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Dedicated to professor Gh. Marcu at his 80th anniversary

REMOVAL OF SOME HEAVY METAL IONS FROM SYNTHETIC WASTEWATERS USING NATURAL ZEOLITES. A COMPARATIVE STUDY

MARIA STANCA[a], ANDRADA MĂICĂNEANU[*,a], SILVIA BURCĂ[a], HOREA BEDELEAN[b]

ABSTRACT. This paper presents some results obtained for removal of lead (II), zinc(II) and iron (II) ions from wastewaters by ionic exchange on natural zeolites from Transilvania. We used zeolitic (clinoptilolitic) volcanic tuffs from Măcicaş (M), Pâglişa (P) and Cepari Vultureni (CV) areas (Cluj county). The experiments were conducted in a batch reactor (static regime) and in a fixed bed column (dynamic regime). The efficiency of removal is high for all the natural zeolites and ions considered. A pretreatment of the zeolite with Na^+ solutions increased the efficiency of the ionic exchange process.

KEY WORDS: Natural zeolites, clinoptilolite, wastewaters, lead, zinc, iron, ionic exchange.

1. INTRODUCTION

It is well known that 70% of the Earth's surface is covered by water, which follows a cycle driven by the absorption of energy from the Sun (evaporation-condensation-precipitation-infiltration to ground water). During this cycle, in which human activities play an important role, water pollution occurs. Heavy metal ions pollution is considered to be of high risk, due to the toxic effect upon the living organisms. Cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc are considered to have high toxicity, while iron and manganese are considered non toxic but with aesthetic effect. Copper and zinc ions are linked to some processes that take place in human body, but if their concentration is too large can become toxic.[1] Other heavy metal ions are highly toxic al low concentrations and can accumulate in the human body leading to different diseases.

Heavy metal ions in water come from natural and anthropogenic sources. Natural sources include rock weathering, soil erosion or dissolution of water-soluble salts. Usually metal ions introduced in water by natural sources are in small quantities and they not have any adverse effects on humans or other living organisms. Anthropogenic sources include municipal wastewater treatment plants, mining, industry (chemical, metallurgic, leather and textile, petroleum refining) corrosion and electroplating. If these wastewaters are not properly treated, heavy metal ions can be transported as

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[*] Corresponding author; e-mail: andrada@chem.ubbcluj.ro

[a] Department of Chemical Technology, "Babeş-Bolyai" University, 11 Arany Janos st., RO - 400028 Cluj-Napoca

[b] *Department of Geology, "Babeş-Bolyai" University, Cluj-Napoca,1 Mihail Kogălniceanu st., RO - 400084 Cluj-Napoca*

dissolved species, can be adsorbed on sediments, volatilize in atmosphere and finally can be taken up by organisms causing deleterious effects.[1,2]

Pollutants removal from wastewaters and water disposal in nature or recycling in the economic circuit is one of the main strategies applied to avoid environmental pollution.

Heavy metal ions removal from wastewaters can be realized using methods like: extraction, reduction, precipitation, electrochemical processes, adsorption or ionic exchange,[2-6] each of them with advantages and disadvantages. The main disadvantage in most of the cases is the high cost of the process.

Adsorption and ionic exchange processes are widely applied to remove heavy metal ions from wastewaters due to their high efficiency even for small concentration of metal. In recent years many researchers oriented their efforts to improve existing materials[7-12] and processes (e.g. use of fluidised bed to remove copper on ionic exchange resin)[13,14] or to find inexpensive materials that can be used as adsorbents or ionic exchangers. In the second category are included natural materials and natural wastes. There were investigated many natural zeolites and clays: Mexican clinoptilolite,[15] Croatian clinoptilolite,[16] American clinoptilolite,[17] montmorillonite,[18-22] scolecite (Brazilian natural zeolite),[23,24] phillipsite (Jordanian zeolite),[25] vermiculite,[26] erionite, chabazite, mordenite,[17] kaolinite,[27,28] dolomite,[29] smectite and hectorite (magnesian smectite),[30-32] gibbsite,[33] sepiolite,[34] micas, illites[35-37] and bentonites.[34-42] Other studies were oriented on the investigation of adsorptive properties of some natural materials and wastes such as apple residues,[43] grape stalk wastes,[44] crab shell particles,[45,46] rice bran,[47] coffee grounds,[48] tree leaves,[49] ash particles derived from palm oil wastes,[50] peanut shell,[51] sheep manure wastes[52,53] or algae and microalgae.[54-56]

In this work we used zeolitic (clinoptilolitic) volcanic tuffs from Măcicaş, Pâglişa and Cepari Vultureni areas (Cluj county) to remove lead, zinc and iron from synthetic wastewaters. The deposits of volcanic tuffs from these areas are very important, from the environmental point of view, due to their clinoptilollite content, which is between 70 and 90% of rock mass. Volcanic tuff samples were collected from two stratigraphical horizons, those from the higher level are marked with “1” and they have a microporous structure, while those from the lower level are marked “2” and they have a mediumporous structure. Physico-chemical and mineralogical characterisation of all the zeolitic volcanic tuffs used in this study will make the object of another paper.

