrum of adsorption and transmittance in IR (Figure 2) is identical with spectra presented in literature for this mineral. The spectrogram separates clinoptilolite from heulandite by the adsorption band at 610 cm^{-1}, for heulandite being of 700 cm^{-1}. The inflection of 1200 cm^{-1} is also characteristic, which indicates, whenever present, contents over 75% clinoptilolite (Valiter et al. 1975).

The spectrum highlights water presence, by adsorption in domains between of 3400 - 3600 cm^{-1}.

The thermogravimetric analysis (TG) and the differential thermal one (DTA) of the Bârsana zeolite tuff was made in an oxidative environment (air) using a crucible Al 100 µl and a tuff amount of 38.9 mg.

The experiment was conducted in a temperature range starting with the room temperature up to 1600 ^{0}C.
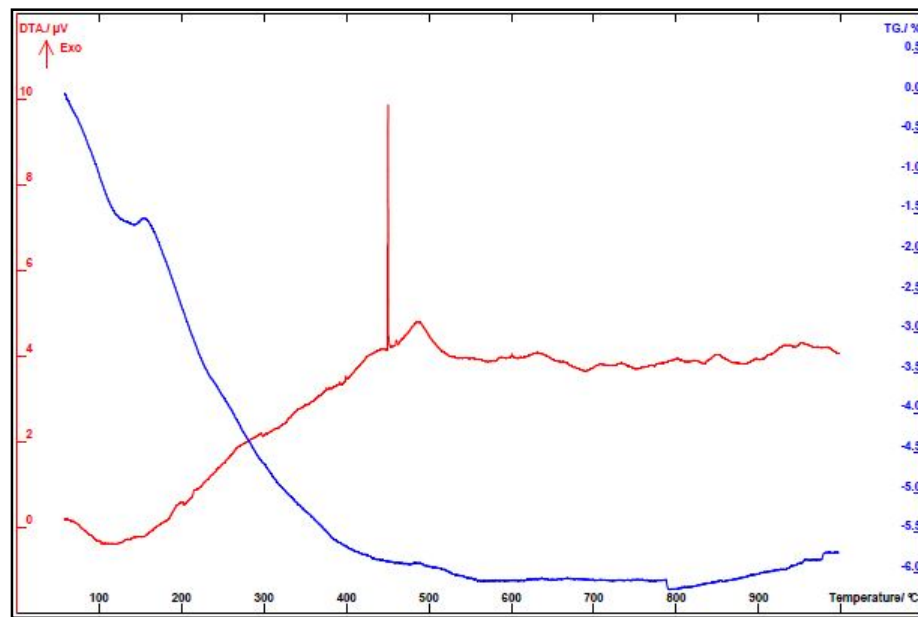

Figure 3. TG-DTA analysis of the Bârsana zeolite tuff.

As it can be seen in Figure 3, at approximately 450 ^{0}C a DTA pick appears which expresses a dehidratation moment of the zeolites from the tuff sample which contain water in different shapes.

The weight loss of the analyzed tuff mass, represented by TG curve, is the most marked in the same area where the pick of DTA appears (about 450 ^{0}C).
At this temperature, a major water loss takes place and after that, both DTA curve and TG curve have a rolling horizontal slope without major changes, which indicates that no important water loss from the tuff structure is registered.

The microstructural characterization of the Bârsana zeolitic tuff was performed by scanning electron microscopy (SEM, Hitachi-S4100) with energy dispersive spectroscopy (EDS, detector Rontec).

The secondary electrons SEM micrograph in Figure 4, complementary made for a Bârsana tuff sample, confirms the major presence of clinoptilolit crystals accompanied by feldspar and opal overgrowing.

