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EXTRACTION OF HEAVY METALS FROM A CONTAMINATED SOIL BY USING CHELATING AGENTS

Abstract: For the experimental study, solutions of EDTMP, NTA, and TA were selected for HM extraction. The influence of extraction time and the ratio of extractant concentrations on extraction efficiency was evaluated. The analysed soil was artificially contaminated with selected HM (Cu, Zn, Pb). Chemical extraction of HM using chelating agents resulted in a reduction of HM concentrations in the soil to the permissible limit values set by the Council Directive 86/278/EEC. The most suitable chelating agents under the conditions of this experiment were the combined chelating agents NTA and TA with an extraction time of 60 minutes. Cu and Zn concentrations were reduced to permissible limits even when using the lowest concentration of NTA and TA (0.1 M), while the 0.5 M concentration and 60-minute extraction time resulted in the lowest concentrations of Cu, Zn, and Pb in the soil - 48 mg/kg, 74 mg/kg, and 78 mg/kg, respectively - and the highest extraction efficiencies of 93.3 %, 91.1 %, and 95.2 %, respectively. The combined chelating agents NTA and TA showed higher extraction efficiencies than the synthetic organic chelating agent NTA alone at different extraction times. The variation in extraction efficiency for the different combined chelating agents is presented as follows: for NTA and TA (0.5 M:0.5 M), Pb > Cu > Zn, and for EDTMP and TA (0.5 M:0.5 M), Cu > Pb > Zn. For chelating agents of synthetic origin only, the series were: NTA - Cu > Zn > Pb, and EDTMP - Cu > Pb > Zn.

Keywords: soil, extraction, heavy metals, chelating agents

Introduction

Heavy metal (HM) concentrations in soil are increasing as a result of natural and anthropogenic factors. Soil pollution with heavy metals is an environmental problem investigated by many scientists [1-8]. The toxicity of HM depends on their chemical state and oxidation number [9]. Due to their high toxicity, HM, even at low concentrations, can pose a threat to human and animal health, and the transport of metal ions through the food chain is becoming a growing public concern [10]. HM are not biodegradable and accumulate in soil in various chemical forms. They can be mobile in the soil solution and bioavailable to plants, depending on soil chemistry. Most HM persist in the environment for long periods [11]. Soils can be contaminated with various heavy metals. Zinc, lead, and copper were chosen for the experimental studies because soils are often contaminated with

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these heavy metals. Based on the Council Directive 86/278/EEC of 12 June 1986 [12], the following pollution sources can be distinguished when increased amounts of selected heavy metals are found in soil in areas affected by industrial and other pollution sources: secondary processing of non-ferrous metals, production of electrical, radio, and electronic devices, production and processing of cast iron and alloyed special steels, production of machine tools, heat treatment of metals, car repair, transport companies, production of lead batteries, printing houses, thermal boiler houses, chemical industry, production of plastics, production of phosphate and other fertilisers, leather processing and footwear production, light industry, production of construction and thermal insulation materials, cement, concrete structures, glass, urban solid household waste used as fertilisers, sewage sludge, contaminated irrigation water, etc. Many studies have summarised the adverse effects of excess Cu on germination, growth, photosynthesis, and antioxidant responses in agricultural crops [13]. Exposure to high levels of Zn may provoke toxic effects in plants, such as reduced growth, damage to pigment contents, and disturbances in enzymatic activities [14]. Lead is a nonessential element, and when taken up by plants, it can negatively affect plant metabolic processes [15]. Contaminated with HM soil is usually excavated and disposed of as hazardous waste. The applicable soil remediation technology should address three aspects of sustainability: economic, environmental, and social [16]. For this reason, it was relevant to investigate the use of chelating agents for the extraction of heavy metals from contaminated soil. Chelating agents exhibit strong complexation with HM and do not adversely affect on soil chemical and physical properties compared to inorganic acids [17, 18]. Although many studies focusing on soil extraction have been conducted in recent years, their mechanisms and practical applications are still limited. In addition, few studies have investigated the innovation of extrahents and the migration and transformation of contaminants in soil using chemical extraction. Very little research has also been carried out on the use of complex chelating agents for effectively reducing HM levels in soil. Therefore, the assessment of soil physicochemical properties and changes in leached HM is an important ecological challenge. At present, researchers have gradually introduced the use of synthetic and natural chelating agents in experimental extraction studies for the removal of HM from soil. The frequent use of these chelating agents is due to their biodegradability, which is likely to leave the soil structure (grain size) unchanged and to have minimal impact on the chemical properties of the soil, which are essential for maintaining soil vitality and returning it to its natural state. The biodegradability of chelates in soil is an important factor in their environmental impact, particularly when used in soil remediation or as fertilisers. While some chelates are known to be persistent, others are readily biodegradable, offering a more environmentally friendly alternative. The biodegradability of a chelate affects its ability to mobilise heavy metals in soil and its potential to leach into groundwater. Chemical compounds such as EDTA and NTA are widely used in industrial applications due to their ability to form stable complexes with metal ions. However, they are highly polar and partially nondegradable, leading to significant environmental release, particularly into aquatic environments [19, 20]. This persistence raises concerns about their potential ecotoxic effects on various aquatic organisms [20]. Tartaric acid derivatives, such as bis-amide ligands, maintain the chelating properties of tartaric acid while being water-soluble [21]. Although specific biodegradability data for tartaric acid complexes are not provided, their water solubility suggests potential for environmental mobility. NTA and EDTA ligands form highly stable complexes with various metal ions. For instance, EDTA binds through four carboxylates

