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BIOAVAILABILITY OF HEAVY METALS IN THE MUNICIPAL SEWAGE SLUDGE

BIODOSTĘPNOŚĆ METALI CIĘŻKICH W KOMUNALNYCH OSADACH ŚCIEKOWYCH

Abstract: Usually chemical form of metal is considered as the most important factor influencing its mobility and bioavailability. In order to determine forms of heavy metals in sewage sludge the speciation analysis is used. The analysis is based on sequential extraction of metals with increasingly aggressive solvents. Reagents chosen for each step extract metal groups with specified properties. The four steps extraction (BCR) gained wide recognition. It extracts metals in following groups: I – exchangeable and associated with carbonates, II – associated with hydrated iron oxides and manganese oxides, III – associated with organic matter, IV – metals that can be found in the residual fraction. Metals found in the first fraction (exchangeable and carbonate) are believed to be mobile. The release of those metals can occur with change in pH or in ionic composition of liquid. Metals bound to hydrated forms of iron and manganese oxides and to organic matter are also available. The fraction of iron and manganese oxides is sensitive to redox changes, whereas metals bound to organic matter are released during mineralization of the substrate. Metals considered to be immobilized are those that can be found only in the residue, which dissolves only in concentrated mineral acids. The speciation analysis of heavy metals in stabilized sewage sludge gives information important for determination of the rate at which heavy metals pass into soil solution and also, as a consequence, their uptake by plants. This information is especially important when considering agricultural usage of sludge.

The purpose of presented studies was compare the amount of metals potentially available for plants with their content in chemicals forms detected with sequential extraction procedure and evaluation the hypothesis that content of metals in some fractions could be equivalent to their bioavailability

The report presents results of BCR sequential extraction procedure of metals (Zn, Cu, Ni, Cd, Pb) from sewage sludge from two WWTP and single extraction with 1 M HCl used for determination of bioavailable forms of metals.

Our studies stated the presence of copper and cadmium generally in the organic fraction, nickel and lead in the residual fraction and zinc both in the organic as well as in the iron and manganese oxyhydroxides fraction. However determined bioavailability significantly differed from the metals content in the fractions regarded as mobile.

Content of zinc in the I and II fraction was on the level 48–51% of the total amount and bioavailability 86–92%. Concentration of copper and nickel in the mobile fractions (I and II) was 2–4% and 22–33%,

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respectively and in bioavailable form 49–63% and 25–41%, respectively. Lead available content in sludge was in the same scheme like copper and nickel (21–22 and 51–62%, respectively).

Bioavailable content detected for analysed metals covered I and II mobile fractions but for Zn, Cu and Ni also significant part of III – potentially immobile fraction. Additionally for Pb even a part of IV – assumed as practically immobile and inactive fraction. Obtained data indicated that speciation forms of metal are not always equivalent to their bioavailability.

Keywords: heavy metals, municipal sewage sludge, bioavailability, four steps extraction BCR procedure, BCR sequential extraction

1. Introduction

The anthropogenic human activities causes production of excess sewage sludge, which proper disposal become more and more urgent. The high content of organic matter and nutrient elements indicates natural application of sludge as fertilizer or regenerator for soil. However, sewage sludge being the final waste material of communal and industrial wastewater treatment processes usually contains transition metals (heavy metals), sometimes on relatively high level and the disposal of such material could result in secondary environmental pollution and is a growing environment problem. 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 [1–3].

Sewage sludge used in nature and agricultural purposes, besides sanitary requirements, have to characterize for acceptable content of heavy metals. Usually, in the stabilized and dewatered sewage sludge the highest content of zinc is observed. Relatively great content of copper and in some cases high concentration of chromium and lead are determined [4–7]. Transfer of heavy metals from sewage sludge to the food chain is done by plants cultivated on soil fertilized with these sludge. Although trace quantities of some heavy metals (as microelements) are necessary in the process of the metabolism of plants and animals, they are able accumulate to phytotoxic levels in organisms and the excessive amounts of them could have the toxic action and stand danger both for plants, animals, as well as human [8–12].

