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EVALUATION OF LOW-COST SORBENTS AS POTENTIAL MATERIALS FOR *IN SITU* REMEDIATION OF WATER CONTAMINATED WITH HEAVY METALS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: The aim of this paper was to examine the possibilities of using various *low-cost* sorbents as material for permeable reactive barrier for efficient removing of lead, cadmium, copper and zinc from contaminated water. Natural zeolite (NZ), iron-modified zeolite (IMZ), apatite, concentrated apatite, kaolin and raw bentonite were examined. The batch test evaluation was used to investigate capturing of heavy metals from contaminated water onto sorbents, as well as retention strength of saturated sorbent. The change of pH values during saturation and leaching of heavy metals was performed in a slightly acidic to neutral area, confirming buffering abilities and environmental acceptability of all investigated sorbents as a material in PRB for protection of groundwater as the most valuable natural resources. The highest saturation ability towards all examined heavy metals was detected with raw bentonite and IMZ. Leaching of heavy metals at pH=2.94-2.98 was confirmed in all saturated sorbents, while at pH=6.07-6.46 it was not detected, except of Pb and Cd in raw bentonite. From the obtained results, the recommendation for selection of sorbent for treatment of water contaminated with lead, cadmium, copper and zinc is given.

KEYWORDS: *low-cost* sorbent, leachability, permeable reactive barrier, heavy metals (zinc, copper, cadmium, lead)

INTRODUCTION

Groundwater is the most valuable natural resource that is extensively used for water supply, irrigation, industry and mining. This source is highly vulnerable to various anthropogenic pollution influences. Therefore, monitoring and maintaining the good quality of groundwater is of great public interest. At localized sources of pollution, a harmful substance is rapidly dispersed and spread out in the form of plumes in direction of groundwater flow. The remediation of such contaminated groundwater can be carried out using various "*in situ*" and "*ex situ*" techniques. Today, more attention is focused on the "*in situ*" technique of a permeable reactive barrier (PRB) due to simplicity of performance and economy benefits. PRB provides a barrier consisted of water-permeable material, set below the surface perpendicular to the groundwater flow. In the case of remediation of groundwater contaminated with heavy metals, by passing contaminated groundwater through the barrier, the reactive material in the barrier keeps heavy metals by different processes such as absorption, ion-exchange, oxidation, reduction, chemical precipitation. Each of mentioned processes

is directly related to the pH of the system. In this regard, the groundwater geochemistry and reactivity of the material are control factors for PRB binding and retention of metal cations. The choice of materials for barriers is important and depends on the contamination source and the type of harmful substances. Material for PRB must demonstrate good binding properties towards contaminants, the ability of their retention, excellent hydraulic properties which allow smooth flow of groundwater through the barrier, and satisfactory mechanical properties for safety performance^{1,2}. The recent investigations of many scientists have focused on investigation of materials which are abundant in nature or waste material from another process. These materials are usually called as "*low cost*"^{2,3}. The purpose of this work is to explore testing of various natural materials such as zeolite, bentonite, kaolin and apatite and investigate the possibility of their use as a material for PRB, which would effectively remove heavy metals such as lead, cadmium, zinc and copper from contaminated groundwater. The results should give an answer which sorbent provides optimal removal of heavy metals from contaminated water and retention strength of saturated sorbent.

EXPERIMENTAL

REAGENTS

Metal aqueous solutions of zinc, copper, lead and cadmium were prepared from nitrates salts with similar initial metal concentrations of $c_o(\text{Zn}) = 10.107$ mmol/l, $c_o(\text{Cu}) = 10.083$ mmol/l, $c_o(\text{Pb})=10.172$ mmol/l and $c_o(\text{Cd})=10.068$ mmol/l. The following *low-cost* sorbent were used in this study: natural zeolite (NZ), iron-modified zeolite (IMZ), apatite, concentrated apatite, kaolin and raw bentonite. Natural zeolite was supplied from Zlatokop deposit in Vranjska Banja (Serbia), with clinotilolite as a major component, while feldspat plagioclase and quartz were in traces^{4,5}. Bentonite originated from Šipovo

deposit (Bosnia), in which montmorillonite was a major component with quartz and calcite in traces⁴. Apatite from ore deposit Lisina, near Bosilegrad (Serbia), prepared by washing and wet milling, with an average content of P₂O₅ of 17.73%⁶. Kaolin was obtained from a plant for production of quartz sand in Rgotina (Serbia), and kaolinite was found as a major component with quartz and mica in traces⁷. Iron-modified zeolite (IMZ) and concentrate apatite was prepared from original zeolite and apatite, respectively, according to well-known procedures^{5,8}. Chemical composition of investigated sorbents is summarised in Table 1.