In the conducted experiment the efficiency of Pb^{2+}, Cu^{2+} and Zn^{2+} adsorption by Bârsana zeolite tuff is followed using a ion exchange column, characterized by ratio D/H=1/10. The solution flow effect on the ionic exchange capacity at the column breakthrough was also monitored.
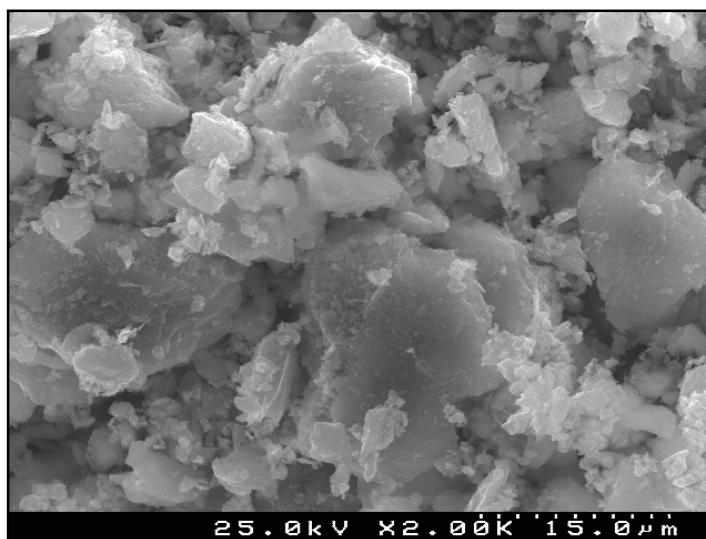
Figure 4. SEM micrograph of the Bârsana zeolitic tuff.

In experiments, synthetic solutions were used having a Pb^{2+}, Cu^{2+} and Zn^{2+} concentration of 100 mg/L and initial pH of 4.0. In Figure 5 the used experimental equipment is presented.

The used installation for the experiment (Figure 5) is made of one column with an inner diameter D=cm having the zeolite tuff height of H=20 cm. A volume of 62.8 ml of zeolite material was used which corresponds to a zeolite amount of 60.28 g (the zeolite bulk density of 0.9598 g/ml was considered having the particles diameter of 1.5 mm).

The solution volume corresponding to the zeolite bed was BV=30.14 ml. The solution flows used in the experiment were 8 BV/h, 10 BV/h and 12 BV/h, which correspond to flows of 4.02, 5.02, respectively 6.03 ml/min. Flows adjustment was made with a peristaltic pump.
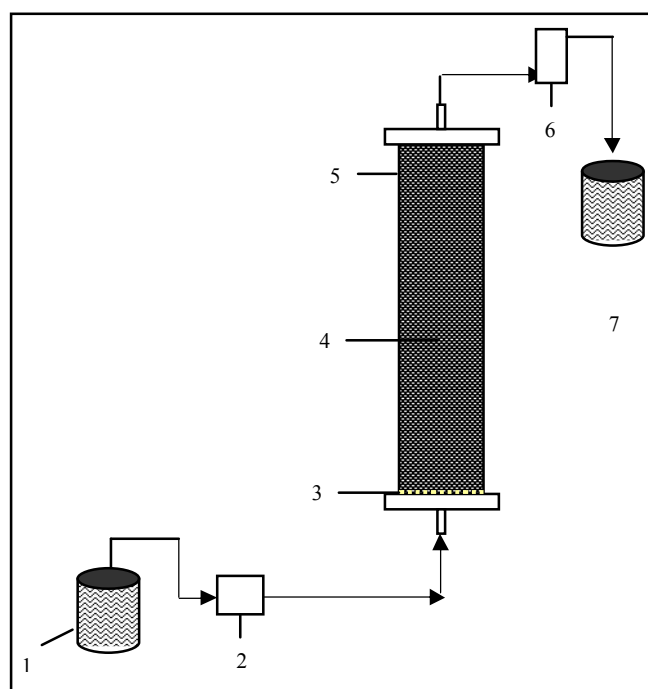

Figure 5. Scheme of the adsorption installation with column and fixed bed: 1 – synthetic solution vessel, 2 – peristaltic pump, 3 – plastic sieve, 4 – natural zeolite bed, 5 – plexiglas column, 6- samples collector, 7 – resulted solution vessel.

