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Changes of metal forms in sewage sludge after EDTA washing

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ABSTRACT

Heavy metals in sewage sludge can be classified as difficult solid waste with potential hazards for environment. This report examined how an aqueous solution of EDTA (ethylenediaminetetraacetic acid) washing changes selected heavy metals' (Zn, Cu, Cd, Ni, Pb) fractionation in sewage sludge. The analyzed sludge was dried and homogenized sewage sludge was obtained from a municipal treatment plant. The samples of sewage sludge were extracted with 0.1 M EDTA solution for 24 h. Primary as well as extracted sewage sludge was examined for the total content of heavy metals and speciation of mentioned heavy metals using BCR sequential extraction procedure. Analyzed sewage sludge samples were quite significantly contaminated with heavy metals. The total content of zinc, copper, cadmium, nickel, and lead in initial sewage sludge was equal to: 2306.5, 263.7, 9.0, 118.0, and 117.0 mg kg^{-1} dM, respectively. After EDTA extraction: 1514.5, 253.5, 7.5, 83.0, and 58.0 mg kg^{-1} dM, respectively. In sewage sludge before extraction, the percentage of metals in fractions I (exchangeable and carbonates), II (Fe and Mn oxides), III (organic matter and sulfides), and IV (residual) was: for Zn 21, 47, 31, 1%, for Cu 0, 0, 99, 1%, Cd 0, 32, 68,0%, Ni 28, 22, 42, 8%, and Pb 6, 3, 34, 57%, respectively. In sludge after extraction, the percentage of metals in fractions was for Zn 17, 47, 33, 2%, Cu 0, 0, 98, 2%, Cd 0, 30, 70, 0%, Ni 13, 20, 46, 21%, and Pb 4, 5, 24, 67%, respectively. EDTA washing resulted in decreasing of nickel and lead percentage in mobile fractions and an increase in fractions strongly bounded to sludge matrix. The effect was most evident for Ni. Efficiency of EDTA solution for zinc, copper, and cadmium fractionation changes was practically negligible. EDTA extraction influenced the content of metals in municipal sewage sludge fractions. The process caused a decrease in each fraction; however, a strong chelating agent removed metals mostly from a dominant fraction.

Keywords: Heavy metals; Sewage sludge; EDTA extraction; Sequential analysis

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1. Introduction

Heavy metals are widely widespread all over the word. Rapid urbanization, industrial, agricultural, and other anthropogenic activity cause accumulation of heavy metals' compounds in particular environmental elements. Sewage sludge being the final waste material of communal and industrial wastewater treatment processes usually contains trace metals, sometimes on relatively high level. The mentioned metals are toxic for humans, animals, and plants; and after consumption by animals, they enter the food chain where man is the last link [1]. Thus, the utilization of sewage sludge would be restricted by the presence of heavy metals compounds. Direct disposal or agricultural application of hazardous sewage sludge containing heavy metals may cause serious soil and underground water pollution problems. The environmental impact of sewage sludge contamination depends not only on the total amount of metals but mainly on their mobility and bioavailability which are influenced by their leaching and interactions with all components of the ecosystem [2,3]. The total metal concentration does not provide sufficient information concerning its potential hazardous effects on environment since the mobility and eco-toxicity of heavy metals depend strongly on their specific chemical forms or binding. To chemical fractionation of metals in environmental samples, the sequential extraction techniques are commonly used [4]. The procedure is based on the extraction of metals from solid matrix with increasingly aggressive solvents. Chemicals for particular step are selected to extract proper metal groups with detailed bounding to sewage sludge. Many sequential extraction procedures have been developed to evaluate heavy metals' behavior in the environment. The method proposed by Tessier et al. [5] was primarily used for the purpose. This method was modified many times and as a result of the studies, the procedure recommended by the Standards, Measurements and Testing Programme of the European Commission (formerly the Community Bureau of Reference) is usually applied now within the European Union, under the name BCR procedure [6]. BCR procedure determines the following groups of metals: I—exchangeable and carbonate bound, II—associated with hydrated Fe and Mn oxides, III—associated with organic matter and sulfides, and IV—residual [7]. Metals detected in two former fractions are believed to be mobile and bioavailable. The bounds for metals in two latter fractions are much stronger and metals are considered to be immobile and inaccessible.

