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Original Research

Sorption of Lead and Cadmium Cations on Natural and Manganese-Modified Zeolite

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Abstract

Our work shows that active masses modified with manganese that are used to remove Mn(II) and Fe(II) can also remove the heavy metals Pb and Cd. The study was conducted for solutions with a concentration of cation 100 mg/L and demonstrated the high correlation between hydroxo-complexs and their potential, and the process of removing investigated metals (Pb and Cd).

Keywords: cleaning water, cleaning waste water, sorption Pb, sorption Cd

Introduction

Contamination of surface and underground waters may be of natural or anthropogenic origin. The extent and type of contamination depends on many factors. Both surface and underground waters may contain metals, such as iron, manganese, lead, or cadmium. Lead present in surface waters is of anthropogenic origin, and it gets to them from chemical and arms factories, ore mining and processing plants, and glassworks and ceramics factories. Its sources include surface flows, especially those from highways (tetraethyl lead is added to petrol), and the lead pipes that are still used in some old water supply systems. Like lead, cadmium can get to surface waters from ore mining and processing plants and with surface flows containing products of oil combustion and vehicle tire wear. Cadmium is also emitted by electroplating plants (in the motor and electronics industries), as well as those producing paints, plastics, fungicides, etc. It also enters surface waters as a result of desorption by humic acids, with which it forms soluble complexes [1-3].

Cadmium in water occurs in a soluble and colloidal form. At pH<8 cadmium is present in a dissociated form as free ions Cd^{2+} or aqua ions $[Cd(H_2O)_6]^{2+}(aq)$. At higher pH values it forms a hydroxo complex $[Cd(OH)]^+$, and in an alkaline environment the following species are present: $[Cd(OH)_2]^-$, $[Cd(OH)_3]^-$, $[Cd(OH)_4]^{2-}$. Ion radiuses are equal to: Cd^{2+} 103 pm, Cd^+ 114 pm; and the atom radius – 148.9 pm. It is rare at oxidation degree +1, e.g. $Cd_2(AlCl_4)_2$. Its ion at +2 forms numerous salts and complexes. Cadmium is strongly toxic and can accumulate in living organisms [7-11].

Lead may occur at one of the following oxidation states: +2, +4, 0, –2. Ion radiuses are equal to: Pb^{2+} 132 pm, Pb^{4+} 84 pm; the atom radius – 175 pm. Pb(II) salts are insoluble in water, except for nitrates and acetates [2]. They occur in surface waters mainly as soluble forms: Pb^{2+} and $[PbCO_{3(aq)}]^o$. In a neutral environment, at pH≈6, Pb(II) and $Pb(OH)^+$ ions occur at the same quantities [4]. In neutral and alkaline environments they form hydroxo complexes $[Pb(OH)_{2aq}]^o$, $[Pb_6(OH)_2]^{-4}$, $[Pb_3(OH)_4]^{-2}$, $[Pb(OH)_4]^{-2}$, $[Pb(OH)_3]^-$. Lead is toxic to humans; it replaces calcium and, consequently, can accumulate in the bone system. Systematic epidemiological studies conducted since 1979 have shown that doubling lead content in a human body (from 10 to 20 μg/dl in blood) has resulted in decreased IQ scores by 1-2 IQ points [5]. Children's blood analyses conducted in 183 urban centres have shown that an increase in lead concentration in water from the background levels to 0.015 mg/L is accompanied by an increase in lead concen-

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tration to the limit value of 10 μg/dl in 13.7% of children. An increase in lead concentration in soil to 400 μg/g increases its blood level to 10 μg/dl in 11.6% of children [6].

Due to their toxic nature, cadmium and lead should be removed from underground and surface waters used for communal purposes. The technological systems currently applied do not have special nodes dedicated to heavy metals removal. It is assumed that the metal concentrations in water are low and they are rarely determined in raw and purified water. At the same time various reports [12-14] have shown that cadmium can be removed by adsorption on goethite, pea and bean husks, fig leaves, zeolite, pumice, vermiculite, and other materials.

