

# Influence of clinoptilolite rock on chemical speciation of selected heavy metals in sewage sludge

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## Abstract

The chemical speciation of Cd, Cu, Pb, Cr and Ni in Torun municipal sewage sludge is investigated with addition of a natural sorbent (clinoptilolite rock). The total contents of the heavy metals in the sludge are substantially lower than the corresponding limits established by European or Polish legislation excepting nickel only. But the metals concentrations excepting lead exceed significantly the natural background (average contents in soils and in the Earth's crust) in dozens. Application of the sequential chemical extraction indicated that the metals in the sewage sludge are bound mainly (over 50%) in the residual fraction. The metals form the following order by parts of the mobile form: Ni > Cd ≫ Cr > Cu ≫ Pb. Addition of the clinoptilolite to the sludge leads to the metals contents fall in all four fractions of the sequential procedure. Concentrations of mobile forms of cadmium, chromium, copper and nickel decrease by 87, 64, 35 and 24%, respectively, as a result of addition of 9.09% of the clinoptilolite. The total decreases of the metals amount after 9.09% clinoptilolite addition to the sludge are around 11, 15, 25, 41 and 51% for copper, nickel, chromium, cadmium and lead, respectively.

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## 1. Introduction

Sewage sludge production is increasing impetuously from year to year in the whole world. The European Union countries have increased sewage sludge production by several percents (3–5%) per year [1,2]. In Poland, production of dry sludge from municipal wastewater treatment had grown from 359,819 tonnes in 2000 to 476,054 tonnes in 2004 [3,4]. Utilization of the mentioned sludge mass was distributed among storing on landfills (34%), agricultural use (14%), utilization for land recuperation (23%), compost production (6%), burning (0.2%) and some other utilization ways (23%) [4]. Obviously, constant increase of sludge production as well as accepted in many countries practice of disposal of the significant sludge mass in landfills may cause serious environmental problems. From this point of view, strategy development of communal wastewater sludge utilization as agricultural fertilizer seems to be prospective thanks

to significant contents of organic matters, nutrients, calcium and potassium [5,6]. Municipal sewage sludge contains usually nitrogen, P<sub>2</sub>O<sub>5</sub>, CaO and K<sub>2</sub>O in amounts (% d.m.) of 2.5–3.5, 1.5–2.5, 0.2–0.8 and to 0.5%, respectively [7].

At the same time, due to the content of heavy metals and pathogenic organisms, the sewage sludge may be considered as unfriendly to environment and therefore, the waste products require an appropriate pretreatment before utilization [8,9]. Application of sludge with high metal concentrations in agriculture may provide unwanted environmental impacts, such as phyto and microbial toxicity with food chain and groundwater contamination. Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health [8,10,11]. In that case, mobile species of heavy metals cause more serious pollution problems since they can be easily taken up by plants and enter the trophic chain or pollute the groundwaters. Cadmium is usually found to be the most extractable among the studied heavy metals [12]. Data about the association of heavy metals with geochemical phases of the soil can be obtained by sequential extraction allowing to detect the distribution of heavy metals in different fractions as

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well as to evaluate mobility and toxicity of metals in soils and sludge [13,14].

Ability of the metal to change chemical form into water-soluble compounds is conditioned by its species existing in the sludge. Parcelling and identification of the heavy metals species accumulated in the sludge with their following quantitative determination are necessary to evaluate the metals' potential environmental influence [15].

Speciation of heavy metals usually includes the fractionation of their total concentrations into soluble, ion exchangeable, acid extractable (carbonate bound), reducible (Fe–Mn oxides bound), oxidizable (organic bound) and residual forms. Sequential extraction of heavy metals from sewage sludge with determination of the present metal species is valuable for forecasting their mobility and bioavailability when sludge are applied to soils [16,17]. It should be noted that sequential chemical extraction may be also considered as a rather arbitrary way of separating different metal species due to inadequate selectivity application of the reagents used towards one particular species, and rare complete dissolution of species [18,19]. In spite of the fact that the method selectivity is sometimes imperfect, the sequential chemical extraction technique is the key one in obtaining data about chemical species of metals in soils and sludge. Different sequential extraction procedures are frequently used to evaluate heavy metal mobility in the environment [20,21]. The sequential procedure recommended by the BCR EUR 14763 EN Union is usually applied now within the European Union [14].

