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Short Communication

Immobilization of selected heavy metals in sewage sludge by natural zeolites

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Abstract

This contribution presents the possibility of application of natural sorbent (Transcarpathian clinoptylolite (KL)) for immobilization of selected heavy metals in the sewage sludge. The influence of ion-exchange parameters (e.g. time, amount of zeolite) were discussed. Process of immobilization was performed using a static method (Batch). It was found that best possible conditions for immobilization of heavy metal ions were as follows: zeolite fraction 0.7–1.0 mm, 5 h of shaking, zeolite/sewage sludge ratio 2/98.

Keywords: Heavy metals; Sewage sludge; Clinoptilolite; Ion exchange; Adsorption

1. Introduction

Sewage sludge formed during sewage treatment constitutes a serious economic problem. The composition of sewage sludge is heterogeneous and diverse. Sewage sludge may contain micro- and macroelements necessary to growth of plants and often xenobiotics (heavy metals and other persistent organic pollutants (POPs), such as phenols, polyaromatic hydrocarbons (PAHs)), pathogenic bacteria, parasites and their eggs. Consequently, it is understandable that these valuable qualities of sewage sludge should be used for practical purposes (Kosobucki et al., 2000).

Physicochemical properties of the sewage sludge can be improve by a addition of e.g. diatomaceous earth, artificial zeolites and natural sorbents (clinoptylolite). Heavy metals content in the sewage sludge decrease after addition of sorbents, this effect is typical for the immobilization of heavy metals on the zeolite surface and pores (Erdem et al., 2004; Sprynskyy et al., 2007).

In the wastewater treatment technology to remove heavy metals ions, adsorption methods and an ion exchange methods are applied successfully and effectively. From the price, physical, chemical, mechanical and hydrodynamic properties point of view natural zeolites are interesting materials to perform these processes. The Transcarpathian clinoptilolites (KL) (from the Ukraine) satisfy this conditions. Clinoptylolite is characterized by a high adsorbing capacity, molecular-sieve ability, considerable selectivity and the ion-exchange capacity as well as resistance to acids treatment and higher temperatures (Sprynskyy et al., 2007).

The selectivity of a sorbent is dependent on the ionic radius, the cation charge, structure of zeolite, distribution of active centers and the temperature of the process (Sprynskyy et al., 2005). The efficiency of the sorption process depends on the pure zeolite content in a mineral, the preparing processes of the mineral, accessibility of active centers, concentration of removed pollution, precipitation types, the hydration degree and the reaction of this suspension also (Lebedynets et al., 2004; Zorpas et al., 2000).

The application of ultrasonic is an alternative way for currently used chemical reagents and permits to apply sewage sludge in agriculture. Recent years show possibilities an ultrasonic engineering in a technological process of wastewater treatment and sewage management (Gronroos et al., 2005). In this work, ultrasonic energy was applied as factor

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increasing the immobilization process. The ultrasonic energy – due to their characteristics – can influence both, the structure and physicochemical proprieties of zeolite and finally can improve of the immobilization process of heavy metals from the sewage sludge.

The possibility of using natural zeolites to reduce the levels of selected heavy metals (Pb, Cr) present in sewage sludge from the municipal wastewater treatment plant in Toruń (Poland) has been a main aim of this study. Batch experiments have been conducted on Transcarpathian clinoptylolite (KL).

2. Experimental part

2.1. Instruments

During the work, the following parameters were determined: total organic carbon (TOC & SSM 5000 Shimadzu (Kyoto, Japan)); digital multimeter CX-732 (Elmetron, Zabrze, PL) was used for measurements of pH with the electrode pH ROSS SURE® – FLOW™ Orion (Beverly, USA); total Kjeldahl nitrogen (TKN) and total phosphorus (TP) determined by the spectrophtometric method using SQ 118 Merck (Darmstadt, Germany); chromium and lead concentrations were determined by flame atomic absorption spectroscopy (FAAS) using an AAnalyst 800 Perkin–Elmer (Shelton, USA) and potassium determined with the atomic emission spectroscopy Philips PU9100X (Cambridge, UK).