Several years ago, active masses containing manganese oxides were first used to catalyze the processes of iron, manganese and arsenic removal. Since cadmium and lead occur in some water intakes, this study attempts to examine the removability of those metals on a zeolite modified with manganese oxides as compared to the process taking place on natural, unmodified zeolite, in order to elucidate the mechanism of removal of the two metals.

Experiment Methodology

- Cadmium and lead ions were determined with a series 3000 Ice atomic absorption spectrometer manufactured by Thermo Jarrell Franklin, USA. Traces of ions were determined using the same apparatus with an AASFG attachment, in accordance with the PN-EN ISO 15586 standard "Water quality: Determination of trace elements by atomic absorption spectrometry with graphite furnace atomic absorption spectrometry" (2005). The effect of interfering agents was evaluated by the use of modifiers such as magnesium nitrate (V) and palladium (II) nitrate (V). Determinations were performed in nitrous oxide and acetylene flame. Lanthanum (III) nitrate (V) was added to the standards and samples to prevent ionisation of the element being determined.
- Pb determination – performed by absorption atomic spectroscopy with flame ionization, in air-acetylene flame, in accordance with PN-ISO 8288 (March 2002). The analyses were performed at a wavelength of 217 nm and slot width of 1 nm.
- Cd determination – performed by absorption atomic spectroscopy with flame ionization, in air-acetylene flame, in accordance with PN-ISO 8288 (March 2002). The analyses were performed at a wavelength of 232 nm and slot width of 0.5 nm.

Qualitative analyses were performed on filtered solutions. The sorption process was examined under static conditions, adopting the optimum sorption time of 120 minutes. The amount of zeolite added to the system was constant and amounted to 15 g/L.

Solutions at concentrations of 100 mg/L, prepared from distilled water and Merck standard solutions of 1,000 mg/L of each of Pb(II) and Cd(II) ions, were used in the experiment. Merck standard solutions were prepared from lead (II) nitrate (V), and cadmium (II) nitrate (V).

The electrokinetic potential and the size of the hydroxo complex particles in relation to the solution pH value were determined in a Brookhaven zetameter by the method of phase analysis of dispersed laser light in a dispersed medium. The method makes it possible to measure individual particles with diameters from 30 nm to 3 μm. A solution of ions at concentrations of 100 mg/L was prepared from distilled water, and solution pH was adjusted with 0.1 mole/L NaOH and HCl. The solution was stirred for 3 minutes and subsequently the electrokinetic potential and the sizes of resulting particles were determined.

The process of sorption was examined under static conditions, adopting a constant dose of the sorbent D_z=15g/L and the initial cation concentration in the solution of C_0=100 mg/L.

Characterization of Materials Used in the Experiment

Natural zeolite (clinoptilolite) from Hungarian deposits was used in the experiment. The zeolite contained 55% of clinoptilolite, 26% of ash and volcanic glass, 6% of quartz, and 13% of montmorillonite. Its density was equal to 2.4 g/cm^3 and its bulk density (ground material) 0.69 g/cm^3. The mineral porosity is 30-50% and the ion-exchange capacity 1.15 mvalMe/g [16]. The mineral was washed with hydrochloric acid and distilled water and subsequently dried at 105ºC (zelite H) and modified with Mn ions (Zeolite Mn).

Zeolite Mn, referred to as "Diapar", was obtained by the method patented by the authors [17]. Zeolite H contains high concentrations of silicon compounds (320 mg/g) and aluminium (60 mg/g) and alkaline earth metals (sodium, calcium, iron, and magnesium), whereas zeolite Mn contains fewer compounds of silicon (290 mg/g) and aluminium (53 mg/g) relative to the total mass, which results from introducing manganese ions to zeolite, owing to which its concentration is quite high (78 mg/g) [18, 19]. Evaluation of the zeolites used in the experiment by infrared spectra analysis showed [2] that the zeolite Mn has better catalytic properties than non-modified zeolite. The active manganese