2. EXPERIMENTAL

Adsorptive and ionic exchange properties of natural zeolites are determined by the structure of their crystalline network, which determine the channel system and also by the negative charge excess due to $[AlO_4]^{5-}$ tetrahedrons compensated by mono- or divalent cations (eg. Na^+, K^+, Ca^{2+}, Mg^{2+}). These counter ions are mobile and can be total or partial exchanged during ionic exchange processes. Heavy metal ions removal was realised on zeolitic volcanic tuff modified by treatment with 1M HCl (Z-H form) and 1M NaCl + NaOH pH = 10 (Z-Na form). There were used two granulations, 0.63-1.0 mm and 0.2-0.4 mm of the zeolitic volcanic tuff. The stages involved in the zeolite preparation are as follows: crushing, grinding, size separation, washing with distilled water, drying at 105°C for 6 hours, treatment with 1M HCl in a stirring reactor with a zeolite acid solution ratio of 1:10, washing with distilled water to pH = 7 and finally drying at 105°C for 6 hours. At the end of this sequence we obtained the zeolite in -H form (Z-H). Also, during the treatment with HCl, zeolite channels are cleaned and pores opened. To bring the zeolite in -Na form which proved to be more efficient in the ionic exchange process,[17] the zeolite is subjected subsequently to an alkaline treatment with strong Na^+ solution (1M NaCl solution brought to pH = 10 with a 1M NaOH solution) according to equation (1). After the alkaline treatment the zeolite samples are washed again with distilled water to pH = 7 and dried for 6 hours at 105°C.

$$\text{Z-H} + \text{NaCl} \rightleftharpoons \text{Z-Na} + \text{HCl} \qquad (1)$$

There were used monocomponent synthetic solutions containing Zn^{2+}, Pb^{2+} or Fe^{2+} ions, prepared from $ZnSO_4\cdot 7H_2O$, $(CH_3OO)_2Pb\cdot 3H_2O$ and $FeSO_4\cdot 7H_2O$ respectively, all analytical purity reagents. Concentrations of the solutions used in this study were selected accordingly to their toxicity and the maximum admissible concentrations in surface and drinking water.[57,58] Determination of heavy metal ions in solution was realised using a Jenway spectrophotometer. Iron was determined as total iron. Experiments were carried out without any modification of the pH for the synthetic solutions.

The ionic exchange process was realised in a batch reactor in static regime using 10 g zeolitic volcanic tuff and 100 ml metal ions solution (zeolite:solution = 1:10). Synthetic wastewater samples were taken every 24 hours until the equilibrium was reached. We also worked on a fixed bed column (d_i = 15 mm) containing 5 g zeolite, with a flow rate of 0,055 ml/s (for all experiments) when samples were collected every 100 ml until the zeolite was exhausted (dynamic regime). The ionic exchange reactions are as follows:

$$2\text{Z-Na} + Zn^{2+} \rightleftharpoons Z_2\text{-Zn} + 2Na^+ \qquad (2)$$

$$2\text{Z-Na} + Pb^{2+} \rightleftharpoons Z_2\text{-Pb} + 2Na^+ \qquad (3)$$

$$2\text{Z-Na} + Fe^{2+} \rightleftharpoons Z_2\text{-Fe} + 2Na^+ \qquad (4)$$

Zeolitic volcanic tuffs used in our study were labelled considering the stratigraphical horizon and their origin as follows: Măcicaş area – M1 and M2, Pâglişa area – P1 and P2 and Cepari Vultureni area – CV.

The ionic exchange efficiencies, η, in %, were calculated with equation (5), considering the final concentration as follows: (a) in static regime – after the equilibrium was reached and (b) in dynamic regime – after 100 ml of synthetic wastewater passed the zeolitic volcanic tuff column bed.

$$\eta = \frac{C_i - C_f}{C_i} \cdot 100 \qquad (5)$$

where

C_i is the initial concentration, in mg/L
C_f is the final concentration, in mg/L.

