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INFLUENCE OF NATURAL MINERALS ON CONTAMINATED SOLUTIONS pH VALUES

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Abstract:

The protection and arrangement of agricultural areas in order to obtain health-safe food is extremely important to know the mobility of heavy metals lead, cadmium, zinc and uranium as radionuclides. This research investigated the influence of mineral raw materials (apatite and zeolite) on the mobility of heavy metals and radionuclides in a column system with constant pressure at different pH values (5.0 and 7.0). The tested solutions were contaminated with metals (lead, cadmium, zinc and uranium), in a concentration of 300 mg/l in time intervals of 30, 60, 90, 120 and 180 minutes. It was experimentally determined that there were significant changes in the pH value of the filtrate. The results showed that both apatite and zeolite successfully immobilized lead at both pH values. Uranium immobilization was better performed in columns with apatite, zeolite showed better properties in cadmium immobilization, and tests on a solution contaminated with zinc showed that both apatite and zeolite show similar affinity. The obtained results were statistically processed using the method of two-factor analysis of variance with repeated measurements. Further research will be based on monitoring the morphophysiological properties of underground and aboveground parts of plants on contaminated soil samples when apatite and zeolite are applied.

Keywords: pH value, natural minerals, contamination, influence

1 INTRODUCTION

Environmental pollution, especially the land on which crops are used for food grow, was a consequence of technological development, especially in the last 70 years. Due to the increasing number of inhabitants, there was an increased request both for food and raw materials. This process inevitably led to the contamination of water, water, and land. New technologies and procedures have been developed in order to reduce the contamination of endangered soils, especially from heavy metals (Pb, Zn, Cd) and radionuclides (U). Due to the increased soil contamination, the process of assisted natural

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remediation was started with the technology of immobilizing heavy metals using natural materials and preventing the mobility of pollutants through complex soil system.

In the constructed column system with mineral raw materials-materials (zeolite, apatite), ion exchange and precipitation processes reduced the content of Pb, Zn, Cd and U contaminants in the filtrate compared to the base solution. According to Jain & Ram, (Jain, 1997) several factors influence these processes such as: mineral composition of the substrate-raw material-filter, filtration coefficient, porosity and pore size, pH value of the base solution, contaminant content.

2 LABORATORY RESEARCH

This first part of the laboratory research in the column system determined the changes in the pH value of the basic solutions of contaminants Pb, Cd, Zn, U (pH=5.00 and pH =7.00) after filtering through columns with zeolite and apatite. Monitoring of changes in the basic solution was performed in 5-time intervals (t1-t5), with the first four intervals (t1-t4) being 30 minutes apart and the t5 interval lasting 60 minutes. Tests in these pH environment conditions (pH 5.00 and pH 7.00) represent a similar model that occurs in the tested soils of the pseudogley and chernozem types because similar conditions of active acidity prevail (acidic, neutral), which is the subject of the second part of the research. Graph 1 shows the change in basic starting pH=5.00 of toxic solutions of Pb, Zn, Cd, U when passing through columns with zeolite and apatite.

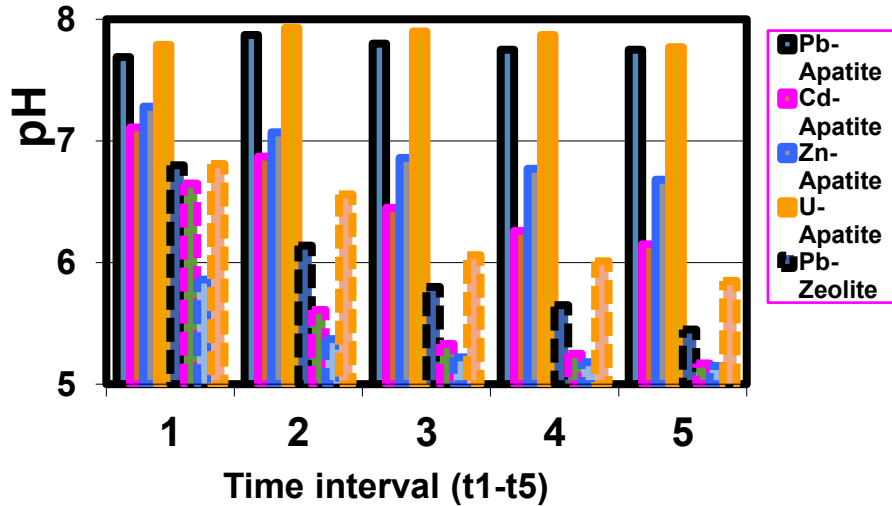
Significant changes in the basic contaminated solution (pH 5.00) were observed, indicating ion exchange processes carried out in zeolite and apatite. The highest pH value of the output solution from the column (filtrate), at pH=5.00, was recorded by the basic solutions of Pb and U through the column filled with apatite in all time intervals, (t1-t5). Contaminated U solutions passed through the apatite column have minimal fluctuations in the pH of the filtrate (0.16), at pH =5.00, varying in a narrow range, 7.77-7.93. A slightly wider fluctuation of the pH value of the filtrate (0.18) through the apatite column was recorded in the Pb solution, 7.69-7.87, during the time interval of 180 minutes.