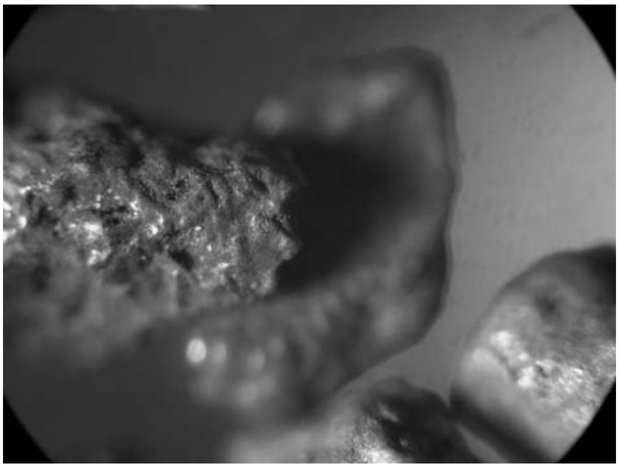

Fig. 1. Photograph of zeolite Mn.

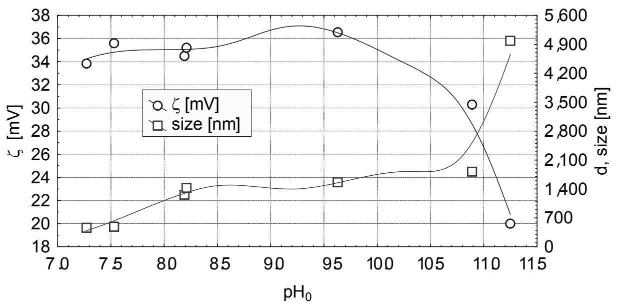

Fig. 2. The zeta potential and the size of Cd hydroxo complex particles.

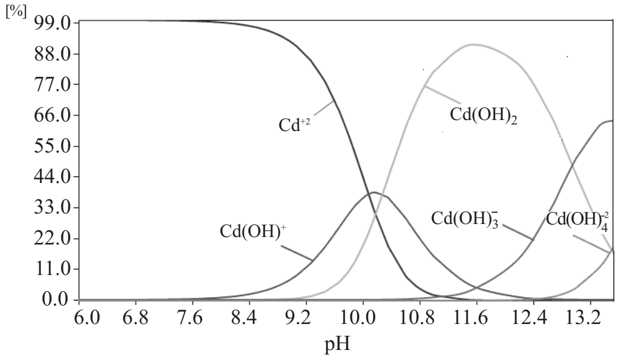

Fig. 3. The effect of solution pH on the occurrence of Cd(II) complexes in aqueous solutions [16].

dioxide that forms on the surface is highly complex and forms various polymorphic varieties, considerably deviating from the stoichiometric formula. Therefore, it has catalytic and sorptive properties. Zeolite Mn is black with a metallic sheen (Fig. 1).

Results and Discussion

The values of zeta potential and sizes of the particles that formed in solutions of cadmium and lead hydroxo complexes are shown in Figs. 2 and 3. The results of examinations of the cations' sorption on zeolites H and Mn are shown in Figs. 4 and 7.

It was possible to measure particle size and zeta potential in the cadmium solution (Fig. 2) within the range of pH values from 6.4 to 11.7. At pH < 6.4 the solution was clear because it contained only dissociated ions. Considerable autocoagulation took place at pH > 11.7; the particles that maintained a stable diameter of about 400 nm throughout the pH range under examination started to grow and their zeta potential started to drop to negative values. These relationships may be explained by the formation of hydroxo complexes (Fig. 3). There are no hydroxo complexes in the solution at pH<6.5, with only dissociated aqua-ion- forming Cd(II) ions present, which explains why the solution in which the zeta potential measurement made was clear within the pH range. The zeta potential has the highest positive values at pH 7-9, when only dissociated Cd^{2+} ions and electropositive Cd(OH)$^+$ hydroxo complexes are present in the solution. At pH values higher than 9.0, negative hydroxo complexes Cd(OH)$_2^-$ are present, which coagulate with Cd^{2+} ions and Cd(OH)$^+$ complexes. At pH>10.5, Cd(OH)$_3^-$ complexes appear, which distinctly reduce the electrokinetic potential of particles, and even switch it from positive to negative values at pH>11. Formation of positive and negative hydroxo complexes distinctly favour autocoagulation, which is indicated by an increase in the size of particles for which the zeta potential measurements were made. A comparative analysis of Figs. 2 and 3 shows that zeta potential can serve as a basis of determination of highly probable types of hydroxo complexes and the relationships between them. Examinations of cadmium sorption on Zeolite H and Zeolite Mn have shown that Cd is better removed on the Zeolite Mn than on the Zeolite H, especially within the pH range of 8-11 (Fig. 4). It is within this range that protons are released from Zeolite H to the solution and they reduce its pH value to the range of 4.2-8.6, within which non-precipitable hydroxo complexes are present in the solution (Fig. 3). Cd removal on Zeolite Mn also takes place due to its precipitation as a result of hydroxo complex formation, especially Cd(OH)$_2$. Sorption of the lowest degree took place in the solution with pH<8.4, with aqua ions dominating. Formation of precipitable hydroxo complexes Cd(OH)$_2^-$ favoured removal of cadmium from the solution, the appearance of consecutive negative complexes in the presence of electropositive complexes enhanced precipitation, and removal of Cd. Obtained dependence of Cd(II)