3. RESULTS AND DISCUSSIONS

3.1. Influence of the chemical treatment on the ionic exchange capacity in dynamic regime.

The influence of the chemical treatment over the ionic exchange capacity was studied on the P1 sample brought in P1-H and P1-Na forms. The experiments were carried out in a column filled with 5 g zeolite with granulation of 0.2-0.4 mm and a synthetic solution containing Zn^{2+} ions, concentration 136.64 mg/L. Our results indicated that the efficiency of the ionic exchange process is almost twice as large in case of the -Na form modified zeolite (figure 1) – 42.03% for P1-H and 76.13% for P1-Na. This result is in agreement with conclusions of some previous studies performed on clinoptilolitic type natural zeolites.[17,59,60] In case of the treatment with NaCl solutions,[17,60] experimental results indicate that natural zeolites improve significantly their ion exchange capacity. Also H^+ radius is 2.08 Å, while Na^+ radius is only 0.95 Å, which will increase diffusion rate through the zeolite channels. If a NaOH treatment was applied,[59] an increase of the crystallinity degree was observed (explained by the amorphous phase reduction), which will improve zeolite exchange properties.

3.2. Comparison between the ionic exchange efficiencies of the zeolitic volcanic tuffs in static regime.

We studied the ionic exchange for zinc (237.58 mg/L) and lead (5.38 mg/L) ions using M1-Na, M2-Na, P1-Na, P2-Na and CV-Na samples with a granulation of 0.63-1.0 mm. Variation of heavy metal ions concentration in time and the ionic exchange efficiency for all the zeolitic volcanic tuffs are presented in figures 2 and 3 for zinc and figures 4 and 5 for lead. The ionic exchange reactions took place for both ions and all zeolitic volcanic tuffs considered (Zn^{2+} and Pb^{2+} concentrations in water decrease), therefore the zeolites under study are considered to be active in the ionic exchange reactions. In case of zinc, the efficiency of the ionic exchange process was higher than 96% for all samples considered.

The equilibrium in case of lead ion was reached more rapidly by comparison to zinc ion, which indicates a favourable kinetic for Pb^{2+} ion. Experimental ionic exchange studies performed on natural zeolites containing as a main component clinoptilolite and multicomponent heavy metal ions solutions showed that Pb ion is in the top of the selectivity sequences (Pb>Cu>Cd>Zn>Cr>Co>Ni).[61-63] In case of lead, ionic exchange efficiencies were over 93% with the exception of M1-Na microporous zeolitic volcanic tuff sample, where the efficiency is only 71.18%. This result can be correlated with the Pb^{2+} ionic radius (1.2 Å), which we assume that is too large by comparison with the pore diameter (microporous sample). After a comparison of ion exchange efficiencies for al the zeolitic volcanic tuffs and each ion, we can conclude that for the CV-Na zeolitic sample were obtained the best results in both cases. Also P1-Na zeolitic sample, in case of lead, and M1-Na zeolitic sample, in case of zinc, showed similar efficiencies for the process under study.

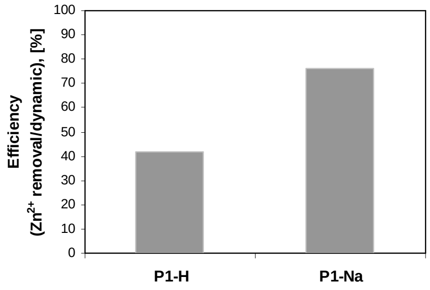

Figure 1. *Ionic exchange efficiency for zinc removal on P1 zeolitic volcanic tuff subjected to acid (P1-H) and acid-alkaline treatment (P1-Na)*

3.3. Comparison between the ionic exchange efficiencies of the zeolitic volcanic tuffs in dynamic regime.

In this part of the work we studied the ionic exchange process in dynamic regime, in a fixed bed column, for Zn^{2+} and Fe^{2+} on M1-Na, P1-Na and CV-Na zeolitic volcanic tuffs. We used each time a 5 g zeolitic sample with granulation of 0.2-0.4 mm and solutions with different concentrations. In case of zinc we studied the influence of concentration over the efficiency of the ionic exchange process using solutions containing 136.64 mg Zn^{2+}/L and 59 mg Zn^{2+}/L, while for iron we considered solutions with 22.93 mg Fe^{2+}/L and 10 mg Fe^{2+}/L. Preliminary tests performed with zeolitic volcanic tuff with granulation 0.63-1.0 mm and higher concentrations for heavy metal ions gave unsatisfactory results, probably due to diffusional limitations.