The mobility and bioavailability of heavy metals are determined by the chemical form of them. Detection of bioavailable fraction and evaluation migration possibilities of heavy metals associated with solid phase is done with single extraction process. However to obtain information allowing the recognition of forms of metal presence, their origin sources, the way of association to solid matrix components, possibilities of the mobilization and transport the sequential multistep extraction procedures are performed [13]. Sequential extraction procedure is realized with increasingly aggressive solutions of substances. For each step there is selected reagent possible to eluate the group of metals compounds with strictly known properties. Procedure initially proposed by Tessier [14] was modified and as a result of work of many groups of researches in framework of Standards, Measurements and Testing Programme of the European Union Commission [15] a shortened, three – step extraction was accepted. The procedure is known as BCR procedure (from the earlier name of this commission: Community Bureau of Reference).

BCR procedure determines the following groups of metals: I – acid soluble, II – reducible (associated with hydrated Fe and Mn oxides), III – oxidizable (associated with organic matter and sulfides) and IV – residual [16–18]. 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 potentially immobile and inaccessible. The residual fraction is considered to be chemically stable and biologically inactive. Metals found in this fraction are not harmful to the aquatic ecosystem. The most mobile, meaning easily dissolved in the soil solution and assimilated by plants, are considered to be acid soluble metals.

Actually there are not uniform procedures for determination of heavy metals bioavailability in sewage sludge used in agriculture. For that purpose, extraction techniques developed for soil are being adopted [18]. The used single step extraction with acids, neutral salts or chelating agents could indicate possibility of transfer of heavy metal from sludge to soil solution and finally to plant, animal and human organisms.

The purpose of presented studies was compare the amount of metals potentially available for plants with their content in chemicals forms detected with sequential extraction procedure and evaluation the hypothesis that content of metals in some fractions could be equivalent to their bioavailability.

2. Material and methods

The analysed material was final, dewatered sewage sludge after hydraulic press station. Sewage sludge samples were taken from two waste water treatment plants in central Poland in autumn 2016. Wastewater treatment plant located in A, with capacity of 9200 m^3 per day, is being conducted by means of activated sludge method, with the use of nitrification, denitrification and biological dephosphatation processes. Wastewater treatment plant located in B, with capacity of 20000 m^3 per day, is being conducted by means of activated sludge with nitrification, denitrification and chemical dephosphatation.

Properties of sludge samples, like hydration, total solids, volatile solids concentration (gravimetric method) were determined.

The samples were initially air-dried under laboratory condition (temperature about 20^{o}C), next dried at 105^{o}C in dryer. Then sludge samples were homogenized in an agate mortar and passed through a stainless sieve with 0.4 mm diameter meshes and kept in plastic container for further analyses. Three different samples of the same sludge were prepared for the analyses. Presented results are the mean values from triplicate measurements.

Sequential extraction was carried out according to the BCR procedure in order to quantify the chemical forms of heavy metals in the sludge samples – Table 1 [16].

Table 1

Sequential extraction procedure, BCR, per 1g of dry matter of sewage sludge

Step	Reagent	Temperature [°C]	Time [h]	Fraction	Nominal target phase(s)
1	40 cm^3 0.11 M CH_3COOH	22	16	Exchangeable, acid soluble	Soil solution, exchangeable cations, carbonates
2	40 cm^3 0.5 M $NH_2OH \cdot HCl$ (pH 2)	22	16	Reducible	Iron and manganese oxyhydroxides
3	10 cm^3 8.8 M H_2O_2 (pH 2–3)	22	1	Oxidizable	Organic matter and sulfides
	—	85	1		
	10 cm^3 8.8 M H_2O_2 (pH 2–3)	85	1		
	50 cm^3 1 M CH_3COONH_4	22	16		
4	2 cm^3 HNO_3 (65%) 6 cm^3 HCl (37%)	120	2	Residual	Silicate minerals

Total content of selected heavy metals (Zn, Cu, Ni, Cd and Pb) was studied after sample mineralization at 120°C with mixture of concentrated acids: HNO_3 and HCl (1 + 3 – aqua regia) for 2 hours.