Table 1 Chemical composition (in %) of investigated low-cost sorbent

	K ₂ O	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	MgO	Fe ₂ O ₃ %	TiO ₂	L.I.	P ₂ O ₅	Total
Apatite	3.18	0.08	9.96	27.95	35.28	0.98	2.42	0.51	1.88	17.73	99.97
Conc. apatite	0.63	0.05	2.40	9.51	49.09	0.16	0.70	0.17	1.67	36.21	100.59
Kaolin	0.79	0.07	28.5	48.29	10.81	0.20	0.83	0.84	9.65	-	99.98
Bentonite	0.38	0.16	25.04	49.24	5.07	1.57	5.67	0.84	11.99	-	99.96
Raw bentonite	0.25	0.16	25.23	51.31	4.54	3.23	3.78	0.34	11.12	-	99.96
NZ	1.26	1.60	13.58	65.15	4.15	0.62	2.27	0.30	11.07	-	100.00
IMZ	4.14	0.87	12.87	64.28	3.47	0.37	4.04	0.60	9.12	-	99.76

SATURATION EXPERIMENT

The saturation of sorbents with heavy metals solutions was examined using batch mode, at solid/liquid ratio of 10 g/l, during 48 hours at room temperature. As our previous experiments have shown that copper in the system of Cu-IMZ precipitates⁹, the pH values of initial copper solutions in this system were adjusted at pH=2.52. During all experiments, pH values were recorded, and concentrations of heavy metals were determined before and after the experiment complexometrically, and checked by AAS. In all suspension, the precipitates were not observed.

LEACHING EXPERIMENT

After loading with heavy metals, leaching of heavy metals from saturated sorbents were performed by using an original approach based on a batch-pH static leaching experiment in ultrapure water of different initial pH values in ranges 2.94-2.98 and 6.07-6.46. The leaching experiments were performed at solid/liquid ratio of 10g/l, during 24 hours at room temperature. During the experiments, pH values of

solutions were recorded, and concentrations of heavy metals after the experiment were determined.

RESULTS AND DISCUSSION

SATURATION EXPERIMENT

Saturation experiments were continuously monitored by measuring pH values of solutions and results are given in Figure 1.

The slight increase of pH of solutions in all examined systems is evident, which is related with decrease of metal concentration in solution and their hydrolyse reaction.

Metals removed quantity on different sorbents q_e (mmol/g) is calculated by equations (1):

$$q_e = (c_o - c_e) \frac{V}{m} \dots\dots\dots (1)$$

where c_o and c_e are initial and equilibrium concentrations of metal cations (mmol/l), V is the volume of the solution (l) and m is the mass of sorbent (g).

The results of metals removed quantity on different sorbents are given in Figure 2.

