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EFFECT OF ULTRASOUND ON EXTRACTION OF HEAVY METALS FROM SEWAGE SLUDGE IN THE CONTEXT OF A POTENTIAL ECOLOGICAL RISK ASSESSMENT

Abstract

The aim of the research was to investigate the effect of ultrasound waves on the recovery of heavy metals (HMs) from sewage sludge. For this purpose, we conducted a three-step sequential extraction process proposed by the Community Bureau of Reference (BCR; presently the Standards, Measurements and Testing Programme). In the experiment use was made of certified reference material ERM-CC144 SEWAGE SLUDGE (Joint Research Centre; JRC). The content of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in certified material was determined by atomic absorption spectrometry using the Avio 200 ICP-OES apparatus (PerkinElmer Inc.). To reduce the sequential extraction time, ultrasound treatment was used instead of long hours of shaking. Sonication was conducted in an ultrasonic bath (Sonic-5; Polsonic). The sonication time was set at 20, 40 and

70 minutes. The frequency, power and temperature during the ultrasound treatment were kept constant. The recovery values of heavy metals obtained by the modified sequential extraction method were at similar levels to those achieved by the conventional one. Moreover, it has also been shown that after only 20 minutes of sonication, the recovery values can be obtained similarly as for the conventional method. In order to check whether the ultrasound waves have a significant impact on the distribution of heavy metals in the chemical fractions of sewage sludge, the percentage share for each element was calculated and the potential ecological risk analysis was conducted. This was possible thanks to the fact that the material used for production of ERM-CC144 (JRC) is sewage sludge of domestic origin. The obtained results revealed that ultrasound treatment does not significantly influence the distribution of analysed heavy metals in the chemical fractions of sewage sludge, with one exception, i.e., Zn. The assessment of the ecological risk was performed using Risk Assessment Code (RAC) index, which includes the content of metals in the most mobile fraction, i.e., bound to carbonates. The calculated values of RAC indicated that Zn posed the highest ecological risk. However, it can be also confirmed that the application of ultrasound treatment in the sequential extraction procedure does not have a significant impact on the interpretation of results of the ecological risk assessment. What is more, it confirms the legitimacy of using the discussed modification in the sequential extraction of heavy metals from sewage sludge.

Keywords: sewage sludge, heavy metals, sequential extraction, ultrasound, ecological risk

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WPŁYW ULTRADŹWIĘKÓW NA EKSTRAKCJĘ METALI CIĘŻKICH Z OSADÓW ŚCIEKOWYCH W KONTEKŚCIE OCENY POTENCJALNEGO RYZYKA EKOLOGICZNEGO

Abstrakt

Celem pracy było zbadanie wpływu oddziaływania fali ultradźwiękowych na wielkość odzysku metali ciężkich z osadów ściekowych. W tym celu przeprowadzono proces trzystopniowej ekstrakcji sekwencyjnej zaproponowanej przez Community Bureau of Reference (BCR; aktualnie Standards, Measurements and Testing Programme). W badaniach wykorzystano certyfikowany materiał odniesienia ERM-CC144 SEWAGE SLUDGE (Joint Research Centre; JRC). Zawartość metali ciężkich (Cd, Cr, Cu, Ni, Pb, Zn) oznaczono przy użyciu spektrometru absorpcji atomowej Avio 200 ICP-OES (PerkinElmer Inc.). Aby skrócić czas ekstrakcji sekwencyjnej, w miejsce wielogodzinnego wytrząsania zastosowano obróbkę ultradźwiękami. Proces nadźwiękawiania prowadzono w łaźni ultradźwiękowej (Sonic-5; Polsonic). Czas nadźwiękawiania wynosił: 20, 40 i 70 minut. Częstotliwość, moc oraz temperaturę podczas obróbki ultradźwiękowej utrzymywano na stałym poziomie. Wartości odzysków dla metali ciężkich uzyskane z zastosowaniem zmodyfikowanej metody ekstrakcji sekwencyjnej były zbliżone do tych otrzymanych dzięki metodzie konwencjonalnej. Ponadto wykazano również, że już po 20 minutach nadźwiękawiania można uzyskać wartości odzysków jak dla metody konwencjonalnej. W celu zbadania, czy fale ultradźwiękowe wpływają istotnie na zawartość metali ciężkich w poszczególnych frakcjach chemicznych osadów ściekowych, obliczono udział procentowy dla każdego z pierwiastków, a następnie przeprowadzono ocenę potencjalnego ryzyka ekologicznego. Ocena ta była możliwa dzięki temu, że w skład materiału ERM-CC144 (JRC) wchodzą osady ściekowe pochodzenia komunalnego. Uzyskane wyniki