and two nitrogens, while NTA can bind via three carboxylates or a combination of carboxylates and nitrogen, depending on the pH and metal-to-ligand ratio [22]. The stability constants of these complexes increase with temperature, indicating strong binding affinity [23]. Tartaric acid-derived ligands form complexes with metals such as nickel(II) and copper(II), exhibiting different electronic and geometric properties depending on stoichiometry [21, 24]. These complexes are characterised by techniques such as potentiometry and X-ray diffraction, confirming their structural stability [21]. The biodegradation of NTA, EDTMP, and tartaric acid in soil is governed by a complex interplay of environmental, chemical, and biological factors. While NTA is relatively biodegradable, EDTMP is persistent, and the fate of tartaric acid is less well quantified. The use of natural chemical compounds is being explored by researchers, including citric acid [22], tartaric acid (TA) [25, 26], acetic acid [27], and oxalic acid [28]. The use of synthetic chemical compounds in extraction is also being investigated, including EDTA [29], GLDA, ISA, PASP, GCA [28], PAA, EDTMP [30], and NTA [31].

Organic chelating agents of natural origin are effective ligands for many metal ions. Organic chelating agents such as glutamic, citric, tartaric, and acetic acids are commonly used for HM extraction [31]. Synthetic chelating agents are also highly effective for reducing soil pollution, as they are capable of forming stable complexes with HM at different pH levels. Recently, research has focused on the combined use of various chemical reagents. Some studies have shown that higher removal efficiencies of HM in contaminated soils can be achieved when sequential extractions are carried out using different extractants. Combined studies on chelating agents of organic acids and inorganic acids have demonstrated that sequential and combined usage can increase the removal efficiency of HM from soil. The combined use of chelating agents reduces the required dose of chemical reagents and results in fewer negative treatment consequences, particularly in cases where synthetic organic compounds are not biodegradable and remain in the soil after treatment [32]. Degradation of citric acid in soil is relatively rapid, whereas synthetic chelating agents such as EDTA and NTA demonstrate low rates of biodegradation [33].

The use of organic acids to mobilise and extract heavy metals from soils is increasingly associated with broader developments in land restoration and contaminant transport control, as highlighted in recent research on surface chemistry, porous media behaviour, and pollutant migration [34-36]. A growing number of studies also examine how organic compounds interact with mineral matrices and alter metal speciation and leaching dynamics, offering valuable insights for improving extraction efficiency [37-39]. Furthermore, advances in biotechnology and materials science demonstrate that organic molecule-driven processes can be incorporated into sustainable soil remediation approaches, including plant-based systems and the use of functionalised materials [40, 41]. Although the application of chelating agents and other chemical compounds for the extraction of heavy metals from soil has been widely studied, most published research to date has been conducted on naturally contaminated or moderately contaminated soils, where heavy metal concentrations are substantially lower. There is a lack of data on the effectiveness of chelating agents under very high contamination levels, typically created artificially, which allow for a precise assessment of extraction limits and chelate interactions under extreme conditions. In this study, we systematically evaluated for the first time the ability of NTA, TA, and EDTMP - both individually and in mixtures - to mobilise Cu, Pb, and Zn from heavily contaminated sandy loam. This experimental design

