Acta Agrophysica, 2001, 51, 237-242

SORPTION AND DESORPTION OF COPPER AND CADMIUM BY NATURAL AND SYNTHETIC ZEOLITES RELATED TO THE pH OF THE POLYMETALIC SOLUTION

B. Kozera-Sucharda, B. Gworek

Department of Soil Science, Warsaw Agricultural University
Rakowiecka 26/30, 02-528 Warsaw, Poland
Institute of Environmental Protection, Krucza 5/11, 00-548 Warsaw, Poland

Abstract. The aim of this study was to determine sorption capacity of five zeolite types with reference to copper and cadmium as well as to investigate pH impact on this process. Moreover, the study determined selectiveness of binding and mobilisations by the analysed zeolites as related to the environmental pH changes.

Keywords: sorption capacity, copper, cadmium, zeolites, pH impact.

INTRODUCTION

Industrialisation is the reason for environment contamination with, among others, heavy metals. To reduce the risk to the environment, it is necessary to identify methods for their inactivation [2,5-8,10,11,15].

Natural and synthetic aluminosilicates could be used for that purpose. These are minerals characterised by high sorption capacity and high ion-exchange capability. From that point of view, zeolites are worth paying attention to, as the minerals of very specific intracristaline structure. In some cases, their sorption capacity of heavy metals exceeds the capacity of soil humus, thus it may enhance inactivation of terato- and carcinogenic elements [1,14,15].

The discussed minerals bind metals in specific conditions of pH and Eh. Hence, by changing one of the factors that influence environment, such as pH, it is possible to determine the optimum sorption and desorption of metals in the specific conditions [2-4].

In the future, the investigated minerals could be more effectively used as remedies for the soils contaminated with heavy metals and for wastewater and sludge treatment [2,5-8,11,14,15].

MATERIAL AND METHODS

A multi-chamber device designed by Camano *et al.* [3,4] was used for the determination of the sorption/desorption mechanism of metals in the solid phase. This method allows to investigate sorption/desorption properties of metals as sorbing agents in the conditions of their competitive reactions. The set consists of a central chamber of 4 dm^3 and six external chambers, 850 ml each. The external chambers are separated from the central chamber by membranes of pores with a size 0.45 μm. They provide free ionic exchange and prevent mixing of solid phases. In all the chambers, the suspended matters are continuously mixed by magnetic stirrers.

Five minerals were selected for the present investigations: synthetic sodium-potassium zeolite type 3A with 0.3 nm channels diameter, synthetic sodium-calcium zeolite type 5A with 0.5 nm channels diameter, synthetic sodium zeolite type 10A with 1 nm channels diameter, synthetic sodium zealot of 0.9 - 1 nm channels diameter (marked with 13X symbol), rock containing zeolite with approx. 90% of klinoptilolite (ZN). For simplification, the solutions above the zeolites were marked with the symbols of the minerals.

The chambers were filled with distilled water. In five external chambers, the following types of sorbing agents were placed: 3A, 5A, 10A, 13X and ZN. The sixth chamber was used as control. The suspension density of individual sorbents was 7 g dm^{-3}. After setting up, the pH in the system (approx. 9) - the pH values in external chambers and in central chamber, was measured. Metal solution in the form of nitrates was added to the central chamber. Their concentrations were: Cu - 604 m g dm^{-3}, Cd - 348 g dm^{-3} and pH of the solution was 4.6. It caused pH reduction of the solution from pH 9 to pH approx. 6.

To continue decreasing the pH value in the system, 1M HNO_3 was added to the central chamber. When the pH in the system set up in the sequence of 6, 5, 4, the solution and the solid phase samples were taken from each of the chambers. The samples, after centrifugation and drying (105 °C) were totally decomposed. The samples were transferred to teflon bombs with HF and $HClO_4$ (7 ml and 3 ml) addition. There, they were melted for 2 hours at a temperature of 130 °C. The content of Cu and Cd in the solutions sampled from the individual chambers, in the zeolites after their transfer to the solution and in the comparative zero sample were detected by the AAS method.

