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HEU-type zeolitic tuff in fixed bed columns as decontaminating agent for liquid phases

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ABSTRACT

The uptake of Cs, Pb, Cu, Zn, Cd, and Mn ions, from aqueous solutions by a HEU-type (clinoptilolite-heulandite) zeolitic tuff was studied in batch and column experiments. The effect of solutions concentration, time contact and flow rate on the uptake was also studied. The uptake sequence was found to be Cs>Pb>Cu>Zn>Cd>Mn. The uptake values were affected by the initial concentration and the flow rate and were inferior in column than in batch experiments. Contact time of 60 min was found sufficient in order for the maximum uptake of Cs^+ to be achieved. Furthermore, the conducted experiments indicate that about 10 kg of HEU-type zeolitic tuff is able to uptake 21.4 g of Mn that corresponds to decontamination of above 1 m^3 of wastes solution with 20 ppm Mn^{2+} concentration. The results suggest that the HEU-type zeolitic tuff could be used as decontaminating agent in a battery of fixed bed columns.

Keywords: HEU-type zeolitic tuff; Clinoptilolite-heulandite; Column; Uptake; Decontamination; Water treatment

1. Introduction

In past and recent years, removal of radionuclides and potentially toxic and hazardous metals has received a great deal of attention in the field of environmental pollution. Problems associated with nuclear accidents and the disposal of the wastes of different kind of industries led to studies of the sorption-uptake properties of clay minerals and zeolites [1–11]. Many natural sorbents based on clay minerals and zeolites are suitable either as the barrier for migration of radionuclides, potentially toxic and hazardous metals in the environment or the means of decreasing their content in water solutions of various origins [4,5,12–19].

Among the nuclear fission products Cs is one of the most soluble, long living and hazardous ones [20,21]. In addition, Pb, Zn and Cu can lead to several adverse effects. Furthermore, manganese content in liquid phases of industrial wastes has strict limitations [22–26].

Conversely, among zeolites, HEU-type zeolite (clinoptilolite-heulandite) shows a high CEC and such a structure that allows many ions to readily access its channels and; hence, shows selectivity to them. The behavior of HEU-type zeolitic tuffs as sorbents depends on their specific chemical, mineralogical and physical characteristics [4,6,13,14,27–35]. The need of decreasing the Mn content of wastes from the production of electrolytically produced MnO_2 is of vast importance. This is associated with the use of cheap sorbents in industrial applications. In addition, the need of decontamination of waters, wash offs, aqueous solutions and industrial wastes led to the study of the behavior in columns of HEU-type zeolitic tuff, for Cs, Pb, Cu, Zn, Cd, and Mn uptake, which is the subject of the present work.

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2. Materials and methods

The HEU-type zeolitic tuff used was from Metaxades, N.E. Greece. The geology, mineralogy and the mineral-chemistry of the Metaxades zeolitic tuffs have been investigated by several authors [35–38]. A homogenized sample with grain size 1–2 mm was prepared after crushing and sieving. The chemical and mineralogical compositions of the sample are given in Table 1. The X-Ray powder diffraction (XRPD) analysis was performed using a Philips diffractometer, Ni-filtered $Cu_{K\alpha}$ radiation on randomly oriented sample. The sample was scanned from 3° to 63° 2θ at a scanning speed of 1.2° min^{-1}. Semi-quantitative estimates were performed using external mixture standards of the identified mineral phases. The chemical composition of the HEU-type zeolitic tuff was determined by atomic absorption spectrometry (AAS). A combination of concentrated hydrochloric, nitric, perchloric and hydrofluoric acids was used for the digestion of the studied tuff. Two laboratory fixed bed columns were used for the experiments with HEU-type zeolitic tuff (Table 2). The concentrations of the cations in the solutions were determined by AAS using a Perkin Elmer Model 503 spectrophotometer. Chloride solutions were used in the experiments, while the Cs used was ^{133}Cs (natural cesium). Batch experiments for comparison reasons were also performed.

3. Results and discussion

The capacity of HEU-type zeolitic tuff used in fixed bed column 1 (Table 2) to uptake Cs, Pb, Cu, Zn, Cd, and Mn ions is presented in Table 3. High concentration solutions (26,840 ppm) were used in order to determine the uptake capacity of the zeolitic tuff. The zeolitic tuff uptake order of the cations studied from the solutions was found to be Cs>Pb>Cu>Zn>Cd>Mn. These results can be related to the radius of hydrated ions and their charge and do not contradict to the selectivity order of HEU-type zeolite [34,39]. The sorption of the various elements from their solutions by the zeolitic tuff is mainly attributed to ion exchange into the micropores of the HEU-type zeolite (clinoptilolite-heulandite) and to a lesser extend to adsorption and surface precipitation processes on the meso- and macro-pores of the zeolitic tuff. Important role in these processes play the surface Brønsted acidic and Lewis basic sites of the HEU-type zeolite crystals [13,15–19,31–33].