makes it possible to identify synergistic or antagonistic effects that do not emerge in soils with lower contamination levels and fills an essential knowledge gap regarding the performance of chelating agents under high heavy metal concentrations. The aim of this study was to evaluate the efficiency of selected chelating agents for the removal of HMs (Zn, Pb, Cu) from contaminated soil to the permissible limit values set by Council Directive 86/278/EEC [12].

Research methodology

Research object and location

Soil samples were taken in accordance with ISO 10381-3:2001 standard [42] from an agricultural site (coordinates 55.74477, 22.98341). For soil analysis, a composite sample consisting of 5 subsamples of the original soil was collected in the field.

Main instruments and tools used: sieves (mesh size 2.0 mm, 0.9 mm, 0.63 mm, 0.2 mm); X-ray fluorescence analyser (SciAps X-200); vibratory shaker (Retsch AS 200); magnetic stirrer (Heidolph MR 1000); pH-meter (Mettler Toledo Seven Multi); analytical balance (Radwag AS 60/220.R2); vacuum system; membrane filters with a pore size of 0.45 μm.

Chemical reagents and solutions used in the study: TA (tartaric acid, $C_4H_6O_6$; 0.1, 0.2, 0.5 M); EDTMP (methylene phosphonic acid, $C_6H_2ON_2O_{12}P_4$; 0.1, 0.2, 0.5 M); NTA (nitrilotriacetic acid, $C_6H_9NO_6$; 0.1, 0.2, 0.5 M); $Pb(NO_3)_2$; $Cu(NO_3)_2$; $Zn(NO_3)_2$; 0.1 N HNO_3; 0.1 N NaOH; 1 M KCl; deionised water.

Determination of soil parameters

The following soil parameters were measured: pH, bulk density, organic carbon content, granulometric composition and soil type, and background content of HM.

Soil pH

Soil pH was measured in accordance with the ISO 10390:2021 standard [43] using a Mettler Toledo Seven Multi pH meter.

Soil bulk density

The ISO 14688-1:2017 standard [44] was used for the determination of soil bulk density.

Organic carbon content

Organic carbon content was determined using a Shimadzu TOC-LCSH/CSN Standalone Model and a Shimadzu SSM-5000A Solid Sample Module. Before analysis, soil samples were chopped, sieved, and dried in a laboratory oven at (105 ±2) °C to a constant weight. Well-dried soil samples were weighed using an analytical balance. The sample was weighed after being placed in a pre-heated sample container [45]. The operation of the device is based on incineration of a dry soil sample at high temperature and quantification of the released carbon dioxide using an infrared detector.

Soil type and granulometric composition were determined according to the ISO 14688-1:2017 [44] and ISO 17892-4:2016 [46] standards.

Background HM concentration

HM concentrations in the soil were measured using a SciAps X-200 XRF analyser. The soil to be tested was sieved through a 1 mm sieve and dried to a constant mass, then mixed with 5 L of deionised water. The soil was mixed in a bucket for 30 minutes using an electric mortar mixer to obtain a homogeneous sample in which the background concentrations of heavy metals were evenly distributed throughout the entire soil volume. The mixed soil was filtered through a 0.45 μm filter to separate the solid fraction from the resulting solution and to remove the mobile forms of heavy metals. The filtered soil was dried at 105 °C to a constant mass. Five 30 g soil samples containing background HM concentrations were taken from different locations within the prepared soil. The tested soil was placed in special capsules to determine background HM concentrations.