RESULTS AND DISCUSSION

The present investigation provided evidence that copper and cadmium sorption by the selected synthetic zeolite species and natural zeolite was differentiated in competitive conditions. The experiments proved that the highest affinity with reference to copper and cadmium was observed in the 5A and 3A synthetic zeolites. In competitive conditions, sorption of the discussed metals by 10X and 13A zeolites was lower by 10% than in the zoelties 3A and 5A under the same conditions. Among the selected aluminosilicates, a natural zeolite showed the lowest Cu and Cd sorption capacity. In comparison to synthetic zeolites, cadmium sorption by the natural zeolite was sometimes even ten times lower (at pH 6). Further pH reduction to approx. 5 and 4 resulted in the further release of metal from the natural zeolite, whereas the highest sorption of these metals by the synthetic zeolites was observed at the pH of 5 and pH 4. Comparing different clay materials (like haloizyte and smectite) to synthetic zeolites, we can say that they all natural and synthetic minerals - showed the highest sorption at pH 5.

The investigation carried out by Helios-Rybnicka and Kyzioł [11] concerning aluminosilicates from such groups as clays like: kaolinite, smectite, serpentite, micas, chlorite, palygorskite and illite-kaolinite prove that within the range of pH changes from 6 to 2 metal release occurs in all the above mentioned aluminosilicates in the following sequence Cu>Cd. The research also showed that heavy metal sorption and release processes are different for natural and synthetic zeolites. In the natural zeolite, both of these parallel processes were apparently shifted towards desorption in comparison to synthetic zeolites (in analysed conditions). For pH 5 and pH 6, the content of the investigated metals in the solutions with synthetic minerals was at the detection limit of the equipment. At the same time, in the natural zeolite, it had similar values for Cd as in control and central chamber (Table 1).

Copper and cadmium binding by the tested zeolites (5A, 3A, 10A, 13X, and ZN) can be presented in a quantitative sequence (in mg kg^{-1} of dry mass):

in solution of pH 6:
Cu: 13X(7800)>3A(6200)>5A(4600)>10A(3000)>ZN(1500)
Cd: 13X(4800)>3A(3800)>5A(3000)>10A(2300)>ZN(400)
in solution of pH 5:
Cu: 5A(11200)>3A(9200)>13X(8200)>10A(7300)>ZN(920)

Table 1. Quantity of copper and cadmium sorbed by natural and synthetic zeolites

Type of sorbent	Solution (mg dm^{-3})			Zeolites (mg kg^{-1})		
	pH 6	pH 5	pH 4	pH 6	pH 5	pH 4
			Copper			
Zeolite 3A	0.012	0.142	1.387	6248	9255	9542
Zeolite 5A	0.052	0.300	1.336	4594	11187	11423
Zeolite 10A	0.302	0.262	1.467	3044	7337	6741
Zeolite 13X	0.054	0.268	1.620	7780	8225	7739
Nat. Zeolite	0.266	7.184	7.070	1459	920	473
Control	23.272	4.520	4.090			
Central	19.948	3.354	3.440			
			Cadmium			
Zeolite 3A	0.030	0.216	0.766	3861	7948	7401
Zeolite 5A	0.044	0.376	1.033	3046	8537	7683
Zeolite 10A	0.058	0.216	0.800	2295	4797	4998
Zeolite 13X	0.039	0.195	0.761	4813	5529	5068
Nat. Zeolite	18.785	3.509	2.899	414	222.4	120
Control	20.399	2.975	2.456			
Central	17.816	2.136	1.981			

Cd: 5A(8500)>3A(7900)>13X(5500)>10A(4800)>ZN (220)

in solution of pH 4:

Cu: 5A(11400)>3A(9500)>13X(7700)>10A(6700)>ZN(470)

Cd: 5A(7700)>3A(7400)>13X(5070)>10A(5000)>ZN(120)

Until now, investigations of heavy metal sorption/desorption on the clay sorbents showed that copper and cadmium release from the natural sorbing agents looks as follows:

Cd>Cu for beidelite,

Cd=Pb for illite and montmorillonite [9].