The effect of contact time in column experiments is given in Table 4. Contact time of 60 min was found to be enough for the maximum uptake to be achieved (Fig. 1). This makes promising the zeolitic tuff used in these experiments as decontaminating agent of liquid phases in column applications. The uptake values at higher concentrations tend to the uptake capacity values of the zeolitic tuff (Table 5 and Fig. 2).

The uptake of Mn^{2+} by HEU-type zeolitic tuff from aqueous solutions in fixed bed column 2 (flow rate 17.76 ml min^{-1}-max available in our experiments) is given in Table 6 and depicted in Fig. 3. The values determined in column exper-

Table 1
Chemical and mineralogical composition of the HEU-type zeolitic tuff sample used (origin: Metaxades, Greece)

Chemical composition		Mineralogical composition	
Oxides	wt%	Minerals	wt%
SiO_2	66.47	HEU-type zeolite	65
Al_2O_3	13.47	Mica	3
CaO	3.25	Clay minerals	3
K_2O	2.6	Quartz	7
Na_2O	2.09	Cristobalite	3
MgO	0.65	Alkali Feldspar	7
$Fe_2O_{3\,tot}$	1.05	Plagioclase	12
TiO_2	0.15		
MnO	0.02		
P_2O_5	0.03		
L.O.I.	10.0		
Total	99.78	Total	100

$Na_{1.0}K_{1.1}Ca_{1.9}Mg_{0.3}Al_{6.8}Si29.3O_{72}20.4H_2O$

Table 2
Characteristics of the two fixed bed columns used for the experiments with HEU-type zeolitic tuff

Characteristics	Column 1	Column 2
Type	Cylindrical	Cylindrical
Height	20 cm	50 cm
Internal diameter	1 cm	5.6 cm
Flow rate	120 ml min^{-1}	various (17.7, 38.7, 52.2, 72.7 ml min^{-1})
Amount of material	10 g	500 g
Solution volume	500 ml and others	2000 ml

Table 3
Capacity of HEU-type zeolitic tuff, to uptake Cs, Pb, Cu, Zn, Cd and Mn ions from aqueous solutions

	Uptake in meq per 100 g	
Ion	Batch*	Column*
Cs^+	138	85
Pb^{2+}	54.2	35.4
Cu^{2+}	47.4	31.2
Zn^{2+}	38.5	20.5
Cd^{2+}	29.2	18.2
Mn^{2+}	21.1	15.6

* 60 min contact time

Table 4
Effect of contact time on uptake of Cs^{+} from aqueous solutions by HEU-type zeolitic tuff in fixed bed column

	Initial solution concentration in ppm				
	50	100	1340	6710	26840
Contact time (min)	Cs uptake in meq per 100 g				
15	3.9	7.2	16	26	54
30	4.2	7.8	28	64	85
60	5.1	9.6	35	78	85
120	5.1	9.8	35	78	85

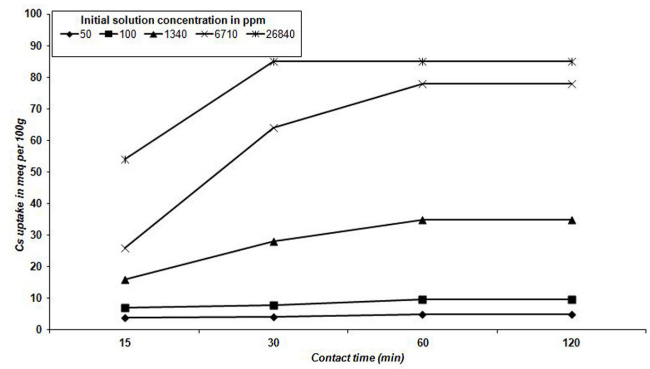

Fig. 1. Diagram showing how contact time effects the uptake of Cs^{+} from aqueous solutions by HEU-type zeolitic tuff in fixed bed column.