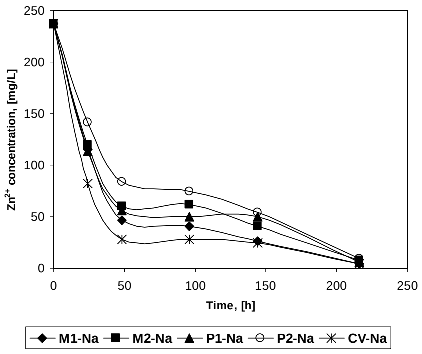

Figure 2. *Comparison between variations of Zn^{2+} concentration (in the synthetic wastewater) in time for all zeolitic volcanic tuffs studied, in -Na form and static regime.*

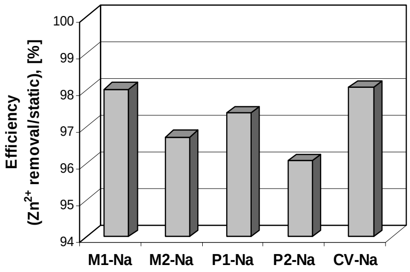

Figure 3. *Ionic exchange efficiency for zinc removal in static regime on all zeolitic volcanic tuffs studied.*

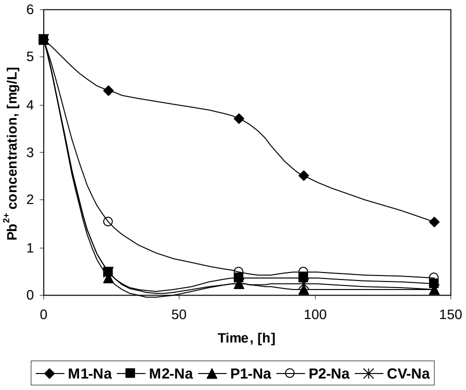

Figure 4. *Comparison between variations of Pb^{2+} concentration (in the synthetic wastewater) in time for all zeolitic volcanic tuffs studied, in -Na form and static regime.*

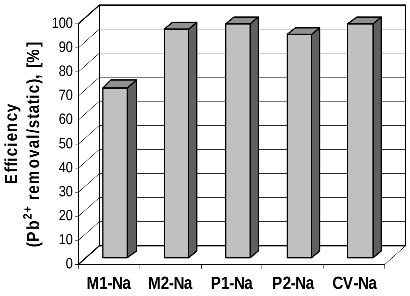

Figure 5. *Ionic exchange efficiency for lead removal in static regime on all zeolitic volcanic tuffs studied.*

For removal of zinc in dynamic regime, were considered M1-Na, P1-Na and CV-Na zeolitic volcanic tuffs, which proved to have higher ionic exchange efficiencies in the static regime study. Results are presented in figures 6 and 7. We found out that in this case, the zeolitic volcanic tuff from Pâglişa area (P1-Na) presents a higher ionic exchange capacity, at the beginning of the process. This might be due to the pores distribution in the P1 sample, which has a surface area smaller than M1 sample, therefore pores are more accessible for the ionic exchange process. In case of P1-Na sample, we also investigated the ionic exchange for a second solution, diluted approximately at half. The efficiency of the ionic exchange process was calculated to be 81.57%, while for the first solution the efficiency was 76.13% after first 100 ml of synthetic wastewater passed the column bed. Also, the wastewater volume that can be processed, before the zeolite exhaustion, increased from 400 ml for the concentrated solution to 1000 ml for the diluted solution.

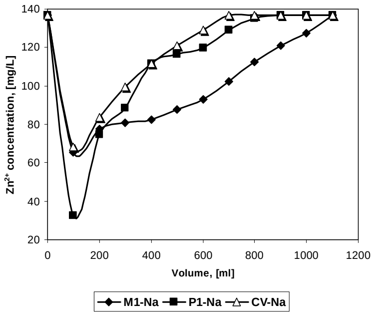

Figure 6. *Comparison between variations of Zn^{2+} concentration (in the synthetic wastewater) with the efluent volume for M1-Na, P1-Na and CV-Na zeolitic samples in dynamic regime.*

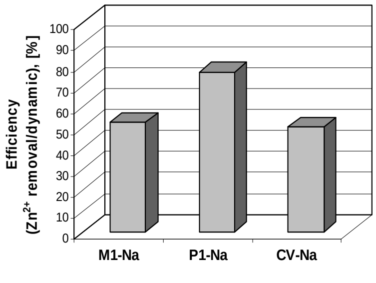

Figure 7. *Ionic exchange efficiency for zinc removal in dynamic regime on M1-Na, P1-Na and CV-Na zeolitic samples*