2.2. Reagents

The chemicals used in the experiments have been obtained as analytical – reagent grade materials from Sigma Aldrich (St. Louis, USA) and *Polskie Odczynniki Chemiczne (P.O.Ch.* Gliwice, Poland). Water used for the preparation of the solutions was taken from Millipore (Molsheim, France) water purification equipment.

2.3. Methodology

Ukrainian clinoptilolite was taken from the Sokirnice mine. This zeolite was applied earlier as the material to adsorption, for example NH_4^+ ions (Lebedynets et al., 2004; Zorpas et al., 2000). Immobilization of the selected heavy metals (Pb, Cr) was performed using static (Batch) method, with raw natural zeolite and natural zeolite, after ultrasonic conditioning.

The crumbled minerals was sieved and three fractions were isolated and used in experiments: 0.5–0.3 mm; 1.0–0.7 mm; 2.0–1.4 mm. Next, clinoptilolite was washed in distilled water, and finally was dried in temperature 383 K in 150 min.

Dewatered anaerobically stabilized primary sewage sludge was collected from the municipal wastewater treatment plant in Toruń (Poland). The part of a raw sample was dried in temperature 378 K and physicochemical analysis were performed. Rest of sewage sludge was mixed with clinoptylolite. Table 1 shows chemical properties of the clinoptylolite and sewage sludge.

Table 1
Physicochemical properties of sewage sludge, clinoptilolite and analysis methods

Parameters and elements	Sewage sludge	Clinoptilolite	Methods
Moisture, (%)	82.55 ± 2.03	1.50 ± 0.05	Drying in 378 K
Loss of ignition, (%)	38.82 ± 1.17	0.21 ± 0.02	Roasting in 823 K
pH (H_2O)	7.32 ± 0.60	5.05 ± 0.08	Potentiometric
Conductivity, (mS/cm)	1.2257 ± 0.40	0.243 ± 0.03[a]	Conductometric
TOC, (%)	31.77 ± 1.89	0.00	TOC Analyser
TKN, (%)	1.81 ± 0.14	19.10 ± 0.05	UV–vis
TP, (%)	2.32 ± 1.45	0.206 ± 0.02	UV–vis
C/N	17.55 ± 5.56	–	–
Ca (CaO), (%)	7.47 ± 0.20	1.55 ± 0.09	Titration
Mg (MgO), (%)	3.30 ± 0.15	1.47 ± 0.05	Titration
K (K_2O), (%)	0.82 ± 0.10	2.51 ± 0.14	FAES
Pb (mg/kg)	31.78 ± 6.82	42.4 ± 0.5	FAAS
Cd (mg/kg)	4.26 ± 1.15	21.8 ± 0.5	FAAS
Cr (mg/kg)	17.54 ± 1.23	24.9 ± 0.5	FAAS
Cu (mg/kg)	23.40 ± 6.50	–	FAAS
Ni (mg/kg)	138.32 ± 3.74	10.8 ± 0.5	FAAS

[a] μS/cm.

The immobilization process was performed using static variant. Two-component mixtures were prepared by a mixing in suitable volumetric ratio clinoptilolite (in extraction thimble) of selected particle sizes with dewatered sewage sludge (Table 2) and finally distilled water to slurry receipt, later mixtures were mechanical stirred.

The containers were mechanical stirred in a definite time (0.5; 1.0; 2.0; 5.0; 10.0; 24.0 h and 1 month, then the adsorbent with the extraction thimble were removed and

Table 2
Mixture compositions for immobilization process research

Fraction (mm)	Sample	Ratio (v/v)	
		Clinoptilolite (%)	Sewage sludge (%)
2.0–1.4	A	0	100.0
	B	0.5	99.5
	C	1.0	99.0
	D	2.0	98.0
	E	5.0	95.0
	F	10.0	90.0
1.0–0.7	A	0	100.0
	G	0.5	99.5
	H	1.0	99.0
	I	2.0	98.0
	J	5.0	95.0
	K	10.0	90.0
0.5–0.3	A	0	100.0
	L	0.5	99.5
	M	1.0	99.0
	N	2.0	98.0
	O	5.0	95.0
	P	10.0	90.0