The bioavailable metal content was analyzed according to procedure proposed for soil [20] with single extraction with 1 M HCl for 1 hour at 20°C.

The contents of studied metals after mineralization, sequential analysis as well as single step extraction with 1 M HCl were detected by an atomic absorption spectrometry method (spectrometer novAA 400, Analytic Jena, Germany).

3. Results and discussion

Analysed sewage sludge samples characterized by hydration and organic matter content equal to 81% and 78%, respectively, for the sewage sludge collected in wastewater treatment plant located in A and 85% and 62%, respectively for the sludge from wastewater treatment plant located in B.

Content of heavy metals (average value) and their percentage distribution over the fractions of sewage sludge (A) and (B) as well as potential bioavailability are presented in Table 2.

Analysed sewage sludge, on account of total heavy metals content (zinc, copper, nickel, lead and cadmium) was in agreement with legislative requirements for sewage sludge used in agriculture, for land reclamation to agricultural and non-agricultural purposes. Despite the total content of heavy metal is useful detector of environmental contamination, it does not provide enough information about potential environmental impact. More detailed data is obtained from single or multi – step extraction procedures indicating mobility and bioavailability of heavy metals [19, 21, 22].

Table 2

Chemical fraction, total and bioavailable content of heavy metals in sewage sludge A and B

Fraction	Zn		Cu		Ni		Cd		Pb	
	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg /kg]	[%]	[mg/kg]	[%]
Sewage sludge A										
I	102.4 ± 0.9	13.3	2.1 ± 0.2	1.8	4.5 ± 0.2	11.7	0.3 ± 0.1	9.4	5.1 ± 0.2	11.9
II	291.7 ± 1.7	37.8	2.2 ± 0.1	1.9	4.0 ± 0.1	10.4	0.9 ± 0.2	28.1	4.3 ± 0.1	10.1
III	354.1 ± 2.6	45.9	101.6 ± 0.7	89.2	7.9 ± 0.2	20.5	1.4 ± 0.1	43.8	12.3 ± 0.3	28.7
IV	22.7 ± 0.4	3.0	8.0 ± 0.3	7.0	22.1 ± 0.4	57.4	0.6 ± 0.1	18.8	21.1 ± 0.5	49.3
Sum	770.9	100.0	113.9	100.0	38.5	100.0	3.2	100.0	42.7	100.0
BAV	665.9 ± 3.8	86.4	71.8 ± 0.5	63.0	9.6 ± 0.2	24.9	1.3 ± 0.3	40.6	21.9 ± 0.5	51.3
Total	876.0 ± 4.2	—	123.7 ± 1.1	—	34.8 ± 0.7	—	3.0 ± 0.3	—	36.0 ± 0.3	—
Sewage sludge B										
I	229.8 ± 2.1	12.9	1.8 ± 0.1	0.9	10.0 ± 0.3	22.9	1.0 ± 0.1	17.2	10.4 ± 0.2	10.3
II	622.5 ± 3.3	34.8	2.1 ± 0.1	1.0	4.6 ± 0.2	10.5	0.8 ± 0.1	13.8	9.8 ± 0.2	9.8
III	827.6 ± 4.4	46.3	181.5 ± 1.5	86.9	10.1 ± 0.2	23.1	2.9 ± 0.2	50.0	9.2 ± 0.2	9.2
IV	108.3 ± 0.8	6.0	23.5 ± 0.4	11.2	19.0 ± 0.3	43.5	1.1 ± 0.1	19.0	71.0 ± 0.6	70.7
Sum	1788.2	100.0	208.9	100.0	43.7	100.0	5.8	100.0	100.4	100.0
BAV	1645.7 ± 5.1	92.0	102.3 ± 1.1	49.0	18.0 ± 0.3	41.2	2.2 ± 0.2	37.9	62.8 ± 0.4	62.5
Total	2044.0 ± 6.9	—	195.8 ± 1.7	—	39.1 ± 0.5	—	4.7 ± 0.2	—	85.0 ± 0.6	—

I, II, III, IV – chemical fraction according to BCR procedure; BAV – bioavailable content of metal.