Environmentally friendly utilization of sewage sludge requires the appropriate treatment method. Application of different techniques applied in order to remove excessive amounts of heavy metals from sewage sludge is one of the ways to obtain environmentally nonhazardous material. Chemical extraction of trace metals from sewage sludge might change the speciation of metals in solid matrix and decrease their mobility and bioavailability. Recently, different chemicals have been regarded as effective agents for metals extraction [8], but EDTA (ethylenediaminetetraacetic acid) seem to be very useful. It presents a high level of complexing capacity, stability during the extraction process, and high extraction efficiency for most metals [2,9].

The purpose of the present studies was to establish the influence of EDTA washing on the distribution of heavy metals forms in sewage sludge using the BCR sequential extraction procedure, which may provide some useful knowledge concerning the changes in potential hazards of heavy metals for the environment.

2. Materials and methods

All chemicals used in this study were of analytical grade and were used without any further purification. Solutions were prepared using demineralized water. All tests were performed in triplicates with a standard deviation less than 5%. Statistical calculations were based on the confidence level equal or higher than 95%.

Municipal sewage sludge was taken from municipal treatment plant in southern Poland. Samples used in the study were in the form of dried granulate. The analyzed sewage sludge was homogenized in an agate mortar and passed through a sieve with 2 mm meshes. Then sludge samples were kept in a plastic container for further studies. Moisture, dry matter, pH, ignition residual, and losses were measured following the standard methods [10]. The basic characteristics of the sewage sludge used for the experiments are given in Table 1.

Table 1
Physicochemical parameters of analyzed sewage sludge

Parameter	Value
pH	7.4
Moisture, %	5.5
Dry matter, g kg^{-1}	945
Ignition residual, g kg^{-1}	560
Ignition losses, g kg^{-1}	385

Removal of heavy metals from sewage sludge was carried out by extracting 5 g sewage sludge samples with 50 mL portion of 0.1 M EDTA, an aqueous solution. The samples were shaken for 24 h, and then extracts were filtered through the filter paper and rinsed with five 50 mL portions of demineralized water. Finally, sewage sludge was air-dried under laboratory conditions (the temperature was about 20℃), homogenized, and dried at 105℃ in a dryer.

Samples of sewage sludge before and after EDTA extraction were examined for the total content of selected heavy metals (Zn, Cu, Cd, Ni, and Pb) after concentrated HNO_3 and HCl (1 + 3—aqua regia) digestion. The results are summarized in Table 3.

Sequential extraction was performed for both types of sewage sludge: EDTA extracted and nonextracted. The four-step BCR procedure was used in order to determine different forms of heavy metals in the sludge [7,11]. Each step was carried out in a 50 mL test tube into which 0.500 g of sludge was placed. The scheme of the procedure is shown in Table 2. All obtained extracts were stored at 4℃ in plastic containers for further analyses.

The contents of heavy metals after digestion as well as sequential analysis were detected by an atomic absorption spectrometry method, using a spectrometer novAA 400, Analytic Jena, Germany.

3. Results and discussion

3.1. Physicochemical characteristics of sewage sludge

The main physicochemical properties of studied sewage sludge are presented in Table 1.

The material was characterized by pH equal to 7.4 and small hydration at the level of 5.6%. Sewage sludge contained 945 g kg^{-1} of dry matter. Dry matter of sludge comprised about 41% of organic matter given as ignition losses.

The total contents of Zn, Cu, Ni, Cd, and Pb in sludge are shown in Table 3. In general, the sludge sample contained the highest amount of zinc (2306.5 mg kg^{-1}dm). Copper, nickel, and lead contents were significant but relatively lower (264.0, 118.0, 117.0 mg kg^{-1}dm, respectively). Cadmium content was the lowest and practically negligible (9.0 mg kg^{-1}dm).

Washing of sewage sludge with an aqueous EDTA solution decreased the total amount of the above-mentioned metals and caused the material to contain 1514.5, 253.0, 83.0, 7.5, and 58.0 mg kg^{-1}dm of Zn, Cu, Ni, Cd, and Pb, respectively. Significant changes were observed for zinc, lead, and nickel. Contents of copper and cadmium were only slightly decreased. Similar to the initial material, the highest content was observed for Zn, lower for Cu, Ni, and Pb, and really low for Cd. Calculated efficiencies of metals' removal during the extraction with 0.1 M EDTA were 34% for Zn, 4% for Cu, 30% for Ni, 17% for Cd, and 50% for Pb. EDTA is known to be a useful agent for heavy metals extraction from sewage sludge as well as other solid matrix [12,13]. Selected metals removal from municipal sewage sludge was in the order: Pb > Zn ≈ Ni > Cd > Cu.