Environment-friendly utilization of sewage sludges evidently requires the appropriate treatment methods. Application of different additives to sewage sludge for immobilization of the excessive amounts of heavy metals is one of the ways for improvement of the physical and chemical properties of the substratum. Although various groups of microorganisms contributing in biosorption of heavy metals are usually the centre of attention as additives [22,23], mineral sorbents are also used to minimize the mobility of heavy metals in the compost [24–27]. Natural zeolites and the clinoptilolite in particular seem to be appropriate amendment materials for sewage sludge taking into account their sorption and exchangeable properties towards the heavy metals. Addition of the clinoptilolite rock to sewage sludge might change chemical speciation of heavy metals in composts and decrease their mobility and bioavailability.

The aim of the present contribution is to establish influence of addition of the natural sorbent (clinoptilolite) on the chemical speciation of heavy metals in sewage sludge samples using the sequential chemical extraction procedure.

## 2. Materials and methods

### 2.1. Sewage sludge sampling

Sludge samples were collected from the tanks after fermentation from municipal wastewater treatment plant in Torun (Poland), where, about 60,000–65,000 m<sup>3</sup> of municipal wastewaters are processed per day. The sludge volume after anaerobic digestion is 80–100 m<sup>3</sup> (per day) on sludge moistures about 80%. The sludge was sampled in polyethylene bags and stored in a

cool room without access of light. The sample moisture was determined by oven-drying at 105 °C for 24 h with the following homogenization in an agate mortar.

### 2.2. Clinoptilolite rock studied

Clinoptilolite rock from Sokyrynysya deposit (the Transcarpathian region, Ukraine) containing about 75% of clinoptilolite was used. Quartz, calcite, biotite, muscovite, chlorite, montmorillonite are the main associated minerals. The exchangeable cations are presented by Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> with prevalence of the last one. Their total contents are determined as 2.53 meq/g. Thermostability of the sorbent is from 923 to 973 K, static water-storage capacity and relative moisture are 9.03 and 10.19%, respectively [28].

### 2.3. Analytical methods

The dry mass of the sample was determined by drying in a dryer at 105 °C up to the constant mass. Losses of ignition were determined as difference between the crucible masses before and after drying in a muffle for 4 h at 550 °C. The pH value was measured in water extracts at sample–deionized water (w/w) as 1:5. The total nitrogen contents were analyzed using Kjeldahl method with the following distillation with water steam. Nitrogen content was evaluated on the basis of determination of ammonium ions concentration in the distillate (Nessler method). The total phosphorus amounts were analyzed by Kjeldahl method too and measured colorimetrically with ammonium molybdate and zinc(II) chloride in glycerine. The total organic carbon was determined using automatic analyzer TOC-5000 with the solid sample module SSM-5000 (Shimadzu). Potassium was evaluated using flame atomic emission spectrometry (FAES). Calcium and magnesium concentrations were determined by standard titration method (EDTA). The total heavy metals (Pb, Cd, Ni, Cr, Cu) contents were analyzed by flame atomic absorption spectrometry (FAAS) after digestion of the samples with aqua regia. Five grams of the sample of dry sludge was dissolved in 20 ml (in 2 ml by turns) of concentrated HNO<sub>3</sub>/HCl (1:3, v/v) mixture and kept for 24 h at 20 °C. The solution obtained was evaporated to dryness. The residue was dissolved in 30 ml of hot water and filtered. The filtrate was diluted in a calibrated flask to 50 ml and analyzed by FAAS (AAS AAnalyst 800 Perkin-Elmer, Shelton, USA).

### 2.4. Sequential extraction

Five compositions with the different zeolite contents 0.99% (100 mg); 2.91% (300 mg); 4.76% (500 mg); 6.54% (700 mg); 9.09% (1 g, w/w) were prepared for the sequential extraction of the sewage sludge with the zeolite addition by placing 10 g of the dried sludge and the transfer mass of the zeolite into flask. Fractionation of heavy metals in these compositions was studied using the sequential extraction procedure described by the BCR EUR 14763 EN Union [14]. Four metallic fractions were determined by means of the sequential extraction scheme: slight exchangeable metals, reducible metals, oxidizable metals

and residual metals. Separate extraction stages were conducted in the polypropylene flasks with the mixture shaking at 50 rpm. After 20 min centrifugation (5000 rpm), the aqueous extract was separated from the solid residue. This residue was washed with 20 cm<sup>3</sup> of distilled water, shaken for 25 min and centrifuged once more. Then the washing water was discarded. The metals extracts were filtrated using 0.45 mm cellulose nitrate membrane filters. The obtained solutions were kept in a cold store at 4 °C for analyzing and the residues were placed into flasks and dried at 105 °C. The heavy metals were divided into four fractions in the following steps:

**Fraction 1** (easy exchangeable and carbonate associated fraction): extraction with 200 ml of 0.11 M CH<sub>3</sub>COOH (pH 7) shaking for 16 h at 20–22 °C.