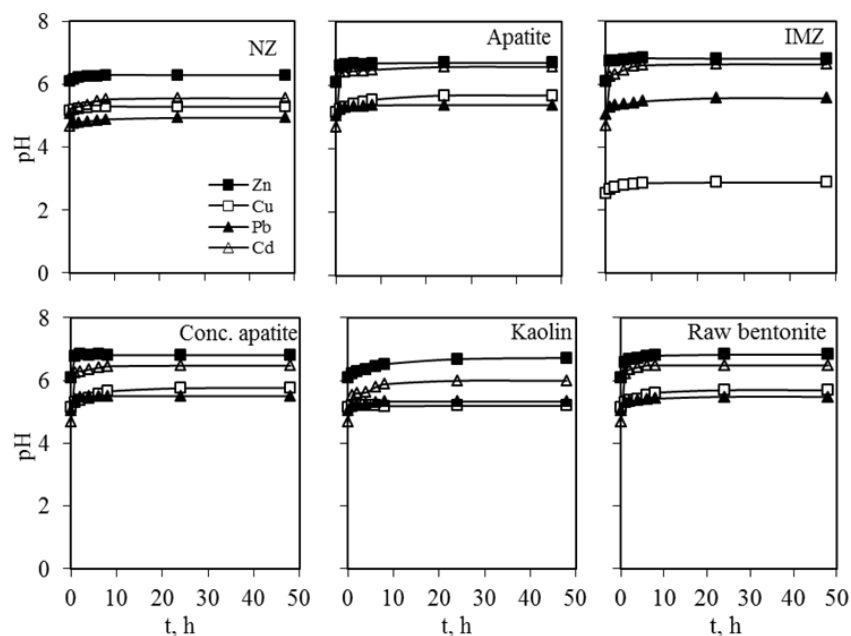


Figure 1. pH values of solution during sorption of zinc, copper, lead and cadmium onto investigated sorbents

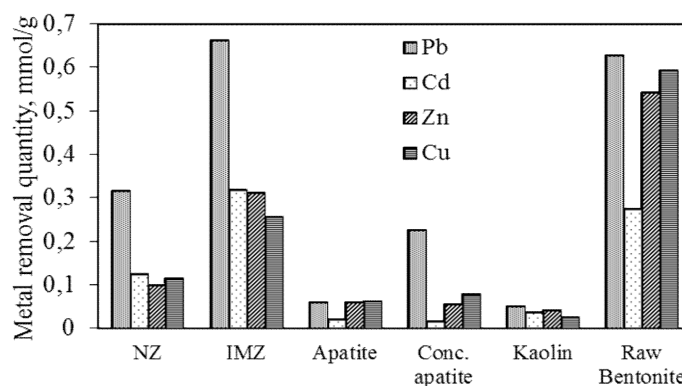


Figure 2. Amount of lead, cadmium, zinc and copper removal on different sorbents

The results indicate that lead was removed in the highest amount in all investigated sorbents, among which IMZ and raw bentonite dominates, followed by NZ and conc. apatite, while the smallest amount was removed by apatite and kaolin. Almost similar amounts of zinc and copper were sorbed onto investigated sorbents, confirming their similar affinities. However, twice higher amount of lead were removed onto investigated sorbent compared to cadmium.

Raw bentonite and IMZ can be selected as materials with the highest potential for removal of heavy metals. Affinity sequence of heavy metals on raw bentonite is in order $Pb > Cu \geq Zn > Cd$, while for IMZ is in order $Pb > Cd > Zn > Cu$.

LEACHING EXPERIMENT

Leaching experiments were followed by measuring the pH values of solutions and results are given in Figure 3.

At $pH=2.94-2.98$, a slight increase of pH values is evident in the system of metal ions with IMZ, conc. apatite and raw bentonite. At $pH=6.07-6.46$, a slight increase is evident for all examined systems, and is most pronounced for conc. apatite.

The amount of metal cations leached from sorbent, q_l (mmol/g) is calculated by equations (2):

$$q_l = c_l \frac{V}{m} \quad (2)$$

where c_l is the concentration of metal cations leached from sorbent (mmol/l).