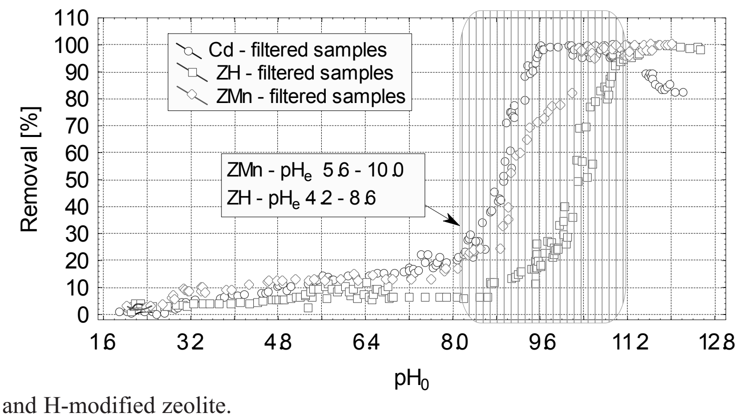

Fig. 4. Cd sorption on Mn- and H-modified zeolite.

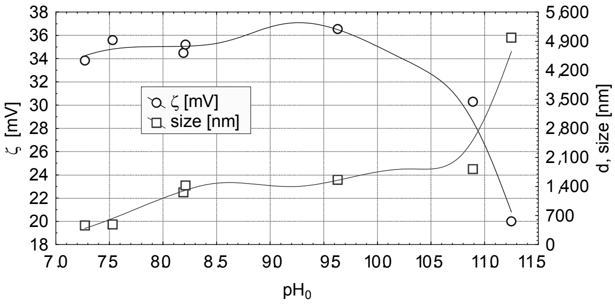

Fig. 5. The zeta potential and the size of Pb(II) hydroxo-complex particles.

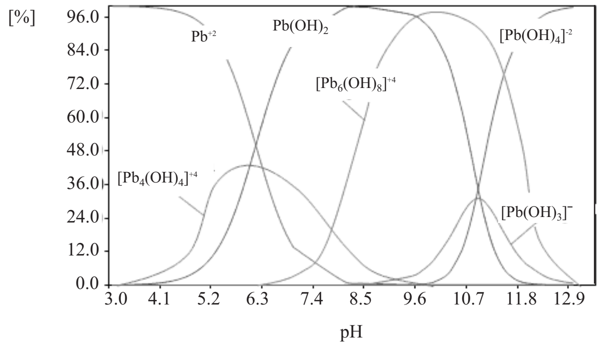

Fig. 6. The effect of solution pH from the occurrence of Pb complexes in aqueous solution [16].

adsorption on the pH solution is similar to those obtained by Davis and Bhatnager [20] in the process of adsorption onto α-Fe_2O_3.

The results of zeta potential measurements, the size of coagulated hydroxo complexes of lead and its sorption process are shown in Figs. 5-8. Measurement of molecule sizes and zeta potential was possible at pH 7.2-11.3. The zeta potential within the range was positive. Its value at pH 7.2-10 was stable and close to 35 mV. At pH values below 10.5, the electrokinetic potential is seen to decrease rapidly to 20 mV at pH 10.25. The relationship is well correlated with the hydroxo complexes formed within the pH range under examination – Fig. 6. Pb^{2+} and $[Pb_4(OH)_4]^{4+}$ ions dominate at pH<6. Electronegative complexes dominate only in a strongly alkaline environment, at pH about 12. This explains why the particles had positive zeta potential within the range under examination.