The content of zinc in both sewage sludge was the highest: 876 and 2044 mg/kg d.m. (dry matter) for A and B samples, respectively. The mentioned metal was the mostly bounded to III and II fraction. Organic matter and sulfides as well as Fe and Mn hydroxides fractions were previously reported as typical for zinc [23].

Copper, lead and nickel total contents were significantly lower and in sewage sludge A were equal to 124, 36 and 35 mg/kg d.m., respectively and in sewage sludge B: 196, 85 and 39 mg/kg d.m. Higher contents of copper were detected in organic matter and sulfides fraction, lead and nickel in residual fraction.

Cadmium characterized the lowest total content on the level: 3.0 and 4.7 mg/kg d.m. for A and B samples, respectively. The highest content of cadmium was detected in Fe and Mn hydroxides fraction. Similar affinity of metals to particular fraction was confirmed by another authors [24, 25].

Dominant role of sewage sludge organic-sulfide fraction in binding zinc, copper, and cadmium, was confirmed by Fuentes et al [26], Stylianou et al [27], Hanay et al [28]. In case of zinc large amount of this metal was found also in iron and manganese oxide fraction, in case of nickel and cadmium – in sludge exchangeable-carbonate fraction. Strong zinc affiliation by iron and manganese oxides in sewage sludge was pointed out by Walter et al [29], Chen et al [24], Jamali et al [25] whereas high concentration of nickel in sludge exchangeable-carbonate fraction was stated by Hanay et al [28], Lasheen and Ammar [30].

The analyses of the sludge indicated low concentration of zinc and cooper in the insoluble fraction (3–11%). The content of lead and nickel in this fraction was 49–71%; 44–57%, respectively. The residual fraction is considered to be chemically stable and biologically inactive. Metals that were found in this fraction are not harmful to aquatic and soil ecosystems. On the other hand in the exchangeable-carbonate fraction, most mobile fraction of metals, the highest concentration of nickel (12–23%) was found. The presence of high concentration of nickel in the mobile fraction indicates that when the outer conditions like: equilibrium in the sorption-desorption system change or pH decrease, the release of metal ions into the soil-water environment can occur. For other metals: zinc, copper, cadmium and lead, their content in the exchangeable-carbonate fraction was 13%; 1–2%; 9–17%; 10–12%, respectively.

Content of metals with distribution over particular sludge fractions with comparison to their potential bioavailability for both types of analyzed sludge samples are presented on Figs. 1–5.

Zinc content in sewage sludge A as well as sludge B corresponded to mobile I and II fraction and additionally to almost all III fraction, commonly called potentially immobile (Fig. 1). Content of zinc in the I and II fraction was on the level 48–51% of the total amount and bioavailability 86–92%. The report of Rajmund and Bozym [19] demonstrated that acidic 1M solution of HCl was the strong but not selective extrahent. It eluate metals bounded to exchangeable, carbonate, iron and manganese oxides as well as with organic matter. The results indicated that mobility and bioavailability could not be considered as parallel and similar parameters. In the last years a number of studies have been done to project and validate methods of measure or predict content of bioavailable forms of metals. Depending on the type of methods used, strength of