Considerable amounts of copper and cadmium bound in synthetic zeolites is explained by their ion-exchange capabilities. All these zeolites contain significant amounts of sodium on exchangeable positions [1,5-7,11]. The ionic radius of the sodium cation is 0.97 Å and 1.01 Å. It is very close to copper ion radius: 0.72 Å for Cu^{+2} and 0.96 Å for Cu^{+1} and for cadmium 0.97 Å and 1.01 Å (cited in [13]). It should be presumed that the cations of these metals substituted sodium cation.

Nevertheless, this analysis does not prove correlation between the channel diameter in zeolites and copper and cadmium sorption. Zeolites 3A and 5A showed higher sorption in comparison to 10A and 13X zeolites although their channel diameters are smaller. Investigations carried out by Gworek *et al.* [5-8] showed higher Cu and Cd sorption by 13X synthetic zeolite than 4A zeolite. This regularity was

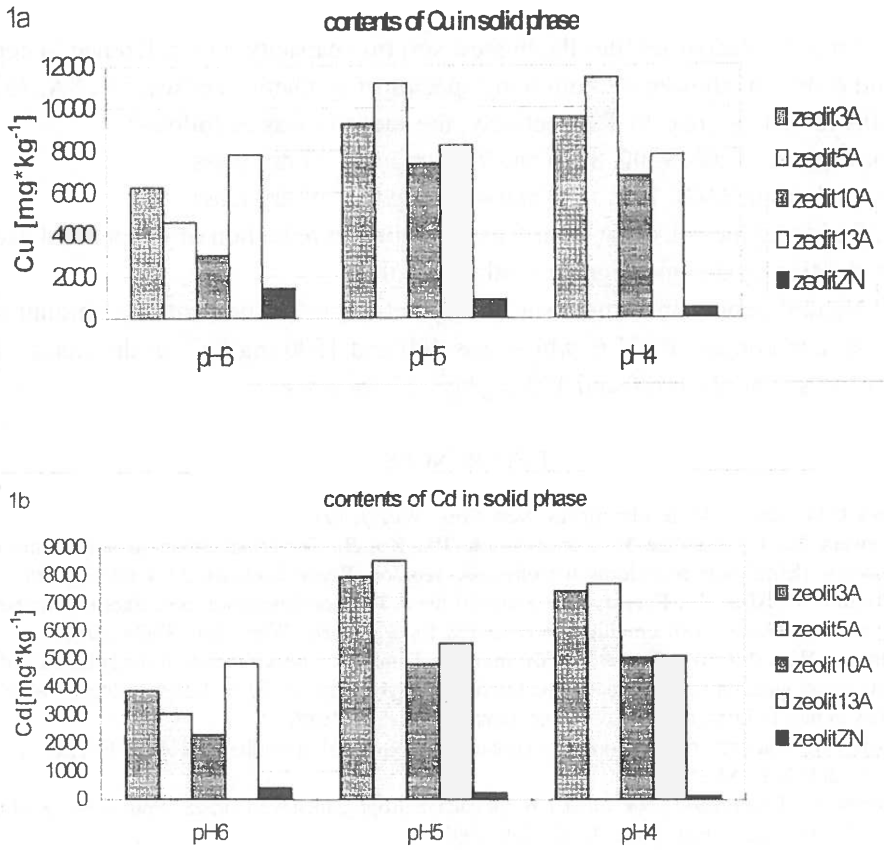

Fig. 1. Quantity of copper (1a) and cadmium (1b) sorbed by natural and synthetic zeolites depending on pH solution.

explained in terms of channel diameter which is bigger in the case of 13X (9-10 Å) than in 4A zeolite of 4.2 Å channel diameter.