wskazują, że obróbka ultradźwiękowa nie wpływa istotnie na udział analizowanych metali ciężkich we frakcjach chemicznych osadów ściekowych, za wyjątkiem cynku. Ocenę ryzyka ekologicznego przeprowadzono przy pomocy wskaźnika Risk Assessment Code (RAC), który uwzględnia zawartość metali w najbardziej mobilnej frakcji, czyli tej związanej z węglanami. Obliczone wartości RAC wskazują, że największe ryzyko ekologiczne powoduje cynk. Można również stwierdzić, że zastosowanie ultradźwięków w procedurze ekstrakcji sekwencyjnej nie wpływa istotnie na interpretację wyników oceny ryzyka ekologicznego. Jednocześnie potwierdza to zasadność stosowania omawianej modyfikacji w procesie ekstrakcji sekwencyjnej metali ciężkich z osadów ściekowych.

Słowa kluczowe: osady ściekowe, metale ciężkie, ekstrakcja sekwencyjna, ultradźwięki, ryzyko ekologiczne

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1. Introduction

Protection of the natural environment against the effects of human activity is one of the greatest challenges the world is facing today. The problem of contamination of all components of the natural environment with heavy metals (HMs) appears to be particularly important. These elements are emitted from many industrial processes, causing the pollution of air, water and soil [1, 2]. Moreover, together with wastewater and surface runoff, heavy metals are introduced to the wastewater treatment plant (WWTP), where they ultimately become accumulated in the sewage sludge – a by-product of wastewater treatment [3, 4, 5]. It is worth pointing out that chemical, physical and biological processes used in WWTPs do not guarantee the complete removal of these elements from wastewater and sludge, which may result in secondary pollution of the natural environment and poses a threat to living organisms, including also humans [1, 6]. According to literature data, it is estimated that annual global production of sewage sludge at WWTPs exceeds 22 million tonnes [7]. Moreover, the use of sewage sludge for agricultural purposes is the most economically attractive method of its disposal due to its low costs and high efficiency [7, 8, 9]. The main restriction is the presence of heavy metals. In European Union (EU), the permissible concentration of heavy metals in sewage sludge for agricultural use is regulated by the Council Directive of 12 June 1986 (86/278/EEC) [10]. However, it is commonly known that the total content of heavy metals allows only assessing the degree of sewage sludge contamination, yet it is not the best indicator of mobility, bioavailability and toxicity, which strongly depend on chemical forms of metals [3, 9, 11]. It must be noted that the release of heavy metals into the natural environment results in the absorption of these elements by crops and then they enter the food chain through surface water and groundwater [3, 4, 12, 13]. This may pose serious environmental and health problems [1, 13]. Consequently,

it is necessary to establish the chemical form in which these elements occur in the sewage sludge in order to properly assess their mobility or bioavailability.

One of the best ways of examining the mobility, bioavailability and toxicity of heavy metals is to carry out a chemical sequential extraction. The most commonly used method is the three-step BCR sequential extraction proposed by the Community Bureau of Reference (BCR; currently the Standards, Measurements and Testing Programme), which is a modification of the Tessier method developed in 1979 [14]. Due to the fact that this method is very time consuming [15], it is necessary to search for techniques that would allow shortening the extraction time (sample shaking), without concomitantly reducing process accuracy. One of such methods, i.e., ultrasound treatment, is a promising and successful technique that allows improving particle dispersion, which causes an increase in the surface area accessible for the reaction with reagents, and at the same time enhances the leaching of heavy metals from the solid matrixes [15, 16, 17]. The most important parameters of sonication process are time, frequency and power. The ultrasound treatment reduces the time of the extraction process from several dozen to several hours [15, 16]. Consequently, it is extremely important to select the optimal process parameters to exclude the differences in fractionation patterns of heavy metals, in comparison to conventional BCR sequential extraction method. Otherwise, this action may lead to analytical errors and have a negative impact on the interpretation of results of the potential ecological risk analysis, which is based among others on the metal content in individual chemical fractions. One of the most commonly used tools for the assessment of ecological risk is Risk Assessment Code (RAC) index [18]. RAC includes the content of heavy metals in the most mobile chemical fraction in sewage sludge, i.e., acid soluble/exchangeable fraction (bound to carbonates). This index has been widely used by many scientists [12, 13, 19].