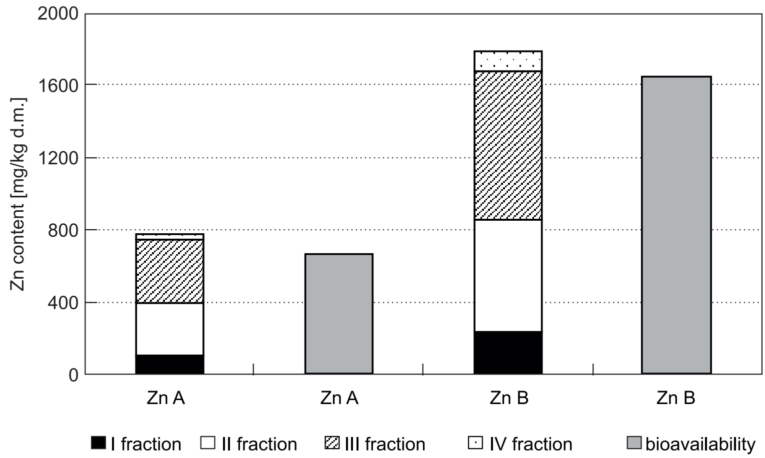

Fig. 1. Chemical fractions and bioavailable content of Zn in analysed sewage sludge samples A and B

extraction solution, variable results could be obtained for selected metal with specific properties. Generally for mobile metals, solutions of neutral salts are recommended for determination of bioavailable forms. For relatively low mobile metals, strongly bounded to solid matrix, extraction with strong acid or chelating agent solution should be selected. For routine analysis usually simple extraction with neutral salt or strong acid is presently proposed [22].

Similar behaviour was observed for copper (Fig. 2) and nickel (Fig. 3). Potentially available for plants content of metals covered not only mobile I and II fraction, but also practically immobile III fraction of metals in sludge A and B. Concentration of copper and nickel in the mobile fractions (I and II) was 2–4% and 22–33%, respectively and in bioavailable form 49–63% and 25–41%, respectively.

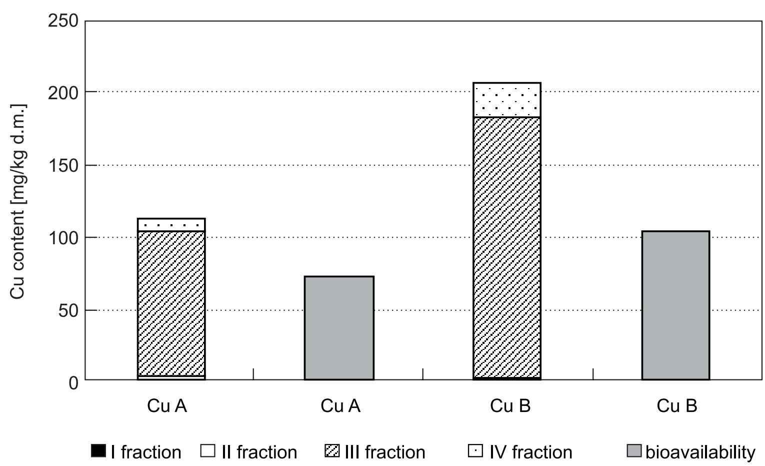

Fig. 2. Chemical fractions and bioavailable content of Cu in analysed sewage sludge samples A and B

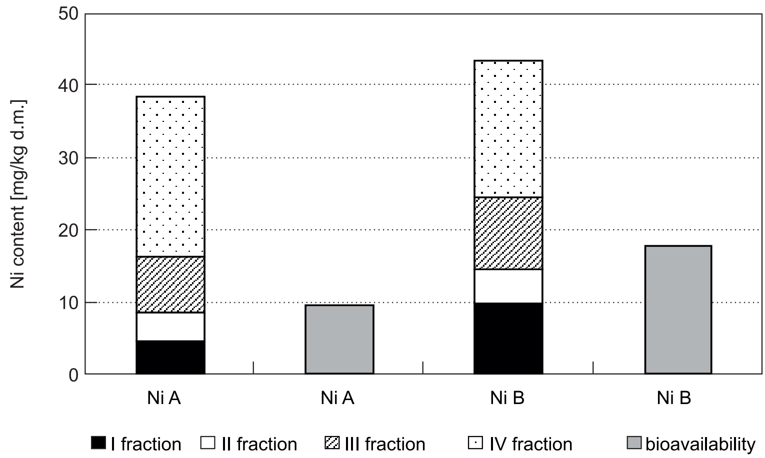

Fig. 3. Chemical fractions and bioavailable content of Ni in analysed sewage sludge samples A and B

Lead available content in sludge A was in the same scheme like copper and nickel (22 and 51%, respectively). A little bit different behaviour of Pb was in sludge sample B (Fig. 4). Its bioavailability covered all I, II and III fraction and significant part of residual fraction, usually considered as immobile and inactive environmentally fraction.