Higher sorption of copper and cadmium obtained as a result of the present study should be explained in terms of a very well developed sorption surface of the minerals which exceeded 1100 me 100 g^{-1} for the 3A synthetic zeolite and only 320 me 100 g^{-1} for the natural zeolite. Similar results were obtained by Helios-Rybicka and Kyzioł [11] who analysed heavy metal sorption for three different kaolinite types. It turned out that metal sorption by various minerals from the same group depends mainly on the sorption capacity of the investigated sorbing agents.

CONCLUSIONS

1. Among selected zeolites the highest sorption capacity with reference to copper and cadmium showed the following species of synthetic zeolites: 5A, 3A, 13X and 10A (at pH approx. 5). Respectively, the capacity was as follows:

for copper: 11200, 9200, 8200 and 7300 mg kg^{-1} of dry mass

for cadmium: 8500, 799, 5500 and 4800 mg kg^{-1} of dry mass.

2. Reducing the pH value from 5 to 4 resulted in reduction of copper and cadmium sorption by the investigated synthetic zeolites.

3. Natural zeolite in comparison to synthetic ones sorbed smaller amount of cadmium and copper, at pH 6, which was 400 and 1500 mg kg^{-1} of dry mass, respectively, and at pH 4-120 and 470 mg kg^{-1} of dry mass.

REFERENCES

1.**Breck D.W.**: Zeolite Molecular Sieves. New York, Willey, 1974.
2.**Borowiak M., Czarnowska K., Lewandowski W., Kot B.**: Dynamika zmian zawartości metali ciężkich w glebach antropogenicznych w obecności zeolitów. Roczn. Glebozn., 37, 4, 67-83. 1986.
3.**Calmano W., Ahlf W., Forstner U.**: Study of metal sorption/desorption processes on competing sediments phases with a multichamber device. Environ. Geol. Water Sci., 77-84, 1988.
4.**Calmano W., Ahlf W., Baade H., Förstner U.**: Transfer of heavy metals from polluted sediments under changing enviromental conditions. [In:] M. Astruc and J.N. Lester (editors), Heavy Metals in the Hydrological Cycle. Selper, London, 501-506, 1988.
5.**Gworek B.**: Inactivation of cadmium in contaminated soils using synthetic zeolites. Environ. Pollut., 75, 269-271, 1992.
6.**Gworek B.**: Unieruchomienie miedzi w glebach antropogenicznych przez syntetyczne zeolity typu 5A i 3A. Arch. Ochr. Środ., 1, 205-209, 1992.
7.**Gworek B., Borowiak M.**: Model studies on mobilization of certain heavy metals by synthetic zeolites. Roczn. Glebozn., 42, 12, 27-35, 1990.
8.**Gworek B., Borowiak M., Brogowski Z.**: The possibility of purification of industrial sewage sludge of heavy metals with the use of synthetic zeolites. Pol. J. Soil Sci., 24/2, 147-152, 1991.
9.**Helios Rybicka E., Calmano.W., Breeger A:**. Heavy metals sorption/ desorption on competing clay minerals; an experimental study. Appl. Clay. Sci., 9, 369-381, 1995.
10.**Helios Rybicka E., Jedrzejczyk B.**: Preliminary studies on mobilisation of copper and lead from contaminated soils and readsorption on competing sorbents. Appl. Clay Sci., 10, 259-268, 1995.
11.**Helios-Rybicka E., Kyzioł J.**: Rola minerałów i skał ilastych w wiązaniu metali ciężkich w środowisku wodnym. Zesz. Nauk. AGH, Kraków, 1991.
12.**Kyzioł J.**: Sorpcja wybranych metali ciężkich na minerałach ilastych. Ph.D. Thesis, AGH, Kraków, 1991.
13.**Polanski A., Smulikowski K.**: Geochemia. Wyd. Geol., Warszawa, 1969.
14.**Sand L., Mumpton F.A.**: Natural Zeolites. Occurrence, Properties, Uses. Pergamon Press, New York, 1978.
15.**Zabiński W.** [ed.]: Sorbenty mineralne Polski. Inst. Geol. i Surow. Mineral., AGH, Kraków, 1991.