**Fraction 2** (reducible fraction or Fe and Mn oxide associated fraction): extraction with 200 ml of 0.5 M NH<sub>2</sub>OH HCl (acidified to pH 2 with HNO<sub>3</sub>) shaking for 16 h at 20–22 °C.

**Fraction 3** (oxidizable fraction or fraction bound to organic matter): extraction by 10 ml of 30% H<sub>2</sub>O<sub>2</sub> with shaking for 1 h at 20–23 °C. Digestion was continued by heating the mixture at 85 °C in a water bath for 1 h and followed by cooling. Then 10 ml of H<sub>2</sub>O<sub>2</sub> was added and the mixture was heated for 1 h at 85 °C. After that, 2 ml of 3 M NH<sub>4</sub>OAc in 20% HNO<sub>3</sub> (v/v) was added with shaking for 16 h at 20–22 °C.

**Fraction 4** (residual fraction): extraction with 6 ml H<sub>2</sub>O and 45 ml 6 M HCl and 15 ml 14 M HNO<sub>3</sub> with shaking for 16 h at 20–22 °C.

### 3. Results and discussion

#### 3.1. Sludge properties

As one can see in Table 1, the significant amounts of such nutrients as nitrogen, phosphorus, potassium and organic matter in the municipal sewage sludge in question allow to consider it as a good fertilizing material. But high contents of toxic heavy

Table 1  
Selected physical and chemical properties of the sewage sludge

Selected characteristics	Values ( <i>n</i> = 3)	Limit (86/278/EEC) <sup>a</sup>	
		In sludge	In soil
Moisture (% d.w.)	82.40 ± 2.57		
Ash (% d.w.)	34.90 ± 1.02		
pH	6.10 ± 0.02		
TOC (% d.w.)	20.55 ± 0.01		
Total P (P <sub>2</sub> O <sub>5</sub> % d.w.)	2.32 ± 1.45		
Total N (% d.w.)	3.16 ± 0.13		
Mg (MgO % d.w.)	3.72 ± 0.12		
Ca (CaO % d.w.)	8.63 ± 0.54		
K (K <sub>2</sub> O % d.w.)	0.82 ± 0.17		
Pb (mg/kg d.w.)	38.12 ± 1.12	750–1200	50–300
Cd (mg/kg d.w.)	13.02 ± 0.96	20–40	1–3
Cr (mg/kg d.w.)	303.40 ± 6.77	–	–
Cu (mg/kg d.w.)	240.40 ± 1.18	1000–1750	50–140
Ni (mg/kg d.w.)	402.80 ± 5.38	300–400	30–75

<sup>a</sup> Council Directive 86/278/EEC on the protection of the environment, and particular of the soil, when sewage sludge is used in agriculture.

metals and cadmium especially may make the sludge usage in agricultural soil improvement dangerous. The low pH value of the sludge would contribute to increase of the heavy metals solubility and hence their availability for uptake by plants or transport to groundwater.

Contents of lead, copper and cadmium in the sludge are considerably lower than the corresponding limits accepted by EU (Directive 86/278/EEC). Only nickel concentration is evaluated about the level defined by the Directive. But the determined metals concentrations in the sludge exceed significantly the established limits for soils. Contents of cadmium and nickel almost by 10 times exceed limits.

Comparison between the heavy metals concentrations determined in the studied sludge and with their average contents in soils and the Earth's crust allows to evaluate measure of the sewage sludge enrichment by the metals relatively to the natural background. As shown in Table 2, cadmium amount in the sludge is more than 10 times more than its average contents in soils and the Earth's crust. The same measure of the studied substrate enrichment is observed for nickel and copper, but concentrations of lead and chromium are not so significant.

Therefore, utilization of the sludge as an agricultural fertilizer without a preliminary treatment for the heavy metals extraction or immobilization may be rather hazardous for environment. It should be noted that although knowledge of heavy metals speciation in sludge is necessary for metal-contaminated waste application, estimation of the geochemical background of an application site is also very important for evaluation of environmental dangerous.