3.2. Sequential extraction of metals form studied sewage sludge

The content of analyzed metals in particular fractions of sewage sludge, before and after EDTA extraction, is summarized in Table 4. The biggest difference in content was observed for zinc in Fe and Mn oxides fraction and exchangeable one. The differences for other studied metals were not much significant. In the case of copper, the highest change was observed for organic matter and sulfides fraction, for nickel in exchangeable and carbonate bounded fractions, and for lead in organic matter and sulfides as well as in a residual fraction. The differences detected for nickel content were insignificant.

Table 2
BCR sequential extraction scheme per 1 g of sludge dry matter

Fraction	Chemicals	Temp. (℃)	Time (h)	Metal form
I	40 mL 0.11 M CH_3COOH	20	16	Exchangeable and carbonate bound
II	40 mL 0.5 M $NH_2OH{\cdot}HCl$, pH 2	20	16	Fe and Mn hydrated oxides bound
III	10 mL 8.8 H_2O_2, pH 2–3	20	1	Organic matter and sulfides bound
		85	1	
	10 mL 8.8 M H_2O_2, pH 2–3	85	1	
	50 mL 1 M CH_3COONH_4, pH 2–3	20	16	
IV	2 mL HNO3 (65%) 6 mL HCl (37%)	120	2	Residual

Table 3
Total content of selected heavy metals in sewage sludge before and after EDTA washing (mg kg^{-1} dm)

Metal	Before washing	After washing
Zn	2306.5	1514.5
Cu	264.0	253.5
Ni	118.0	83.0
Cd	9.0	7.5
Pb	117.0	58.0

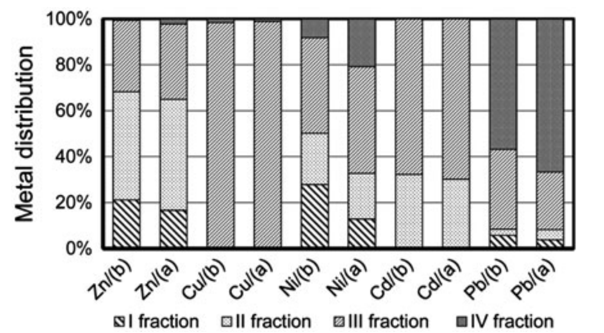

Fig. 1. Distribution of selected heavy metals over sewage sludge fractions before (b) and after (a) extraction with 0.1 M EDTA.

The obtained results indicated that EDTA was a strong chelating agent extracting metals even from dominant fractions.

Fig. 1 shows the percentage distribution of analyzed heavy metals over municipal sewage sludge fractions before and after EDTA washing. The metals were classified into four chemical forms as exchangeable and carbonates bound, Fe–Mn oxides bound, organic matter and sulfides bound as well as residual fractions. The metal solubility and bioavailability decreased gradually from the exchangeable fraction to the residual fraction [5].

The sequential extraction revealed that the highest concentration of zinc in the sludge before EDTA extraction was found in the Fe and Mn hydrated oxides fraction (about 47%), next in the fraction of organic matter and sulfides (31%), and finally in the exchangeable fraction (21%). Zinc content in a residual fraction was very low and was equal to 1%.

EDTA extraction caused a decrease in the total zinc concentration and slight enrichment of zinc content in fractions of iron and manganese oxides (48%), organic matter and sulfides (33%), and residual (2%). Distribution of zinc in an exchangeable fraction decreased and was equal to 17%. Strong attraction of zinc to Fe and Mn oxides was previously reported in the literature [14–16].

In the case of copper and cadmium, the process of chemical extraction did not significantly influence metal distribution in sewage sludge. In the initial sludge, a dominant phase for copper was organic matter and sulfide fraction (99%), and residual (only 1%). After EDTA washing, similar distribution was observed: 98% and 2% for organic matter and sulfides, and residual fraction, respectively. Such domination of copper in organic and sulfides fraction have been pointed out by other authors [4,17].

Cadmium content in analyzed sewage sludge was very low and the changes in its speciation during EDTA extraction were, similarly to copper and zinc, insignificant. Initial distribution of Cd was: 68% organic matter and sulfides, and 32% Fe and Mn oxides, and after extraction 70% and 30%, respectively. Similar distribution for cadmium was reported in various papers [7,14].