Table 5
Uptake of Cs^{+} by HEU-type zeolitic tuff from aqueous solutions

Initial concentration (ppm)	Uptake in meq Cs^{+} per 100 g	
	Batch	Column
50	6.2	5.1
100	12.0	9.8
250	26.0	19.2
500	41	29
1340	57	35
2680	82	52
6710	115	78
13420	128	82
26840	138	85

Column 1, flow rate 120 ml min^{-1}, contact time 60 min

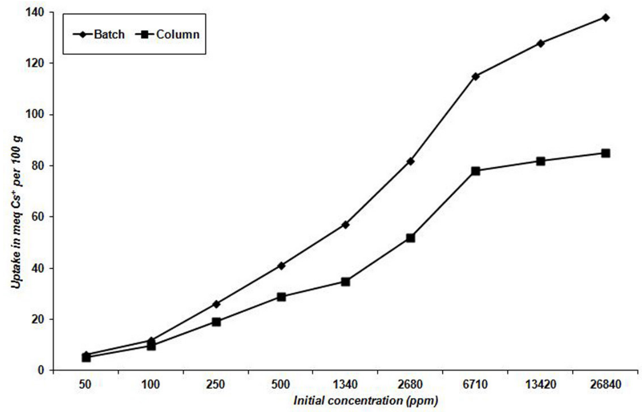

Fig. 2. Diagram showing the uptake of Cs^{+} by HEU-type zeolitic tuff from aqueous solutions.

Table 6
Uptake of Mn^{2+} by HEU-type zeolitic tuff from aqueous solutions

Initial concentration (ppm)	Uptake in meq Mn^{2+} per 100 g	
	Batch	Column 2
50	6.0	4.9
250	7.7	5.9
500	8.7	6.3
750	10.6	7.6
1000	11.3	8.2
1250	16.7	11.4
1500	17.8	12.9
1750	20.2	14.6
2000	21.1	15.6

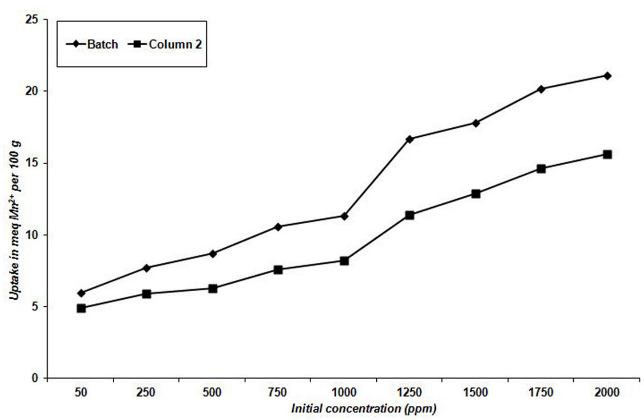

Fig. 3. Diagram showing the uptake of Mn^{2+} by HEY-type zeolitic tuff from aqueous solutions.

Table 7
Effect of flow rate and contact time on the ability of HEU-type zeolitic tuff to uptake Mn^{2+} from aqueous solutions in fixed bed column No 2

Flow rate (ml min^{-1})	Contact time (min)	Uptake in mg Mn^{2+} per g of the rock	
		Initial concentration Co = 10 ppm	Initial concentration Co = 20 ppm
17.76	20.00	1.56	2.14
38.71	9.16	0.77	0.95
52.17	6.80	0.54	0.64
72.70	4.90	0.24	0.30

Solution with concentration of 10 or 20 ppm of Mn^{2+} was feeding to the column. Feeding stopped when Mn^{2+} was detected at the exit of the column.

iments were found to be lower than the ones determined in batch experiments. This can be attributed to column characteristics, in general. Column values are always found to be inferior to the batch ones.

The effect of flow rate and contact time on the ability of HEU-type zeolitic tuff to uptake Mn^{2+} from aqueous solutions in fixed bed column is given in Table 7. Flow rate, which is connected to contact time (since no alteration was made in materials quantity and dimensions of the column), affect strongly the uptake ability.

The concentrations of 10 and 20 ppm of Mn^{2+} were used because these are the ones of wastes in specific steps of electrolytic MnO_2 production that could be treated with a decontaminating agent. Following simple calculations and using the experimental results of Table 7, about 10 kg of HEU-type zeolitic tuff is able to uptake 21.4 g of Mn that corresponds to decontamination of above 1 m^3 of wastes solution with 20 ppm Mn^{2+} concentration. This suggests that, this material could be applied, in the studied case, as decontaminating agent. Fixation of the sorbed elements within HEU-type zeolitic tuff has been reported [17,18].

4. Conclusions

The uptake sequence of ions from their aqueous solution by HEU-type zeolitic tuff used in fixed bed column was found to be Cs>Pb>Cu>Zn>Cd. The uptake values were affected by the initial concentration and the flow rate, and were inferior in column than in batch experiments. Contact time of 60 min was found to be enough in order for the maximum uptake of Cs^+ (85 meq per 100 g) to be achieved. From low concentrations solutions of 10 and 20 ppm Mn^{2+}, the HEU-type zeolitic tuff used was found able to uptake 1.56 mg g^{-1} and 2.14 mg g^{-1} (for 17.7 ml min^{-1} flow rate), respectively, which suggests potential use as decontaminating agent in a battery of fixed bed columns.

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