Such changes in pH value indicate the conclusion that the reactions of apatite with a contaminated solution of Pb and U and an acidic environment are very fast and stable, thanks to the sufficient amount of exchangeable carbonates present. As for the changes in the pH value of basic solutions (pH=5.00) contaminated with Zn, Cd, through the column filled with apatite, the values also record changes in the pH value of the solution, but of a slightly weaker intensity during the entire duration of the experiment of 180 minutes. Base contaminated solutions of Cd and Zn (pH =5.00) passed through the apatite column have lower filtrate pH values and record a linear, slight decrease in filtrate pH values for Zn (7.28-6.68) and slightly faster for Cd (7.11-6.15) over time. (t1-t5) of 180 minutes.

In the article by Knox et al. (Knox, 2003), the pH of the soil solution did not remain constant comparing the control and two mineral supplements (phillipsite, apatite). The pH value of the soil solution in the control variant was 3.84 (± 0.01), in the variant with apatite it was 4.89 (± 0.05) and for phillipsite it was 4.26 (± 0.05). The increase in pH with mineral raw materials is probably the result of alkali action from the apatite, as a hint of the relatively high calcium carbonate content. The obtained results, at pH=5.00, indicate that good quality apatites were used and that they can have a wide and varied application, due to the speed and ability to react, because most phosphate-apatites are not good for soil remediation. For good results, the mineral raw material from the apatite group should: 1) have as much exchangeable carbonate as possible, 2) no fluorine in exchangeable form, 3) have traces of harmful metals in the initial structure, 4) be poorly crystalline or equally amorphous, and 5) has high internal porosity (Conca, 1997).

Changes in the pH value of basic contaminated (Pb, Zn, Cd, U) solutions, pH = 5.00, were also recorded after passing through the columns that were filled with zeolite, but at a much lower intensity. The range of new changes in the pH value of the base solution after passing through the zeolite columns ranges from pH = 5.15 for the Zn filtrate in the time period t5 to pH = 6.81 for the U filtrate in the time period t1. The largest oscillations of the pH value of the filtrate in the time interval t1-t5 on zeolites, at pH=5.00 of the basic solution, were recorded by the contaminated Cd solution (6.65-5.17), which decreased by 1.48 pH units. A similar tendency was also observed with the Cd solution (7.11-6.15) that was passed through the column with apatite, where the pH change was slightly lower, 0.96 pH units. New changes in the pH value of the basic contaminated solution (pH=5.00), after passing through the zeolite columns, have the same distribution of the influence of contaminants (U, Pb, Zn, Cd) as in the case of apatite. The biggest changes in pH value, between the basic solution and the filtrate solution, occurred in the solution with U, then Pb, and the least with Cd and Zn. This indicates the possibility of a great similarity between apatite and zeolite in the affinity towards certain toxic elements, regardless of the difference in the chemistry of their action (adsorption/precipitation).