The change in metal fractionation in the sewage sludge after EDTA extraction was obvious for nickel and lead. Before extraction of the sewage sludge, nickel was dominantly present in the organic matter and sulfides fraction (42%) and at a similar level in exchangeable and carbonate as well as in Fe and Mn oxides fractions: 28% and 22%, respectively. Similar distribution was confirmed by other studies [7,15]. The smallest percentage was detected in residual fraction, 8%. After extraction process, metal distribution over the organic matter and sulfides fraction, exchangeable and carbonate fraction, Fe and Mn oxides fraction, and residual fraction was

Table 4
The content of metals in municipal sewage sludge fractions before (b) and after (a) 0.1 M EDTA extraction (mg kg^{-1}dm)

	Zn		Cu		Ni		Cd		Pb	
Fraction	b	a	b	a	b	a	b	a	b	a
I	448,5	235,7	0	0	32	9,5	0	0	6,3	2,1
II	998,7	689	0	0	25,7	14,7	2	1,6	2,8	2,5
III	656	466,3	244	213,3	48	34,4	4,2	3,7	38	14
IV	15,5	32,3	4,2	2,4	9,4	15,4	0	0	62	37,2

changed and was equal to 46, 13, 20, and 21%, respectively. The rise in the content of nickel in residual fraction is the highest and the smaller one is observed for organic matter and sulfides fraction. A slight decrease was noted in Fe and Mn oxides fraction. The percentage of nickel in exchangeable and carbonate bound form decreased significantly and reached 13%.

In primary sewage sludge, lead was found to be principally distributed in the residual (57%) and organic matter and sulfides (35%) fractions. Distribution of Pb over mobile fractions: exchangeable and carbonate bound as well as Fe and Mn oxides was 6 and 2%, respectively. The dominant accumulation of lead in a residual fraction was also confirmed by other authors' results [6,11]. After EDTA extraction, 67% of lead was present in the residual fraction and 25% in the organic matter and sulfides fraction, whereas 4% in exchangeable and carbonate as well as Fe and Mn oxides fractions. Distribution over chemically stable and biologically inactive residual fraction increased, forming more stable and environmentally safe material.

Extraction of heavy metals from sewage sludge caused decreasing in portion of Ni and Pb in mobile fractions of sewage sludge (exchangeable and Fe—Mn oxides) and their stabilization in resistant fractions: residual as well as the organic matter and sulfides fraction. This effect was the most obvious in the case of nickel. For Cu and Cd, the changes in metal distribution over sewage sludge fractions were negligible. Those mentioned metals were present in sewage sludge generally in nonmobile forms before extraction.

The change in metal distribution in the sewage sludge as a result of EDTA extraction caused some improvement concerning environmental safety of sewage sludge. Heavy metals bounded to last fractions should be practically insoluble and their migration among the elements of environment is not observed.

4. Conclusions

The total content and fractionation of selected heavy metals were studied in samples of municipal sewage sludge. Analyzed sewage sludge contained a different concentration of zinc, copper, nickel, cadmium, and lead. The highest concentration was detected for zinc, much lower for copper, nickel, and lead and insignificant one for cadmium. The distribution of them among sewage sludge fractions was different. Distribution pattern of Zn and Ni was found to be similar;metals were detected in the most mobile fractions. Zinc was in exchangeable and Fe and Mn oxides fractions, and nickel was in organic matter and sulfides fractions in the most, however, significant amounts were detected in both exchangeable and Fe and Mn oxides fractions. On the other hand, all copper, cadmium, and lead were distributed in the most resistant fractions. Cu was present mainly in the organic matter and sulfides fraction and Cd was found in organic matter and Fe and Mn oxides fractions. In the case of Pb, the highest percentage was detected in a residual fraction as well as in organic matter and sulfides fractions.

The process of EDTA extraction involving heavy metals' removal from sewage sludge caused a decrease in the total amount of all analyzed metals, but the efficiency of removal varied widely and changed in the order: for $Pb > Zn \approx Ni > Cd > Cu$.

EDTA extracted washed metals from each fraction, especially from the dominant fraction of particular metals. EDTA washing influenced the distribution of metal between chemical fractions of sewage sludge, but in a different way for different metals. Distributions for zinc, copper, and cadmium change only slightly and they were quite similar before and after extraction. For nickel and lead, the changes were more evident. The percentage of analyzed heavy metals in mobile fractions decreased and increased in immobile fractions, especially in a residual fraction. The presence of heavy metals in a residual fraction is regarded as safe for the environment. Therefore, EDTA extraction of sewage sludge produced the material which is characterized by a lower amount of heavy metals which are in environmentally more stable forms of metals.

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