The aim of this study was to investigate the effect of ultrasound waves on the recovery of heavy metals (HMs) from sewage sludge and the potential ecological risk assessment. However, despite the interest of scientists in this research area, there is a little literature available on this topic.

2. Materials and methods

2.1. Material and total heavy metal determination

The research material was the certified reference material ERM-CC144 SEWAGE SLUDGE (JRC). The material used for production of ERM-CC144 (JRC) is sewage sludge material of domestic origin.

The total concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in sewage sludge were determined by atomic absorption spectrometry using the Avio 200

ICP-OES apparatus (PerkinElmer Inc.). For this purpose, 0.5 g of sewage sludge sample was digested with 5 ml of 65% nitric acid (HNO_3) and 15 ml of 35% hydrochloric acid (HCl). The resulting mixture was subjected to microwave digestion using the Multiwave 3000 system (Anton Paar GmbH, Graz, Austria). After cooling, the solution was filtered through paper filters and diluted with 5% HNO_3 to a volume of 50 ml. The obtained samples were stored at 4°C until laboratory analysis. The obtained results are expressed in mg/kg_{DM} (DM; dry matter).

The content of heavy metals in obtained extracts was analysed according to the same procedure as the other samples, excluding mineralization process. The entire analysis was performed in duplicate.

2.2. Sequential extraction methods

Chemical forms of heavy metals in sewage sludge were determined with the use of the three-step BCR sequential extraction [20, 21]. The above-mentioned method includes also one additional step (Step 4), which is optional. Fraction 1 and 2 are considered mobile. 0.5 g of sample material was used for extraction.

To reduce the sequential extraction time, the ultrasound treatment was introduced instead of long hours shaking. A comparison of conventional and ultrasound-assisted sequential extraction methods is shown in Table 1.

Tab. 1. Comparison of the conventional and ultrasound-assisted sequential extraction methods

Step	Fraction (F)	Reagents	Conventional extraction	Ultrasound-assisted extraction
			Extraction conditions	
S1	F1; Acid soluble/ exchangeable fraction; bound to carbonates	20 ml CH_3COOH (0.11 M)	16 hrs of shaking	30 min of shaking and 20, 40 or 70 minutes of sonication
S2	F2; Reducible fraction; bound to Mn and Fe oxides	20 ml $NH_2OH{\cdot}HCl$ (0.1 M, pH=2)	16 hrs of shaking	30 min of shaking and 20, 40 or 70 minutes of sonication
S3	F3; Oxidisable fraction; bound to organic matter and sulphides	5 ml H_2O_2 (8.8 M, pH=2), heat to 85°C for 1h (repeated twice); 25 ml CH_3COONH_4 (1 M, pH=2)	16 hrs of shaking	20, 40 or 70 minutes of sonication
S4	F4; Residual fraction	15 ml HCl/ 5 ml HNO_3	-	-

Source: prepared on the basis of [20, 21] and own study

The sonication was conducted in an ultrasonic bath (Sonic-5; Polsonic). The time of sonication was set at 20, 40 and 70 minutes. The frequency (40 kHz), power (2x320 W) and temperature (30±5°C) during the ultrasound treatment were kept constant. Before the sonication of samples in the 1st (S1) and 2nd step (S2) of extraction, 30 minutes of shaking was carried out to ensure greater contact of the solid sample with extraction reagents. The set used for the ultrasound treatment is presented in Figure 1.