For every studied heavy metal ion (Pb^{2+}, Cu^{2+} and Zn^{2+}) a sample of resulted solution was taken at every 50 ml solution in order to establish the column breakthrough according to the solution flow.

Results and Discussion. In Figures 6-8 the variations of experimental data are graphically presented as a result of studying the influence of solution flows on the column breakthrough ion exchange capacity.

As it results from the graphics, the zeolite column breakthrough appears first for the solution flow of 12 BV and much later at 8 BV. This explains the fact that the slower the solution flows the later the column breakthrough appears.
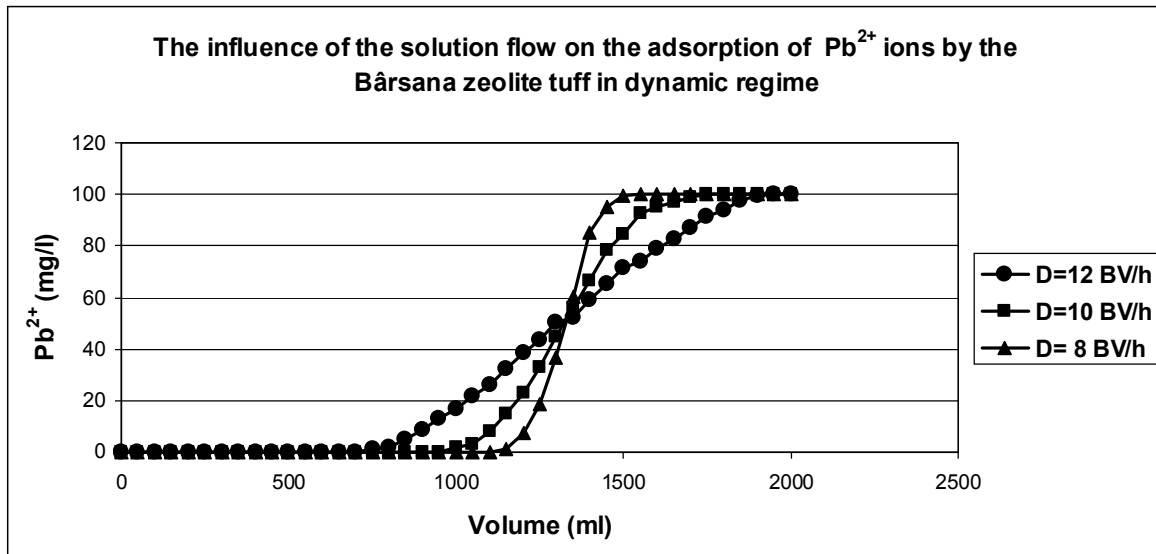

Figure 6. The influence of the solution flow on the adsorption of Pb^{2+} ions by the Bârsana zeolite tuff.
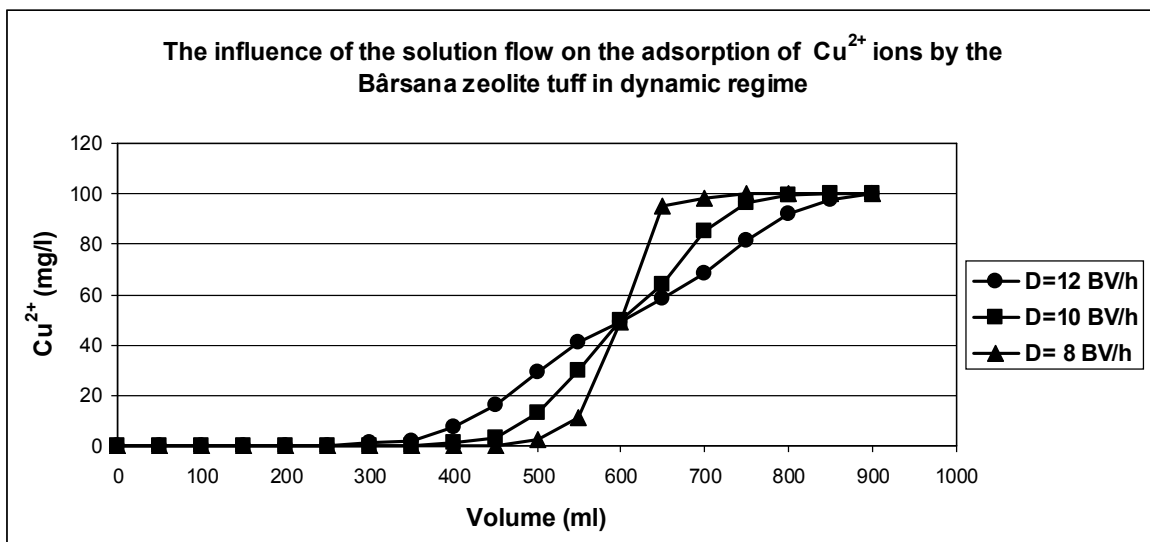