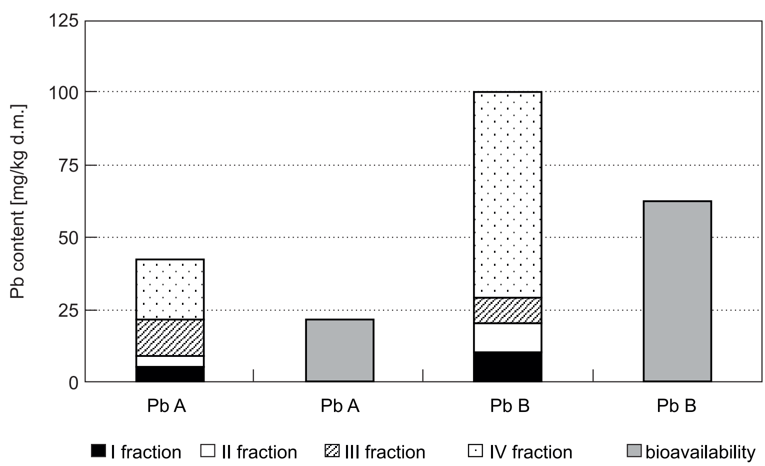

Fig. 4. Chemical fractions and bioavailable content of Pb in analysed sewage sludge samples A and B

Cadmium behaviour was in agreement with typical approach that first two fraction of metals in sewage sludge are equivalent to metal bioavailability (Fig. 5). Content of metal assumed as bioavailable covered in practise only I and II fraction (31–41%).

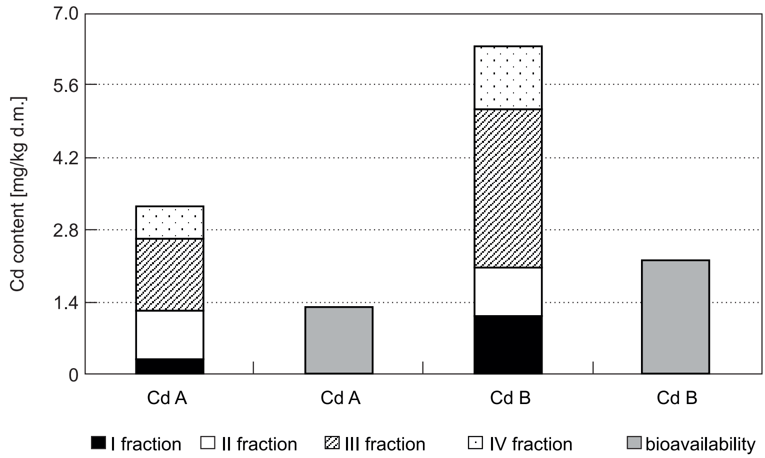

Fig. 5. Chemical fractions and bioavailable content of Cd in analysed sewage sludge samples A and B

4. Conclusions

Our studies stated the presence of copper and cadmium generally in the organic fraction, nickel and lead in the residual fraction and zinc both in the organic as well as in the iron and manganese oxyhydroxides fraction. It was detected that heavy metals mobility (content in the exchangeable, carbonate and iron and manganese oxyhydroxides fractions) changed in the order: Zn > Cd > Ni > Pb > Cu. However determined bioavailability significantly differed from the metals content in the fractions regarded as mobile. Results obtained after washing of metals with 1M HCl allowed the ordering of metals with decreasing bioavailability: Zn > Pb ~ Cu > Cd > Ni. The extraction of metals from sewage sludge samples with mentioned above solution was in the range from 25 to 92%. Similar values of bioavailable content of metals were reported previously [19].