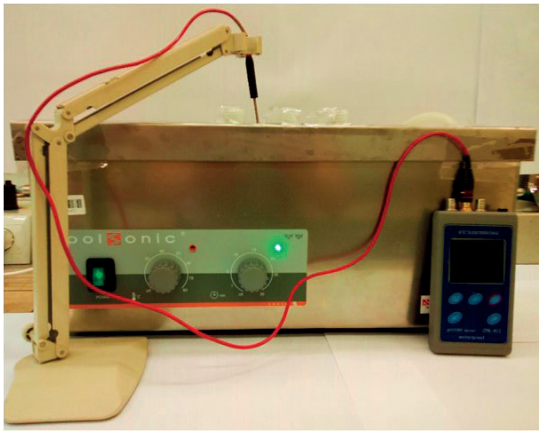

Fig. 1. Set for the ultrasound treatment

Source: own study

2.3. Recovery rate of heavy metals

In order to check the accuracy of the applied procedure and to verify results obtained by the proposed protocol, the recoveries for both methods (R; %) were calculated. For this purpose, the sum of heavy metal concentration in the four chemical fractions (F1+F2+F3+F4) obtained by both the test methods was compared with the total concentrations of heavy metals (TC) in the ERM-CC144 (JRC) certified material (Equation 1) [11]. This formula was applied both for the conventional and ultrasound-assisted sequential extraction method.

$$R = \frac{F1 + F2 + F3 + F4}{TC} \times 100; \% \quad (1)$$

2.4. Potential ecological risk assessment

In order to determine whether the ultrasound waves influenced significantly the distribution of heavy metals in the chemical fractions of sewage sludge, a calculation was made of the percentage share for each element. For the assessment of potential

ecological risk of heavy metals in sewage sludge, the widely used index was applied, i.e., Risk Assessment Code (RAC) by Perin 1985 [18] (Equation 2). This index is preferentially used to evaluate the ecological risk associated with metals bound to the most mobile chemical fraction in sewage sludge, i.e., in the acid soluble/exchangeable fraction (F1).

$$RAC = F1; \% \quad (2)$$

Where: RAC ≤ 1% – no risk; 1% < RAC ≤ 10% – low risk; 10% < RAC ≤ 30% – medium risk; 30% < RAC ≤ 50% – high risk; RAC > 50% – very high risk

3. Results and discussion

3.1. Results of sequential extraction methods

To express the difference between the obtained results, percentage differences between the total content of each heavy metal in all four chemical fractions of sewage sludge, obtained with the use of two extraction methods, were calculated. A comparison of the above-mentioned results is presented in Table 2.

Tab. 2. Comparison of results obtained by two methods of sequential extraction

Heavy metals	Conventional extraction (sum of F1–F4)	Ultrasound-assisted extraction (sum of F1–F4)			Percentage differences between conventional and ultrasound-assisted extraction methods		
		20 min	40 min	70 min	20 min	40 min	70 min
	mg/kg$_{DM}$				%		
Cd	15.6	15.3	15.0	15.5	1.9	3.9	0.6
Cr	137.5	148.7	144.6	135.3	7.8	5.0	1.6
Cu	390.2	346.8	384.7	388.3	11.8	1.4	0.5
Ni	76.9	82.7	81.3	76.8	7.3	5.6	0.1
Pb	147.6	150.8	152.8	145.6	2.1	3.5	1.4
Zn	975.0	930.2	971.4	985.6	4.7	0.4	1.1

Source: own study

Generally, the percentage differences between the total concentrations of analysed heavy metals in sewage sludge, in four chemical fractions, obtained by two extraction methods ranged from 0.1% to 11.8%. However, the obtained results indicated that the highest percentage differences between the total content of analysed heavy metals were recorded after 20 minutes of ultrasound treatment (from 1.9 to 11.8%), while the

lowest ones after 70 minutes (from 0.5 to 1.4%). The highest percentage difference was observed in relation to Cu content (11.8%). In some cases, we noted higher summary concentrations of heavy metals in chemical fractions after ultrasound treatment, e.g. in case of Cr, Ni and Pb (after 20 and 40 minutes of sonication) and Zn (after 70 minutes of sonication). Similar observations were made by other scientists who noted higher summary concentrations of Pb and lower concentration of Cu and Zn in the four chemical fractions of sewage sludge – after ultrasound treatment [22], but contrary to our experiment those differences were significant.