Figure 7. The influence of the solution flow on the adsorption of Cu^{2+} ions by the Bârsana zeolite tuff.
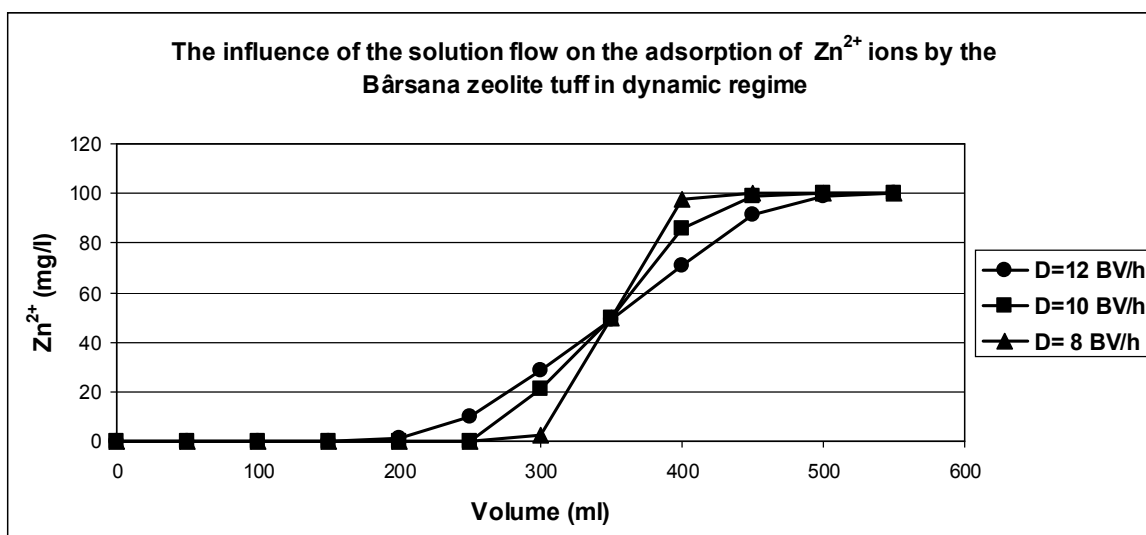
Figure 8. The influence of the solution flow on the adsorption of Zn^{2+} ions by the Bârsana zeolite tuff.

In Tables 1-3 the variation of the breakthrough ion exchange capacities and the total ion exchange capacity of the zeolite tuff are presented according to the solution flows. In Figure 9 the influence of solution flow on the breakthrough ion exchange capacity tuff zeolite is presented graphically for every heavy metal ion.

As it can be observed, the increase of the flow from 8 BV/h to 12 BV/h generates for the three heavy metal ions a decrease of the breakthrough ion exchange capacity by 36.37% for Pb^{2+}, 39.99% for Cu^{2+} and 33.34% for Zn^{2+}, respectively.