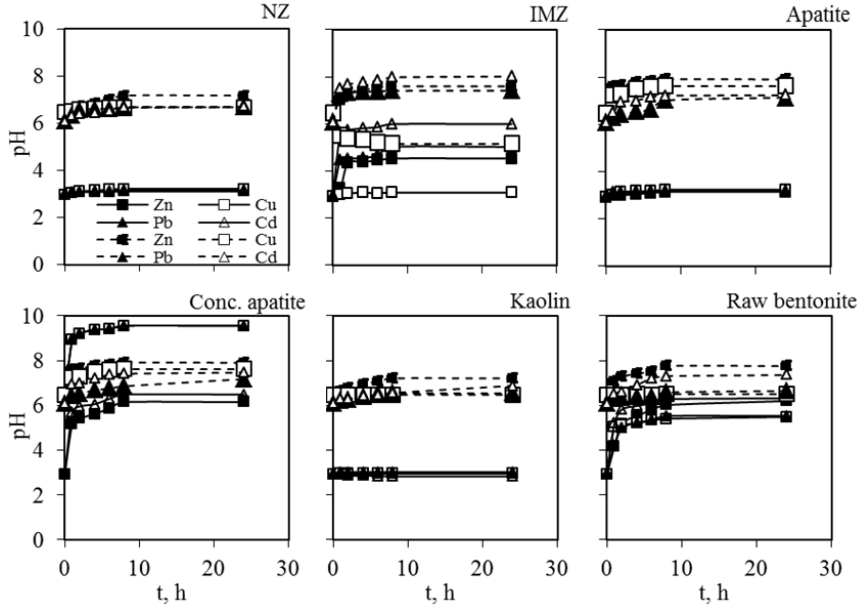


Figure 3. pH values of solution during metal leaching experiment from solution of pH=2.94-2.98 (full lines) and 6.07-6.46 (dash lines)

Leaching of heavy metals from metal-saturated sorbents in ultrapure water solution of pH=2.94-2.98 is given in Figure 4. Leaching in ultrapure water so-

lution of pH=6.07-6.46 was only recorded for lead and cadmium from raw bentonite (thus graphical presentation of these results is not given).

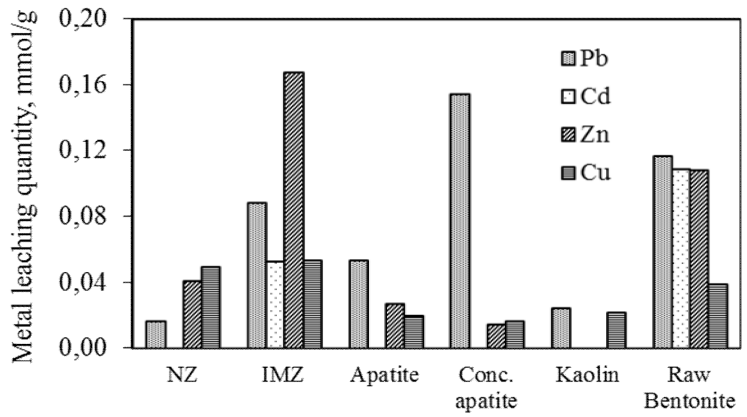


Figure 4. Leaching amount of heavy metals from saturated sorbents in solution of pH=2.94-2.98

At pH₀=2.94 leaching of zinc and copper is evident for all examined sorbents except leaching of zinc from kaolin. Absence of zinc leaching from kaolin is a consequence of a lower amount of sorbed zinc during the saturation experiment.

Also, leaching of lead is evident from all examined sorbent, while leaching of cadmium is evident from saturated IMZ and raw bentonite. Lower pH value encourages competition of H⁺ ions, thus leaching of all examined heavy metals is more pronounced.

CONCLUSION

During saturation of zinc, copper, cadmium and lead on investigated sorbent, the highest removal of heavy metals was achieved by IMZ and raw bentonite. Leaching of heavy metal in acidic medium at pH=2.94-2.98 was recorded in almost all saturated sorbents, due to the presence and competition of higher amounts of H⁺ ions. Leaching of heavy metals from slightly acidic to neutral medium at pH₀=6.07-6.46 was recorded for lead and cadmium from raw bentonite.

Thus, although raw bentonite has excellent removal properties toward lead and cadmium, recorded leaching at pH pH=6.07-6.46 indicate that this material is not suitable for PRB for removal of lead and cadmium.

Based on the obtained results, the following recommendations for the selection of investigated sorbents as materials for PRB for remediation of water contaminated with heavy metals can be given: for zinc removal, among examined sorbents, raw bentonite and IMZ show the highest potential as materials in PRB. As in the system of Cu-IMZ precipitates creates due to the increase of pH, raw bentonite can be selected as a material for PRB for copper removal. For removal of lead and cadmium, IMZ shows the potential to be used as a material in PRB.

Application of the "low-cost" sorbents as materials in a barrier makes the overall process economically and environmentally acceptable.

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