The analysed sewage sludge exhibited higher concentrations of heavy metals bound to the immobile fractions (F3 and F4), except Cd and Zn, which was also observed in our previous studies [6, 12]. The average percentage distribution of each heavy metal in different chemical fractions of sewage sludge, for two investigated methods, has been shown in Figure 2. Despite the fact that the concentration of Cu in the third chemical fraction (immobile), obtained after 20 min of ultrasound treatment, was lower than those achieved by the conventional method, the percentage shares for other heavy metals, i.e., Cd, Cr, Ni, and Pb in chemical fractions of sewage sludge were similar for both extraction procedures. The other exception was Zn (regardless of sonication time). Zn extracted from the sewage sludge using the conventional procedure presented a higher percentage share in the first two chemical fractions (F1 and F2), compared to the ultrasound-assisted method, i.e., by about 9% and 7%, respectively, and a lower one in the third fraction (F3) (of ca. 15%). This suggests that in the case of ultrasound-assisted extraction method, the entire loss from the two first fractions was passing into the third one (immobile). It is worth noting that zinc occurs in one of the highest concentrations in sewage sludge, as has also been confirmed by other scientists [3, 7, 8, 22]. Moreover, this metal is usually less toxic than cadmium or mercury that occur in sewage sludge, at very low concentrations [6]. It is difficult to say what caused the changes in zinc distribution, between particular chemical fractions of the sewage sludge after ultrasound treatment. Frequency, power and temperature during sonication were constant. Therefore, it is necessary to conduct further research to determine conditions for sequential extraction of zinc from sewage sludge using the ultrasound treatment.

To verify the BCR sequential extraction procedure we compared the sum of the four chemical fractions with the total concentrations of heavy metals in sewage sludge and calculated the recovery rate (R). The conducted research reveals that after only 20 minutes of ultrasound treatment, similar recovery values can be obtained as for the conventional method. The recovery rate of heavy metals ranged from 91% to 123% and 90% to 123%, for conventional and ultrasound-assisted method, respectively. The obtained results confirmed that the ultrasound-assisted BCR sequential extraction procedure is adequate and reliable for analysing the speciation of heavy metals considered in this study. The recovery values for analysed heavy metals are presented in Table 3.