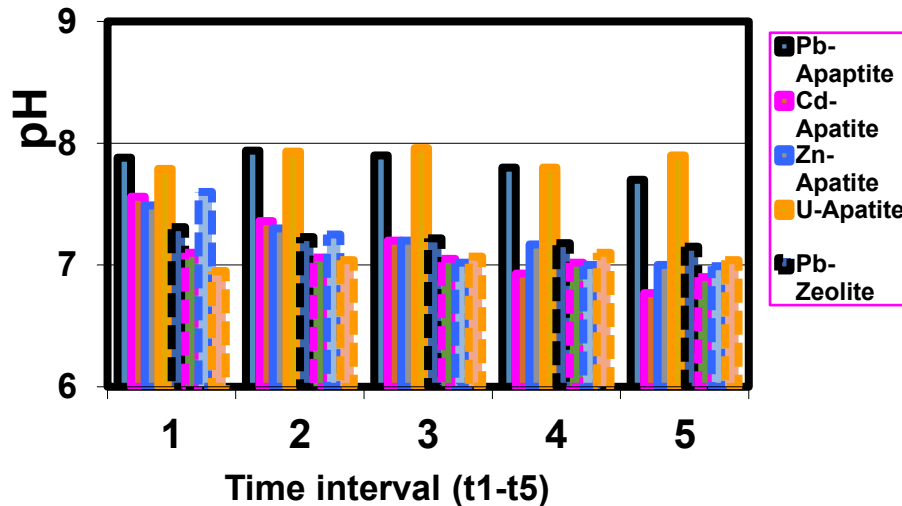
The shown difference in the pH value of the initial solution and the filtrate solution, the dynamics of changes between mineral raw materials (apatite, zeolite) after treatment, occurred due to the composition, dynamics of receiving and the amount of adsorptive cautions that can influence such changes. It is known that the greatest affinity of apatite is for lead and uranium if they are found as contaminants, because they create stable complexes, precipitates. Apatite in its adsorptive complex has a slightly higher content of calcium, sodium and magnesium, which caused the newly created changes in pH value. The obtained results clearly indicate the affinity of certain mineral raw materials for toxic metals, as well as the degree and speed of possible success in establishing the dynamic balance of the adsorption or precipitation process. Graph 1 clearly shows the uniformity and stability of pH filtrate with Pb and U through the apatite column.



Graph. 1 Changes in the pH value of the basic solution pH = 5.00 after passing through columns with zeolite and apatite

Such a trend of uniformity was not established for the contaminants Zn and Cd (pH=5.00) by passing through apatite columns. Even greater oscillations in the time period (t1-t5) of 180 minutes, and lower differences compared to the base solution pH = 5.00 were recorded in the columns with zeolite, with the largest increases in the pH value of the filtrate compared to the base solution being recorded in the first two time intervals (t1-t2), in the first 60 minutes. Changes in the pH value of the filtrate of the solution with Pb, Zn, Cd and U also occurred when the basic contaminated solution, whose pH value was 7.00, was passed through the columns with zeolite and apatite (graph 2). The newly formed changes at pH value 7.00 are significantly less fluctuating compared to the base solution pH = 5.00, and the variations range from 6.77 to 7.96.

The same trend with the pH = 7.00 solution, that is, the biggest changes in the pH value, occurred as with the basic contaminated pH = 5.00 solution in the Pb and U filtrate obtained through the apatite column. The pH values of the filtrate are quite uniform with the apatite column for the contaminated solutions with Pb (7.70-7.94) and U (7.79-7.96).



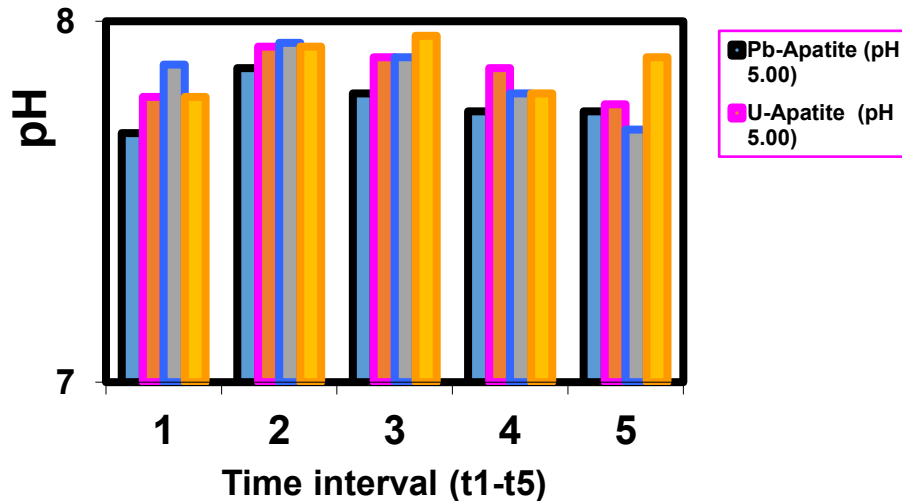
Graph. 2 Changes in the pH value of the solution for apatite and zeolite, after treatment with a toxic solution of pH 7.00

The resulting filtrate through apatites for Cd and Zn have a similar linear decrease in pH value in time t1-t5, for Cd from 7.56 to 6.77 and for Zn from 7.49 to 7.00. As with the basic contaminated solution pH =5.00, and in environmental conditions pH =7.00, the widest ratio of filtrate during time t1-t5 was recorded for Cd (0.79) and Zn (0.49) solutions.