#### 3.2. Distribution of the metals species in the sewage sludge

Data on the metals species distribution in four fractions of the sewage sludge without the zeolite addition obtained as a result of the sequential extraction procedure is shown in Fig. 1. As the figure indicates, the metals differ from one another by quantitative grouping in separate chemical species in the sludge. This grouping is specific for each metal.

The metals formed the following orders by relative contents of the species:

Cu (residual >> oxidizable >> reducible > exchangeable);

Cr (residual >> oxidizable > exchangeable > reducible);

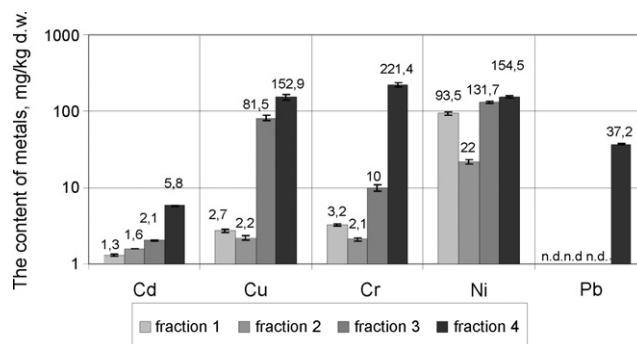


Fig. 1. The distribution of the metal species in the sewage sludge.

Table 2

Comparison of the heavy metals contents in the studied sludge and the average contents in soils and the Earth's crust

Contents of heavy metals (mg/kg d.w.)	The studied sludge	Soils, average [29]	Farming soils, average [30]	The Earth's crust, average [31]
Pb	38	10	36	12
Cd	13	0.5	0.44	0.2
Cr	303	200	25	100
Cu	240	20	15	55
Ni	403	40	15	75

Pb (residual);

Ni (residual > oxidizable > exchangeable > reducible);

Cd (residual > oxidizable > reducible > exchangeable).

The similar metals speciation in the sewage sludge was established by Walter et al. [12] excepting lead. As a result of the sequential extraction application Alvarez et al. [32] described that metals distribution was different for each fraction and the highest levels of copper and chromium were found in the oxidizable fraction, the highest contents of nickel were distributed among the exchangeable and the reducible fractions, the predominant part of lead was accumulated in the residual fraction. Although, our study results correspond well to the results reported by Alvarez et al. [32] concerning lead and nickel, the main parts of copper and chromium in our case were concentrated in the residual fractions with the significant amount of copper in the oxidizable fraction. It is clear that differences in the metals speciation as well as in their total concentrations are conditioned by a number of factors with the municipal industry specification in the first place.

The metals concentrations as a percentage of the four fractions sum are shown in Fig. 2. The results indicate the highest mobility of nickel and cadmium in the analyzed sludge. The shares of their mobile forms (Fractions 1 and 2) are 29 and 27%, respectively. The mobile parts of lead, copper and chromium do not exceed 3%. The highest contents of cadmium and nickel in exchangeable fraction were also reported by Kazi et al. [19]. According to their parts in the mobile forms the studied metals form the following order: Ni > Cd  $\gg$  Cr > Cu  $\gg$  Pb. All metals are concentrated mainly in the residual fraction. The parts of nickel, cadmium, copper and chromium in the residual fraction

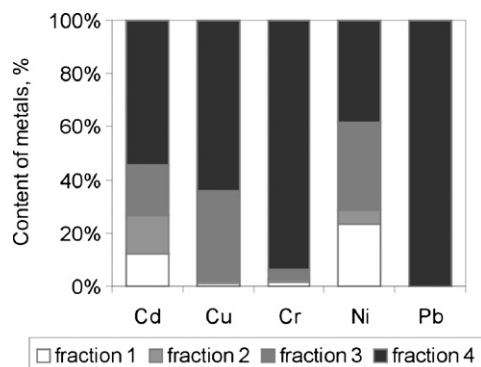


Fig. 2. The heavy metals percentage in the individual fractions of the sequential extraction.

are 39, 54, 64 and 94% of the total metal extracted amounts, respectively, while lead is connected almost completely with the residual fraction. The dominant accumulation of lead in this fraction agrees well with the other authors results [12,33]. Although, the mobile forms of the metals usually seem to be more dangerous for environment, their low concentrations, in forms bound with oxidizable or residual fractions, may also be a source for the metals discharge into environmental objects.