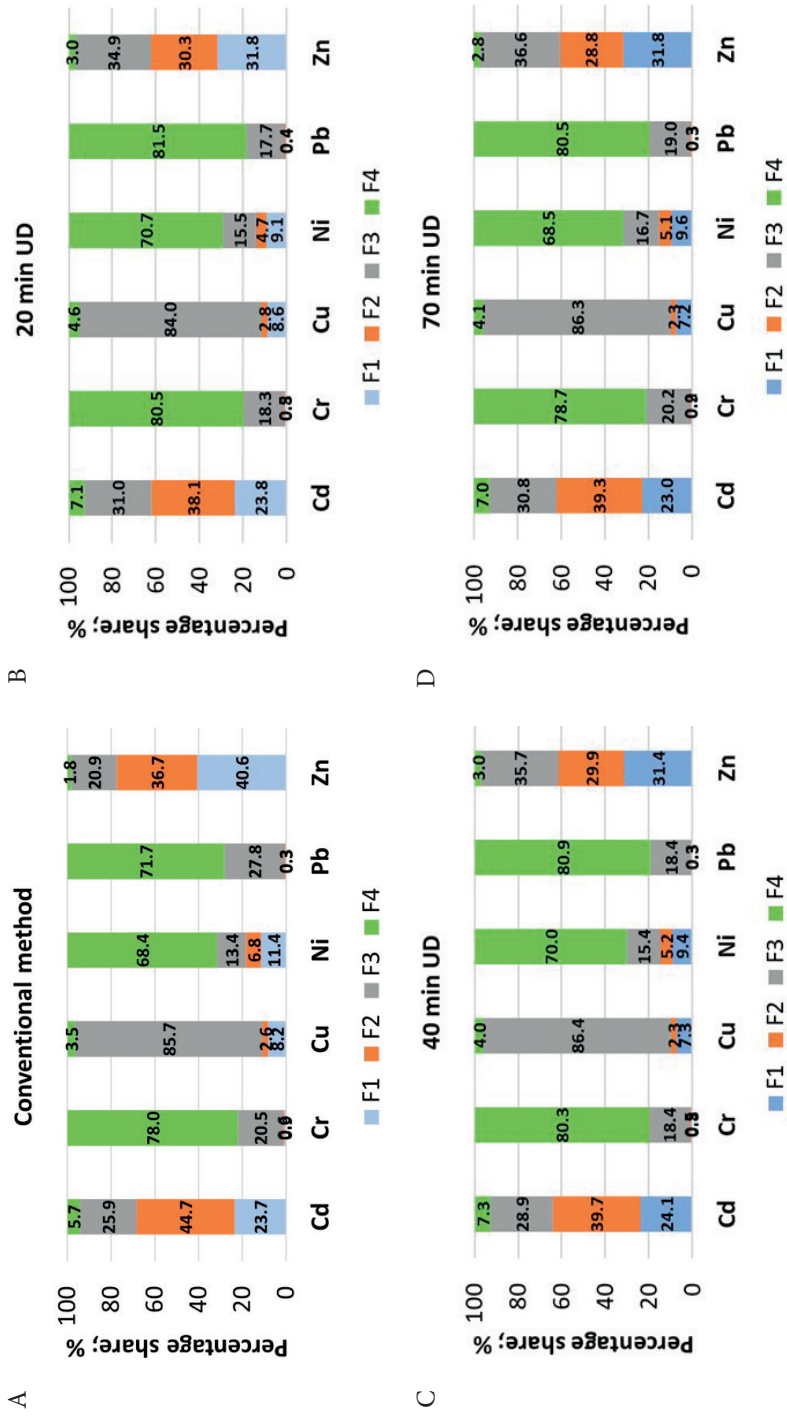

Fig. 2A-D. The average percentage distribution of each heavy metal fraction in sewage sludge

Source: own study

Tab. 3. Comparison of recovery values for heavy metals in sewage sludge

Extraction method	Sonication time	Cd	Cr	Cu	Ni	Pb	Zn
	min	R; %					
Conventional extraction	0	123	91	111	92	97	105
Ultrasound-assisted extraction	20	121	98	99	99	100	100
	40	119	96	109	97	101	105
	70	123	90	110	92	96	106

Source: own study

3.2. Results of potential ecological risk assessment

The results of potential ecological risk assessment are presented in Table 4. The heavy metals risk assessment is connected with the evaluation of the hazardous properties of those elements and their adverse influence on soil properties, which is associated with absorption of these pollutants by plants and their penetration into the food chain of animals and humans. However, total concentrations of heavy metals in sewage sludge used for production of ERM-CC144 (JRC) did not exceed the permissible standards for sewage sludge in EU (86/278/EEC) [10]. What is more, the obtained results reveal that regardless of the extraction method used, zinc and cadmium were found to have the highest potential of migration and contamination. Similar observations were made by other scientists [19, 23]. The calculated RAC values for zinc amounted 41% (high risk) for the conventional extraction method and from 31% to 32% (high risk) for ultrasound-assisted one, while in relation to cadmium 24% (medium risk) and from 23% to 24% (medium risk), respectively. The conducted research also shows that the percentage differences in the share of zinc in individual chemical fractions of sewage sludge do not have a significant impact on the results of the potential ecological risk assessment.

Tab. 4. RAC values

Extraction method	Sonication time	Cd	Cr	Cu	Ni	Pb	Zn
	min	RAC; %					
Conventional extraction	0	24	1	8	11	0.3	41
Ultrasound-assisted extraction	20	24	1	9	9	0.4	32
	40	24	1	7	9	0.3	31
	70	23	1	7	10	0.3	32

Source: own study

4. Conclusions

The conducted research has shown that ultrasound-assisted sequential extraction method gives similar results to those obtained with the conventional one. Moreover, the ERM-CC144 (JRC) certified material, produced from sewage sludge of domestic origin, exhibited higher concentrations of most tested heavy metals bound to the immobile fractions. Only Cd and Zn were present in higher in mobile fractions of sewage sludge. It was also ascertained that the percentage shares of heavy metals in chemical fractions were similar to both extraction methods, with one exception, i.e., Zn. The obtained recovery rates were similar to both exanimated methods, which confirm that ultrasound-assisted extraction procedure is adequate and reliable for detecting the speciation of analysed heavy metals. Moreover, the obtained results reveal that regardless of the extraction method applied, Zn is a metal that poses the highest potential ecological risk in the analysed sewage sludge. Furthermore, it was found that the difference between the distributions of this element in the individual chemical fractions of sewage sludge did not have a significant impact on the results of the ecological risk assessment. However, considering the obtained outcomes, it is necessary to continue research in order to determine the appropriate conditions for extraction of Zn from sewage sludge by sequential extraction method assisted with ultrasound waves.

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