It could be concluded that metals mobility, bioavailability and content in given fractions detected in sequential extraction procedure are not equivalent and mentioned parameters have to be analysed separately.

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Abstrakt: O mobilności i biodostępności metali ciężkich decyduje przede wszystkim forma chemiczna ich występowania. W celu określenia form metali wykonuje się analizę specjacyjną opartą na ekstrakcji sekwencyjnej, która polega na stopniowym wydzielaniu metali z osadów roztworami o wzrastającej agresywności. Do każdego etapu dobiera się reagenty, które są zdolne wyekstrahować grupę połączeń metali o znanych właściwościach. Szerokie uznanie zdobyła czterostopniowa ekstrakcja (BCR), której zastosowanie umożliwia wydzielenie metali: I – wymienialnych i związanych z węglanami, II – związanych z uwodnionymi tlenkami żelaza i manganu, III – z materią organiczną oraz IV – pozostałych. Za mobilne uważa się metale występujące w pierwszej frakcji (wymiennej i węglanowej), z której ich uwalnianie następuje pod wpływem zmiany pH, składu jonowego cieczy. Także metale związane z uwodnionymi tlenkami żelaza i manganu oraz z materią organiczną są dostępne. Frakcja tlenków żelaza i manganu jest wrażliwa na zmiany potencjału redox, natomiast metale związane z substancją organiczną są uwalniane w procesie mineralizacji tego substratu. Za metale unieruchomione uważa się te, które są zgromadzone w pozostałości rozpuszczalnej dopiero w stężonych kwasach mineralnych. Wykonanie analizy specjacyjnej metali ciężkich w ustabilizowanych osadach ściekowych jest szczególnie istotne przy rolniczym wykorzystaniu osadów, pozwala bowiem ocenić szybkość przechodzenia metali do roztworu glebowego, a w efekcie ich pobranie przez rośliny.

Celem przedstawionych badań było porównanie ilości metali potencjalnie dostępnych dla roślin z ich zawartością w formach chemicznych oznaczonych w sekwencyjnej procedurze ekstrakcyjnej i ocena hipotezy, że zawartość metali w niektórych frakcjach może być równoważna biodostępności.

W celu oznaczenia form metali ciężkich (Zn, Cu, Ni, Cd, Pb) w osadach ściekowych pobranych z dwóch mechaniczno-biologicznych oczyszczalni ścieków zastosowano ekstrakcję sekwencyjną BCR, natomiast do oznaczenia biodostępnych form metali pojedynczą ekstrakcję 1 M HCl.

Badania potwierdziły występowanie miedzi i kadmu głównie we frakcji organicznej, niklu i ołowiu we frakcji pozostałościowej, natomiast cynku zarówno we frakcji oragnicznej, jak i tlenków żelaza i manganu.

Natomiast oceniona biodostępność znacznie się różniła od występowania metali we frakcjach uważanych za mobilne.

Zawartość cynku we frakcji I i II wynosiła 48–51% całkowitej ilości, natomiast biodostępność 86–92%. Zawartość miedzi, niklu i ołowiu w formach mobilnych (I i II) wyniosła odpowiednio 2–4%; 22–33% i 21–22%, natomiast w biodostępnych odpowiednio 49–63%; 25–41% i 51–62%.

Biodostępna zawartość analizowanych metali została oznaczona we frakcji I i II, ale dla Zn, Cu i Ni, również w znaczącej ilości we frakcji III – potencjalnie mobilnej. W przypadku Pb biodostępność dotyczyła także części frakcji IV – przyjętej jako praktycznie niemobilnej. Uzyskane dane wskazywały, że formy chemiczne metali uznane jako mobilne nie są zawsze równoznaczne formom biodostępnym.

Słowa kluczowe: metale ciężkie, komunalne osady ściekowe, biodostępność, czterostopniowa procedura ekstrakcji BCR, ekstrakcja sekwencyjna BCR, BCR