Furthermore, one should realize that the sequential extraction procedure is not absolutely selective concerning the metal forms. For instance, not only weakly bound ion exchangeable forms or forms associated with calcium carbonate, but also metals forms bound with some organic functional groups or iron hydroxides and oxides may be extracted using 0.11 M acetic acid. Application of BCR sequential extraction procedure for metals from individual mineral phases of seawater sediment demonstrated that the majority of metals released by CH<sub>3</sub>COOH were associated with calcium carbonate, kaolinite, potassium-feldspar and ferrihydrite [18]. At the same time, this extractant is considered to be able to dissolve carbonates without attacking organic matter, Fe and Mn oxides and aluminosilicates [33]. Whalley and Grant [18] reported that the recovered metals were extracted by hydroxylamine hydrochloride during the third stage of the procedure from montmorillonite and MnO<sub>2</sub> too. The residual fraction is also defined by Kazi et al. [19] as “pseudo residual”. It may be suggested that metals bound with some organic compounds occurring in strong sorbed forms in mineral matter are also associated with the residual fraction. In the same cases, relative contents of metals in the different fractions may vary depending on sludge type, ratios between sludge and extractant solutions, contact time, reagent concentration, intensity of mixing, pH value, experiment temperature, etc.

We suppose that heavy metals of the residual fraction may be immobilized in the sulfide minerals in the sludge. It seems to be especially probable for cadmium, lead and copper. Metal sulfides could form as a result of sulfate reduction in a sludge fermentation process. The heavy metals may also be strongly connected in the clay minerals structures or in organic matters as hydroxides.

### 3.3. Influence of the clinoptilolite rock addition to the sewage sludge on heavy metals speciation

Results of the sequential analysis of the sewage sludge with the natural zeolite demonstrate that the heavy metals contents decrease in all four fraction due to the sorbent addition



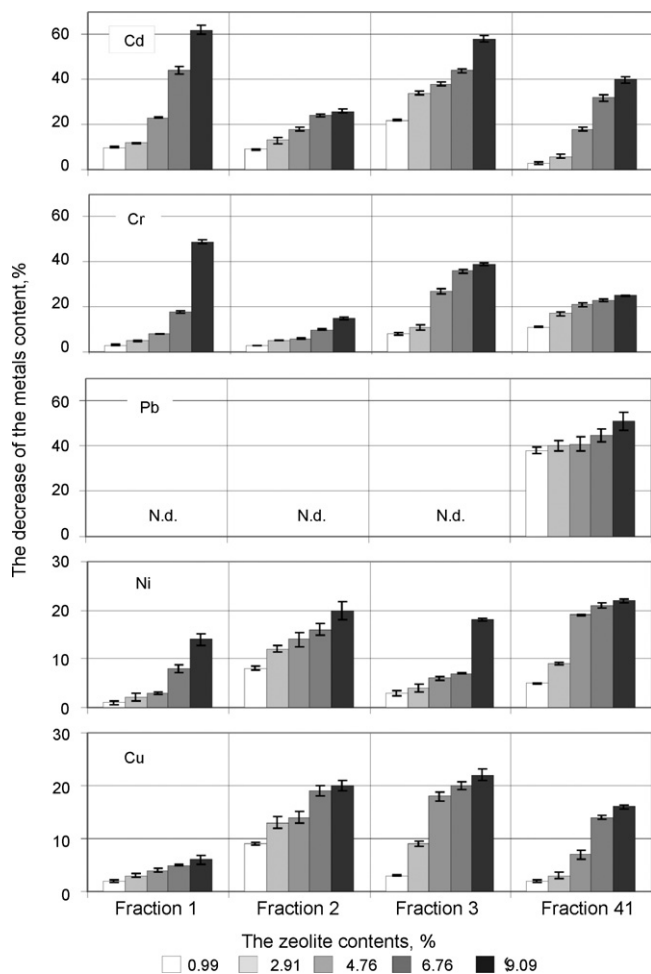


Fig. 3. Efficiency of the clinoptilolite addition for decrease of the heavy metals contents in the different fractions of the sludge.

(Fig. 3). Among mobile forms, the most significant decrease was observed for cadmium. As a result of 9.09% (w/w) of the zeolite application cadmium amounts were reduced by 62, 25, 58 and 40% in the first, the second, the third and the fourth fractions, respectively. The total fall of the metal concentration comparing with its total concentration without the zeolite application was 41%. Taking into account, the high toxicity and the significant content of cadmium in the sludge, the obtained results are encouraging with regard to the use of clinoptilolite rock as an effective additive for this metal immobilization.