At pH values above 10.7 there is approximate equilibrium between the amount of positive and negative complexes. Therefore, they distinctly autocoagulate in alkaline solutions. The particles grow rapidly to achieve a diameter of 4,900 nm at pH 10.25. At the same time, the zeta potential decreases rapidly and is close to zero. The precipitability of hydroxo complexes is the highest at the pH value that is indicated by the concentration of the element in the filtrate (Fig. 7). Dependence of pHe (final) from pH$_0$ (initial) in the Pb adsorption process are shown in Fig. 8. Effective sorption on Zeolite H and Zeolite Mn, not associated with complex

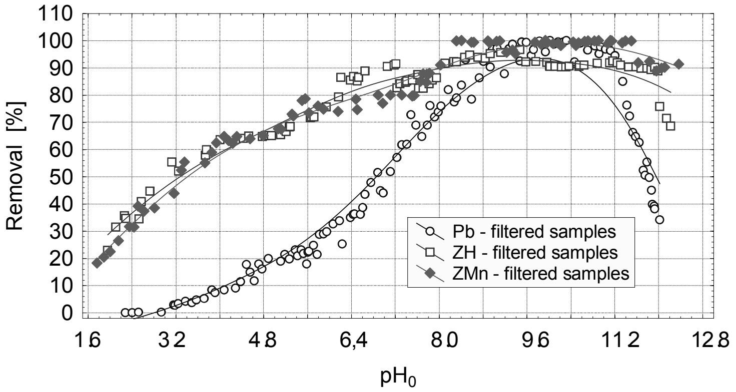

Fig. 7. The effect of pH$_0$ on removal of Pb ions in the adsorption process. Zeolite dose D_z=15 g/L, cation concentration C_0=100 mgPb/L.

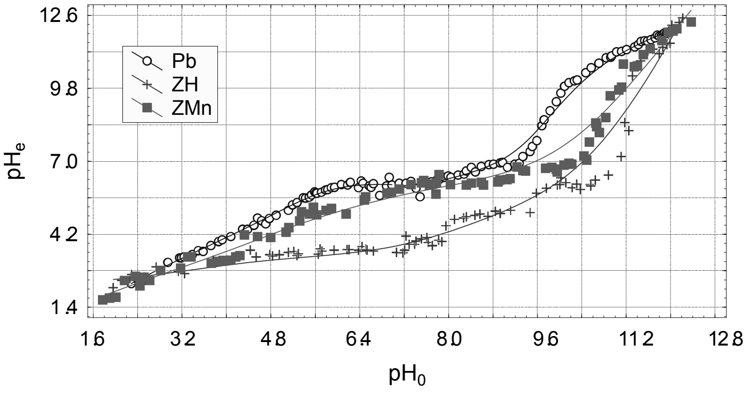

Fig. 8. The effect of pH$_0$ (initial) on pH$_e$ (final) in the Pb adsorption process. Zeolite dose D_z=15 g/L, cation concentration C_0= 100 mgPb/L.

precipitation, takes place at pH<8.5, when positive charge dominates. Hence, it may be concluded that the sorption process is caused by electrostatic attraction. Moreover, the presence of positive hydroxo complexes is important rather than that of free ions. Sorbent porosity is a limiting factor. The size of its pores is about 0.78-0.4 nm, whereas a majority of hydroxo complex particles (ca. 60%) has a diameter >700 nm at pH>7.5. This explains why the effectiveness of sorption (the area between the Pb as well as ZMn and ZH curves), which includes particle precipitation, is about 40%, despite favourable conditions that result from electrostatic affinity.

Conclusions

Our experiment leads to the following conclusions:

- Measurement results for zeta potential and sizes of hydroxo complex particles provide the basis for determination of their probable affinity to a sorbent with known surface potential.
- Electropositive hydroxo complexes participate in the process of Pb sorption on zeolite H and zeolite Mn. The appearance of negative hydroxo complexes in the solution favours autocoagulation of positive and negative complexes, which results in metal precipitation.
- The effectiveness of sorption is affected by the size of hydroxo complex particles and sorbent (molecular sieve) porosity.
- The presence of zeolite H reduces Cd removability from the solution as a result of proton release from zeolite and a decrease in the solution's pH.
- A correlation is observed between the hydroxo complexes and their zeta potential and the resultant value that arises from autocoagulation.