Table 1

Variation of the ion exchange capacity according to the solution flow for Pb^{2+}

No.	Flow(BV/h)	BIEC* (mg/g)	TIEC** (mg/g)
1	8	1.8248	2.1537
2	10	1.493	2.1586
3	12	1.1612	2.1478
4	TIEC dynamic regime		2.15

* Breakthrough ion exchange capacity
** Total ion exchange capacity

Table 2

Variation of the ion exchange capacity according to the solution flow for Cu^{2+}

No.	Flow(BV/h)	BIEC* (mg/g)	TIEC** (mg/g)
1	8	0.8294	1.0315
2	10	0.6635	1.0432
3	12	0.4977	1.0419
4	TIEC dynamic regime		1.039

Table 3

Variation of the ion exchange capacity according to the solution flow for Zn^{2+}

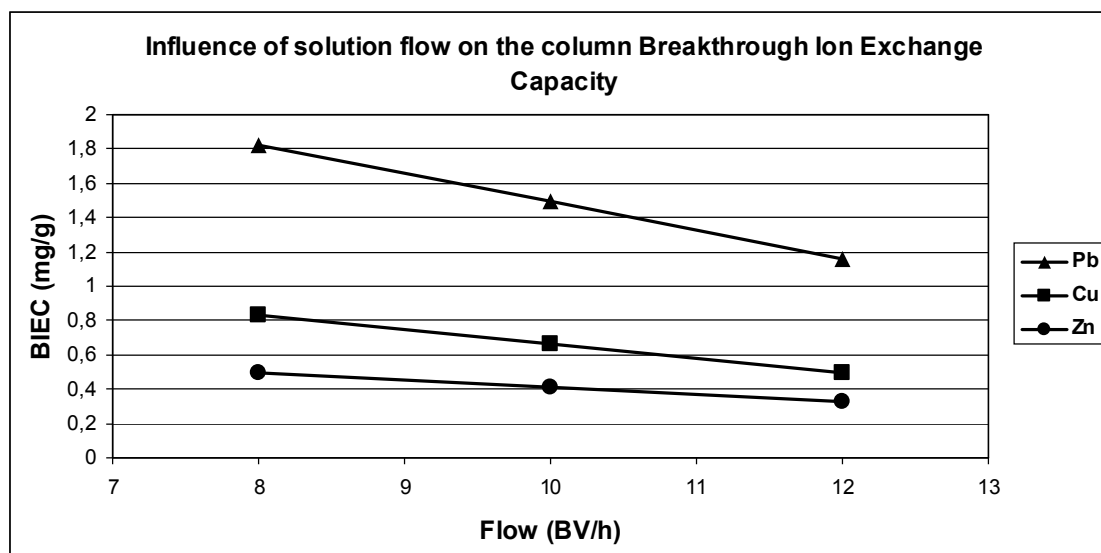| No.	Flow(BV/h)	BIEC* (mg/g)	TIEC** (mg/g)
1	8	0.4976	0.6214
2	10	0.4147	0.6174
3	12	0.3317	0.6219
4	TIEC dynamic regime		0.620

Figure 9. The influence of the solution flow on the column Breakthrough Ion Exchange Capacity of the Bârsana zeolite tuff.

Conclusions. The physical and mineralogical analyses performed on the Bârsana zeolite tuff used in this experiment show a major content of clinoptilolite which confers it a high capacity of retention of the heavy metals from the wastewaters. As the graphics in Figures 6-8 show, the zeolite column breakthrough appears at higher flows of the heavy metal solutions which explains that the higher the solution flows the sooner column breakthrough appears.

The natural zeolite tuff used in this experiment shows a higher affinity for the Pb^{2+} ions and the best adsorption was registered for the lowest contact solution flow (8 BV/h). That is confirmed by the total ion exchange capacity of the used tuff in the experiment illustrated in Tables 1-3 where the biggest TIEC value is registered for Pb^{2+} ions.

The flow increase from 8 BV/h to 12 BV/h, generates for the three heavy metal ions a decrease of the BIEC by 36.37% for Pb^{2+}, by 39.99% for Cu^{2+} and by 33.34% for Zn^{2+}.

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