Chromium content has also decreased most after the zeolite addition in the first fraction (by 49%). In the following three fractions, there was a fall of chromium concentrations by 14, 40 and 25%, respectively. Copper was characterized by somewhat weaker binding with the zeolite and by more even fall by fractions. Copper contents decreased by 15, 20, 20 and 22% for the studied fractions, respectively. The least fall of the mobile forms and of ion exchangeable form in particular (6%) was observed for nickel. The metal amounts of the other fractions lowered by 16–20%. The zeolite addition had no influence on lead speciation in the sludge. All lead con-

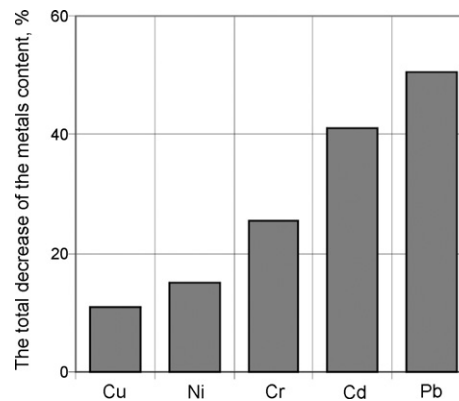


Fig. 4. The total decrease of the metals concentrations as a result of the sludge treatment process.

tinued to remain in the residual fraction with decrease of its concentration by 51%. Wong and Selvam [27] reported that lime addition to sewage sludge had also no influence on lead speciation, but caused increase of its content in the residual fraction.

Addition of 9.09% of the zeolite (w/w) lead to the most significant decrease of the total lead content (50.6%) evaluated in four fractions. The total concentrations of the other metals (Cd, Cr, Ni and Cu) fell by 41, 25, 15 and 11%, respectively (Fig. 4). Wong et al. [23] found that bioleaching of heavy metals from anaerobically digested sewage sludge using  $\text{FeS}_2$  caused corresponding decrease of chromium, copper, lead and nickel contents by 12, 41, 32 and 38%, respectively. Hsiao and Lo [24] applied lime, cement and sodium silicate as additives for leaching of heavy metals from sewage sludge by bench processes. The best results for chromium and lead concentration decreases (by 39 and 41%) were obtained in lime-treated sludge (10% lime), whereas in lime–sodium silicate (20 g lime plus 15 ml sodium silicate per 200 g sewage sludges) treated sludge for copper (52.5%). Study of biological leaching of metals (Mn, Al, Zn, Cu and Ti) in an anaerobic sewage sludge using microorganism *Thiobacillus ferrooxidans* demonstrated 24% efficiency for copper [34].

Composting of sewage sludge with natural zeolite (clinoptilolite) Zorpas et al. [26] observed that the zeolite (25%, w/w) can take up 100% of Cd, 32% of Cu, 40% of Ni, 18% of Cr and 17% of Pb. The metals formed the following order by immobilization degree: Cd > Cu > Ni > Cr > Pb. We have obtained somewhat other order: Pb > Cd > Cr > Ni > Cu. Taking under consideration that we added two and a half as less amount of the clinoptilolite, the relative contents of the immobilized metals were comparable in both studies. The presented data differ considerably from results of Wong and Selvam [27] for lead and to a smaller degree for cadmium. Obviously these differences are conditioned mainly by specific chemical composition of sewage sludge in question.

Decrease of the metals concentrations in all four extracts of the sequential procedure due to the zeolite addition to the sewage sludge seems to be interesting result of the present study. A negative balance between the metal contents in the sludge with the

zeolite addition and without the same was obtained. On one hand, this fact substantiates definition of the residual fraction of the used procedure only as “pseudo residual fraction” and on the other hand, it may testify that heavy metals are immobilized by the considered clinoptilolite to a large measure in firmly bonded adsorbed forms. Such bonded form of the metals (lead and cadmium especially) is caused by their location in adsorption process in inner crystalline space of the clinoptilolite. It is apparent that the metal bonds in the zeolite porous structure are significantly more solid than in sewage sludge. It may also be assumed that at separation of the clinoptilolite from the sewage sludge after composting the metals concentrations in some extraction, fractions could be lesser than in the conducted experiment.