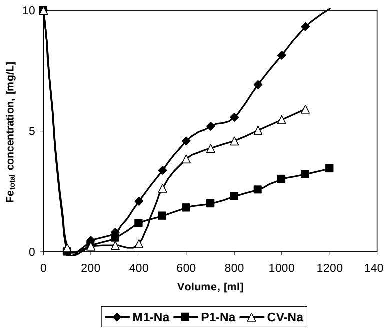

Figure 8. *Comparison between variations of Fe$_{total}$ concentration (in the synthetic wastewater) with the effluent volume for M1-Na, P1-Na and CV-Na zeolitic samples in dynamic regime.*

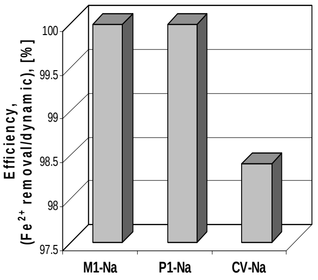

Figure 9. *Ionic exchange efficiency for iron removal in dynamic regime on M1-Na, P1-Na and CV-Na zeolitic samples*

The same zeolitic volcanic tuffs were used to study the removal of iron from synthetic wastewaters (initial solution 10 mg Fe^{2+}/L). Results are presented in figures 8 and 9. All zeolitic samples demonstrated high efficiencies for iron removal. Iron was completely removed after first 100 ml of synthetic wastewater passed the zeolitic bed for M1-Na and P1-Na zeolitic samples, while for CV-Na zeolitic sample an efficiency of 98.4% was calculated.

We also carried out tests on P1-Na zeolitic sample using a second, more concentrated solution (figure 10). We observed that for the concentrated solution the exhaustion of the zeolite sample took place after we processed 900 ml wastewater. In case of the diluted solution after 1200 ml, when we stopped the experiment, the residual concentration of iron in solution was only 3.43 ml Fe$_{total}$/L (the ionic exchange process takes place until the initial concentration of iron is reached after the solution passed the zeolitic volcanic tuff bed, as a consequence of the ionic exchanger exhaustion). During the experiment we observed that Fe(OH)$_3$ brown precipitate started to build up on top of the zeolite sample, leading to an increase of the pressure drop, which modifies the hydraulic regime across the column.

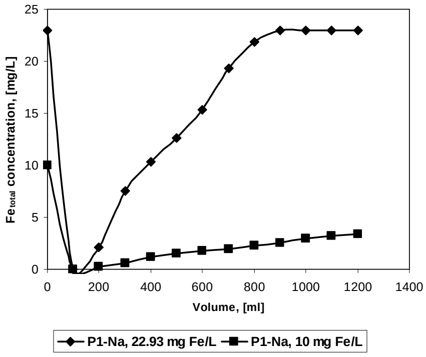

Figure 10. *Comparison between variations of Fe$_{total}$ concentration (in the synthetic wastewater) with the effluent volume for P1-Na zeolitic sample in dynamic regime for two concentrations of iron solutions.*

4. CONCLUSIONS

(1) All zeolite samples considered can be used in wastewaters treatment to remove lead, zinc and iron.

(2) Our results indicated that the efficiency of the ionic exchange process is almost twice as large in case of the -Na form modified zeolite by comparison with the –H form.

(3) In static regime the most efficient samples were CV-Na and M1-Na for zinc removal and CV-Na and P1-Na for lead removal.

(4) The equilibrium in case of lead ion (static regime) was reached more rapidly by comparison to zinc ion, which indicates a favourable kinetic for Pb^{2+} ion.

(5) In case of dynamic regime for zinc removal, the most efficient sample was P1-Na. Also the ionic exchange process was more efficient and column exhaustion took place after a larger volume of wastewater was processed when solution concentration is lower.

(6) The iron was removed completely after 100 ml wastewater passed on M1-Na and P1-Na samples and the life of the zeolite was extended when diluted solution was used.

(7) After the heavy metal ions removal from wastewaters, the zeolites samples in metal ion form ($Z\text{-}Me^{n+}$) can be regenerated and reused in the same process with metals recovery[2] and as catalysts in flue gas treatment to remove NO_x[64] or in Fenton type processes to remove organic pollutants from wastewater.[65]

(8) Further studies will consider multicomponent synthetic solutions and wastewaters collected from industrial effluents.

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