References

1. SONGHUYUAN, ZHIMIN XI, YI JIANG, JINZHONG WAN, CHAN WU, ZHONGHUA ZHENG, XIAOHUA LU. Desorption of copper and cadmium from soils enhanced by organic acids. Chemosphere **68**, 1289, **2007**.
2. HORANYI G. Specific adsorption of simple organic acids on metal (hydroxides: a radiotracer approach. J. Colloidal Int. Sci. **254**, 214, **2002**.
3. WASAY S.A., BARRINGTON S., TOKUNAGA S. Organic acids for the in situ remediation of soils polluted by heavy metals; soil flushing in columns, Water Air Soil Pollut. **127**, 301, **2003**.
4. DOJLIDO J.R. Chemistry surface waters. Economics and environmental. Bialystok **1995**.
5. WATT G.C.M., BRITTON A., GILMOUR H. G., MOORE M.R., MURRAY G.D., ROBERTSON S.J. Food and Chemical Toxicology **38**, S73, **2000**.
6. LANPHEAR B. P., BURGOON D. A., RUST S. W., EBERLY S., GALKE W. Environmental Research, **76**, 120, **1998**.
7. TANGAROMSUK J., POKETHITIYOOK P., KRUATRACHUE M., UPATHAM E.S. Cadmium biosorption by Sphingomonas paucimobilis biomass. Bioresource Technology **85**, 103, **2002**.
8. WAISBERG M., PIUS JOSEPH, BEVERLEY HALE, DETMAR BEYERSMANN. Molecular and cellular mechanisms of cadmium carcinogenesis. Toxicology **192**, 95, **2003**.
9. MOMOSE Y., IWAHASHI H. Bioassay of cadmium using a DNA microarray: genome-wide Saccha expression patterns of Saccharomyces cerevisiae in response to cadmium. Environ. Toxicol. Chem. **20**, 2353, **2001**.
10. KALICANIN BILJANA M. Determination of very toxic metal – Cadmium in natural water samples. Desalination **249**, 58, **2009**.
11. DE CONTO CINIER CH., PETIT-RAMEL M., FAURE R., GARIN D., JOUVET Y. Kinetics of cadmium accumulation and elimination in carp Cyprinus carpio tissues. Comparative and Physiology Part C **122**, 345, **1999**.
12. BENAISSA H. Screening new sorbent materials for cadmium removal from aqueous solutions. Journal of Hazardous materials B **132**, 189, **2006**.
13. CHIN-HSING LAI, CHIH-YU CHEN, BAI-LUH WEI, SHU-HSING YEH. Cadmium adsorption on goethite-coated sand in the presence of humic acid. Water Research **36**, 4943, **2002**.
14. PANUCCIO M. R., SORBONA A., PIZZO M., CACCO G. Cadmium adsorption on vermiculite, zeolite and pumice: Batch experimental studies. Journal of Environmental Management **90**, 364, **2009**.
15. ANIELAK A.M. The physicochemical properties of manganese dioxide-modified clinoptylolite. Przemysł Chemiczny **7**, 487, **2006**.
16. UFNALSKI Ionics equilibrium, algorithms, calculations and computer simulation. N-T, WNT, **2004**.
17. Patent application 369803 ANIELAK A.M.
18. ANIELAK A.M., SCHMIDT R. Adsorption of As(III) on natural Clinoptilolite Modified with Manganese. Polish Journal of Environmental Studies. **16**, (2A), 239, **2007**.
19. ANIELAK A.M., ŚWIDERSKA-DĄBROWSKA R., MAJEWSKI A. Removal of arsenic from underground waters on modified clinoptilolite. Environmental Engineering Taylor & Francis Group, London, UK, **2007**.
20. DAVIS A.P., BHATNAGAR V. Adsorption of cadmium and humic onto hematite. Chemosphere, **30**, (2) 243, **1995**.