#### 4. Conclusions

1. Generally total contents of the heavy metals in the sewage sludge from Torun municipal wastewater treatment plant are substantially lower than the corresponding limits established by European or Poland legislation excepting nickel only. The metals concentrations excepting lead exceed significantly the natural background (average contents in soils and in the Earth's crust) in dozens.
2. Sewage sludge is the strong industrial accumulator of heavy metals and may be a source of environmental contamination, but huge volumes of communal sewage sludge with high content of fertilizing compounds may be sufficiently used for agricultural purposes. However such use of sewage sludge requires lowering of contents of heavy metals and other toxic components to undangerous levels.
3. The application of the sequential chemical extraction indicated that metals in sewage sludge were bound mainly (over 50%) in the residual fraction. Nickel distributed evenly in residual, oxidizable and exchangeable fractions was the only exception. Nickel (27%) and cadmium (29%) were characterized by the highest concentrations in the mobile reducible and exchangeable fractions. The metals form the following order by parts of the mobile form: Ni > Cd >> Cr > Cu >> Pb. The significant parts of nickel, cadmium and copper (33, 19 and 34%, respectively) are also bonded with organic matter (oxidizable fraction).
4. Addition of the natural clinoptilolite to the sewage sludge led to the metals contents fall in all four fractions of the sequential procedure. Concentrations of mobile forms of cadmium, chromium, copper and nickel decreased by 87, 64, 35 and 24%, respectively, as a result of the addition of 9.09% of the clinoptilolite.
5. The total decreases of the metals after 9.09% clinoptilolite addition to the sludge were around 11, 15, 25, 41 and 51% for copper, nickel, chromium, cadmium and lead, respectively.
6. The clinoptilolite rock may be considered as a suitable material to heavy metals immobilization by their bond into firmly sorbed forms of the pseudo residual fraction.

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#### References

- [1] J.E. Hall, F. Dalimier, Waste management—sewage sludge: survey of sludge production, treatment, quality and disposal in the EC. EC Reference No.: B4-3040/014156/92, Report No.: 3646, 1994.
- [2] J. Werther, T. Ogada, J. Werther, T. Ogada, Sewage sludge combustion, *Prog. Energy. Combust. Sci.* 25 (1999) 55–116.
- [3] Information and statistical papers, Environment Protection, Main Statistical Government, Warsaw, 2001 (in Polish).
- [4] Information and statistical papers, Environment Protection, Main Statistical Government, Warsaw, 2004 (in Polish).
- [5] A.L. Shober, C. Stehouwer, E. Macneal, On-farm assessment of biosolids effects on soil and crop tissue quality, *J. Environ. Qual.* 32 (2003) 1873–1880.
- [6] F. Caravaca, C. Garcia, M.T. Hernandez, A. Roldan, Aggregate stability changes after organic amendment and mycorrhizal inoculation in the afforestation of semiarid site with *Pinus halepensis*, *Appl. Soil. Ecol.* 19 (2002) 199–208.
- [7] J. Siuta, G. Wasiak, Composting waste products and compost use, IOŚ, Warsaw, 2000 (in Polish).
- [8] A. Bhogal, F.A. Nicholson, B.J. Chambers, M.A. Shepherd, Effects of past sewage sludge additions on heavy metal availability in light textured soils: implications for crop yields and metal uptakes, *Environ. Pollut.* 121 (2003) 413–423.
- [9] A.M. Chaudri, C.M.G. Allain, V.L. Barbosa-Jefferson, F.A. Nicholson, B.J. Chambers, S.P. McGrath, A study of the impacts of Zn and Cu on two rhizobial species in soils of a long-term field experiment, *Plant Soil* 221 (2000) 167–179.
- [10] M.B. McBride, B.K. Richards, T. Steenhuis, J.J. Russo, S. Sauve, Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application, *Soil Sci.* 162 (1997) 487–500.
- [11] C.D. Stalikas, A.Ch. Mantalovas, G.A. Pilidis, Multielement concentration in vegetable species grown in two typical agricultural areas of Greece, *Sci. Total Environ.* 206 (1997) 17–24.
- [12] I. Walter, F. Martanez, V. Cala, Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses, *Environ. Pollut.* 139 (2006) 507–514.
- [13] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 231–235.
- [14] Ph. Quevauviller, A. Ure, H. Muntau, B. Griepink, Conclusions of the workshop: single and sequential extraction in sediments and soils, *J. Environ. Anal. Chem.* 51 (1993) 129–134.
- [15] A. Dube, R. Zbytniewski, T. Kowalkowski, E. Cukrowska, B. Buszewski, Adsorption and Migration of Heavy Metals in Soil, *Pol. J. Environ. Stud.* 1 (2001) 1–10.
- [16] P. Flyhammar, Use of sequential extraction of heavy metals on anaerobically municipal solid waste, *Sci. Total Environ.* 212 (1998) 203–215.
- [17] D.C. Su, J.W. Wong, Chemical speciation and phytoavailability of Zn, Cu, Ni and Cd in soil amended with fly ash-stabilized sewage sludge, *Environ. Int.* 1060 (2003) 1–6.
- [18] C. Whalley, A. Grant, Assessment of phase selectivity of the European Community Bureau of Reference (BCR) sequential extraction procedure for metals in sediment, *Anal. Chem. Acta* 291 (1994) 287–295.
- [19] T.G. Kazi, M.K. Jamali, G.H. Kazi, M.B. Arain, H.I. Afridi, A. Siddiqui, Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test, *Anal. Bioanal. Chem.* 383 (2005) 297–304.
- [20] J. Scancar, R. Milacic, M. Strazar, O. Burica, P. Bukovec, Environmentally safe sewage sludge disposal: The impact of liming on the behaviour of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, *J. Environ. Monit.* 3 (2001) 226–231.