Pollution of soil samples with HM

Soil samples (300 g each) were placed in glass bottles and contaminated with aqueous solutions of the heavy metals to be tested: $Pb(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$, to achieve heavy metal concentrations at least twice higher than the permissible limit values set by Council Directive 86/278/EEC [12], taking into account background HM concentrations. The prepared solution was mixed and poured into a glass bottle containing 300 g of dried soil. An additional 100 mL of deionised water was added. After contamination with HMs, the soil solution in the glass bottle was stirred with a "Rotoshake RS12" sample mixer for 2 hours. After mixing, the soil was filtered through a 0.45 μm filter. The solid fraction was placed in an open plastic container and mixed. Heavy metal concentrations in the soil were determined using the XRF method. After contamination, soil samples were mixed in a common container. Five soil samples of 30 g each were taken from different parts of the contaminated soil, placed into Petri dishes, and dried. The dried samples were transferred into special capsules, and heavy metal concentrations were determined using an X-ray fluorescence spectrometer.

Extraction was used to remove HM from contaminated soil, and the main parameters of the experiment are presented in Table 1.

Table 1

The main parameters of the experiment

Chelating agent	Concentration [mol/L]	pH [-]	Temperature [°C]	Extraction time [min]
NTA	0.1, 0.2, 0.5	3.0	20.5 ±2	10, 30, 60
EDTMP				
NTA and TA	0.1:0.1, 0.1:0.2; 0.2:0.2, 0.2:0.5, 0.5:0.5			
EDTMP and TA				

A constant pH value of 3.0 was chosen, at which organic acids with functional groups (–COOH, –OH, etc.) can easily bind with HM and achieve high extraction efficiency [28].

A pH of approximately 3 may be selected as a compromise value because the efficiency of heavy metal extraction with organic acids increases as pH decreases. In an acidic environment, H^+ ions compete with metal cations for sorption sites in the soil, facilitating metal desorption and their transfer into the solution.

However, when pH decreases below 3, undesirable processes begin to occur: the leaching of base cations essential for soil fertility (Ca^{2+}, Mg^{2+}, K^+) intensifies, and base

saturation declines. In addition, the mobility of elements such as Fe, Mn, and Al increases, and their elevated concentrations may become phytotoxic and negatively affect plants. Although extraction efficiency at pH = 3 is relatively high, the most favourable conditions for soil microorganisms are typically at pH 5-7. Therefore, after extraction, it is recommended to neutralise the soil by liming to restore optimal pH, microbial activity, and suitable conditions for plant growth.

The extraction times (10, 30, and 60) min were chosen according to the results of experimental studies by Yan [47]. It was found that HM content in soil remains constant when chelating agents are used for extraction times longer than 60 minutes.

Data quality assurance

High purity chemical reagents (p.a), prepared solutions and deionised water were used in the experiment. The pH-meter was calibrated using buffer solutions, to ensure accurate pH measurements. The Sigma-Aldrich certified reference material (soil matrix CRM) was used as a quality control tool to ensure the accuracy and traceability of heavy metal (HM) concentration measurements obtained with the SciAps X-200 portable X-ray fluorescence analyser. This CRM, which has an internationally certified elemental composition and a matrix closely matching real soil, enables assessment of measurement accuracy, verification of calibration stability, confirmation of result traceability, and evaluation of matrix effects. In this way, the use of CRM increases the reliability of analytical data and allows a well-founded assessment of the quality of HM concentration determinations using the SciAps X-200. The data, means, and standard deviations of the results were calculated using Excel 2016. SigmaPlot 15.0 and the Python Matplotlib library were used for graphing. Each experimental condition was analysed using three independent replicates to ensure reproducibility. Differences between measurements were evaluated using a two-tailed Student's t-test, with statistical significance accepted at $p < 0.05$. The *t*-test allows a statistical assessment of whether the means of three replicates differ by more than would be expected due to random variation in measurement, using a significance level of $p < 0.05$. When the calculated p-value is less than this threshold, the null hypothesis is rejected and the observed difference is considered statistically significant, meaning it is likely to reflect a real effect rather than chance.

Research results and discussion

The influence of the concentration ratio of chemical reagents on the efficiency of the process

Determination of soil parameters

Determined soil parameters were as follows: bulk density - 1.207 g/cm³; the soil consisted of approximately 87 % sand, 12.4 % silt, and 0.6 % clay. Based on the results of experimental studies, the analysed soil was classified as sandy loam. The organic carbon content in the soil was 0.73 %. Organic carbon content is an important soil parameter, as it increases the adsorption capacity for HM.