Matusik et al. (Matusik, 2012) determined that hydroxy apatite affects the reduction of Cd content in the solution at different pH values of the basic solution 3, 5 and 7 and leads to an increase in the pH value of the basic solutions to 6.07, 6.90 and 7.21, respectively. In the experiment with natural apatite, the initial pH values were slightly changed to 3.59, 6.45 and 6.90. Such changes in the pH value of the solution can be explained by the influence of H^+ ions in the formation of different phosphate-anion species: HPO_4^{2-} , $H_2PO_4^-$ and H_3PO_4 (Manecki, 2000).

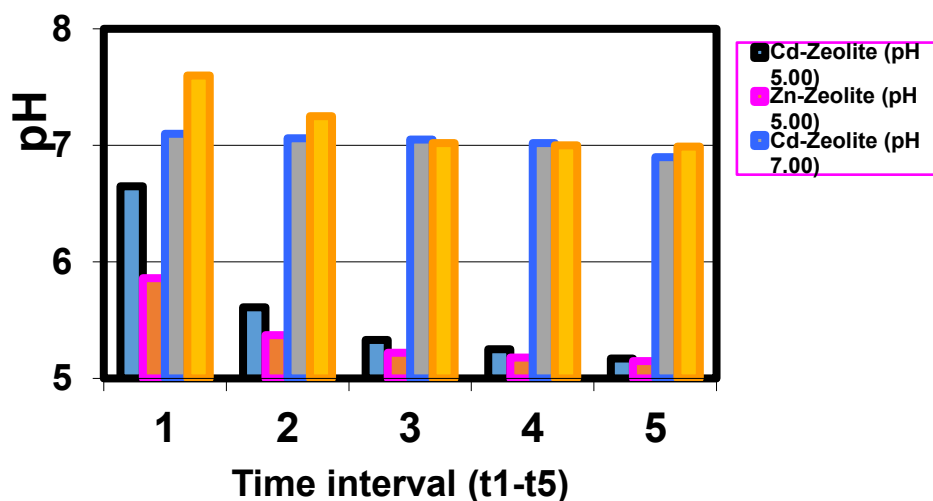
The zeolite-adsorbent, as a filter in the columns, affected the changes in the pH value of the basic contaminated solutions (Pb, Zn, Cd, U) pH=7.00, but with a much smaller impact compared to the same conditions where the filter filling was apatite. Zeolite as an adsorbent in the column had a greater influence on the filtrates when the initial contaminated solution with toxic metals (Pb, Zn, Cd, U) was acidic, pH = 5.00. Solutions with Pb (7.31-7.23-7.22-7.18-7.15) and Zn (7.60-7.25-7.02-7.00-6.99) had sudden changes in the filtrate passed through the zeolites and a trend of decreasing pH value

with time (t1-t5). Graph 2 clearly shows that the change in the pH value of the basic contaminated solution (pH =5.00, pH =7.00) did not significantly affect the change in the pH value of the filtrate obtained through apatites for U and Pb contaminants.



Graph. 3 The influence of the pH value of the basic contaminated solution, pH 5.00 and 7.00, on the changes in the pH value of the filtrate through apatite columns for U and Pb

The increase in the pH value of the solution during the adsorption process of Pb, Cu, Ni, Co, Zn on zeolites indicates that the zeolite is subjected to ion exchange mechanisms with the introduction of toxic metals and that the maximum level of exchange follows the order Pb^{2+} (2530 mmol g⁻¹) > Cu^{2+} (2081 mmol g⁻¹) > Ni^{2+} (1532 mmol g⁻¹) > Co^{2+} (1242 mmol g⁻¹) > Zn^{2+} (1154 mmol g⁻¹) (Qui, 2009).



Graph. 4 The influence of the pH value of the basic contaminated solution, pH 5.00 and 7.00, on changes in the pH value of the filtrate through the zeolite columns for Cd and Zn

3 CONCLUSION

By measuring changes in the pH value of the solution, the cyclic process of zeolite saturation can be very successfully monitored, which can successfully indicate the point of saturation and the end of the regeneration process, which is very important for practical application. The column experiment showed that the best efficiency is obtained if the initial lead concentration is $1,026 \text{ mmol l}^{-1}$ and the flow rate is 2 ml min^{-1} (Vukojevic, 2006).

The filtrate obtained from the column with zeolite for the basic contaminated solutions of Cd and Zn strongly depends on the pH value of the basic solution, such differences, the dependence of Zn and Cd on the pH of the environment in which they are found, indicates that the adsorption properties of the zeolite towards Cd and Zn will depend a lot on pH of the environment (graph 4).

ACKNOWLEDGMENTS

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