- [21] M. Pueyo, G. Rauret, D. Lack, M. Yli-Halla, H. Muntau, Ph. Quevauviller, J.F. Lopez-Sanchez, Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following collaboratively tested and optimised three-step sequential extraction procedure, *J Environ. Monit.* 3 (2001) 243–250.
- [22] H.W. Ryu, H.S. Moon, E.Y. Lee, K.S. Cho, H. Choi, Leaching Characteristics of Heavy Metals from Sewage Sludge by *Acidithiobacillus thiooxidans* MET, *J. Environ. Qual.* 32 (2003) 751–759.
- [23] W.C. Wong, L. Xiang, X.Y. Gu, L.X. Zhou, Bioleaching of heavy metals from anaerobically digested sewage sludge using  $\text{FeS}_2$  as an energy source, *Chemosphere* 55 (2004) 101–107.
- [24] P.C. Hsiau, S.L. Lo, Extractabilities of heavy metals in chemically-fixed sewage sludges, *J. Hazard. Mater.* 58 (1998) 73–82.
- [25] L.R. Nissen, N.W. Lepp, R. Edwards, Synthetic zeolites as amendments for sewage sludge-based compost, *Chemosphere* 41 (2000) 265–269.
- [26] A.A. Zorpas, D. Arapoglou, K. Panagiotis, Waste paper and clinoptilolite as a bulking material with dewatered anaerobically stabilized primary sewage sludge (DASPSS) for compost production, *Waste Management* 23 (2003) 27–35.
- [27] J.W.C. Wong, A. Selvam, Speciation of heavy metals during co-composting of sewage sludge with lime, *Chemosphere* 63 (2006) 980–986.
- [28] F.D. Ovcharenko, N.Ye. Shcherbatyuk, Yu.I. Tarasevich, V.A. Suprychyov, Sorption properties of the Transcarpathian clinoptilolite, *Clinoptilolite, Mentseniereba, Tbilisi* (1977) 136–140 (in Russian).
- [29] D.P. Maluga, Biochemical method of search of ore fields, AS SSSR, 1963 (in Russian).
- [30] H. Poletschny, Sewage sludge—useful or dangerous for agriculture. In: *Entsorgungspraxis-Spezial, Klarschlamm Entsorgungspraxis-Spezial, Klarschlamm* (1988) 10–13 (in German).
- [31] S.R. Teylor, Trace element abundances and the chondritic Earth model, *Geochimica et Cosmochimica Acta* 28 (1964) 1989–1998.
- [32] E.A. Alvarez, M.C. Mochon, J.C.J. Sanchez, M.T. Rodriguez, Heavy metal extractable forms in sludge from wastewater treatment plants, *Chemosphere* 47 (2002) 765–775.
- [33] S.C. Wong, X.D. Li, G. Zhang, S.H. Qi, Y.S. Min, Heavy metals in agricultural soils of the Pearl River Delta, *Environ. Pollut.* 119 (2002) 33–44.
- [34] A.T. Lombardi, O. Garcia Jr., Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by *Thiobacillus ferrooxidans* and its effect on metal partitioning, *Water Research* 36 (2002) 3193–3202.