Soil pH decreased steadily with increasing concentrations of chelating agents, irrespective of the extraction time. A comparison of HM concentrations in the soil before and after pollution is presented in Table 2.

Table 2

Comparison of HM concentrations in the soil before and after pollution

Concentrations of HM in the soil	Cu	Zn	Pb
Background concentration [mg/kg]	27.9	12.3	13.1
Council Directive 86/278/EEC [12] [mg/kg]	75	300	80
HM concentration in the artificially polluted soil [mg/kg]	712 ±16	840 ±22	1,624 ±31

The revised HM limit values (RVp) are presented for each heavy metal, taking into account the organic carbon content in the soil. HM (Cu, Zn, Pb) concentrations in the contaminated soil exceeded the limit values specified in the Council Directive 86/278/EEC [12] by more than twofold: Cu - 9.5 times, Zn - 2.8 times, and Pb - 20.3 times.

Soil homogeneity can be inferred from the low dispersion of HM concentrations across different sampling sites, which was 2.3 % for Cu, 2.6 % for Zn, and 1.9 % for Pb. The highest recorded concentrations of heavy metals in urban soils worldwide are: Cu up to 12,986 mg/kg, Pb up to 5,780 mg/kg, and Zn up to 3,420 mg/kg. The heavy-metal levels selected for this experimental study did not exceed internationally reported contamination thresholds for urban soils [48].

Extraction dependence on acid type, concentration and extraction time using combined chelating agents

Remaining concentrations of HM in soil after extraction with the combined chelating agents - EDTMP and TA; NTA and TA are presented in Figures 1 and 2. With different concentrations of (NTA and TA) and different extraction times (10, 30 and 60) min, the concentrations of Cu varied from 105 mg/kg to 48 mg/kg, the concentrations of Zn varied from 253 mg/kg to 74 mg/kg and concentrations of Pb varied from 575 mg/kg to 78 mg/kg.

The highest removal efficiency was for Pb up to 78 mg/kg (95.2 % efficiency) and for Cu up to 48 mg/kg (93.3 % efficiency) at concentrations of NTA and TA of 0.5 M and an extraction time of 60 min (Fig. 1e). Comparing the extraction efficiencies of NTA and TA at 0.2 M : 0.5 M with NTA and TA at 0.5 M with an extraction time of 60 minutes, the difference in efficiency was negligible. The efficiency of HM removal was similar when using lower concentrations of synthetic chelating agents, i.e., 92.4 %, 86.8 % and 93.3 % for NTA 0.2 M and TA 0.5 M for HM (Cu, Zn, Pb), respectively, and 93.3 %, 91.1 %, 95.2 %, respectively, when increasing the concentration of NTA to 0.5 M.

The use of lower concentrations of the combined chelating agents shows a similar extraction efficiency to that achieved with higher acid concentrations, as no significant change in efficiency is observed between the higher and lower concentrations of NTA. With increasing concentrations of NTA and TA and longer extraction times, the most effective reduction of Pb was observed in the soil. Using different amounts of NTA and TA and an extraction time of 60 min, Pb removal efficiency ranged from 64.7 % to 95.2 %. When using NTA 0.2 M and TA 0.5 M, the removal efficiency exceeded 91 %, indicating that effective HM removal can be achieved even with lower concentrations of chelating agents.

The extraction efficiency for the removal of HM from soil was lower when using different concentrations of EDTMP and TA compared with the use of NTA combined with TA. Extraction efficiencies obtained with various EDTMP concentrations and extraction times ranged from 46.0 % to 87.9 %. The highest extraction efficiencies achieved were

87.9 % for Cu, 75.9 % for Zn, and 84.5 % for Pb. Using the highest concentrations of EDTMP and TA and an extraction time of 60 min, Cu removal ranged from 712.5 mg/kg to 86.4 mg/kg, Zn from 840 5 mg/kg to 200.5 mg/kg, and Pb from 1,624 mg/kg to 252 mg/kg (Fig. 2e).

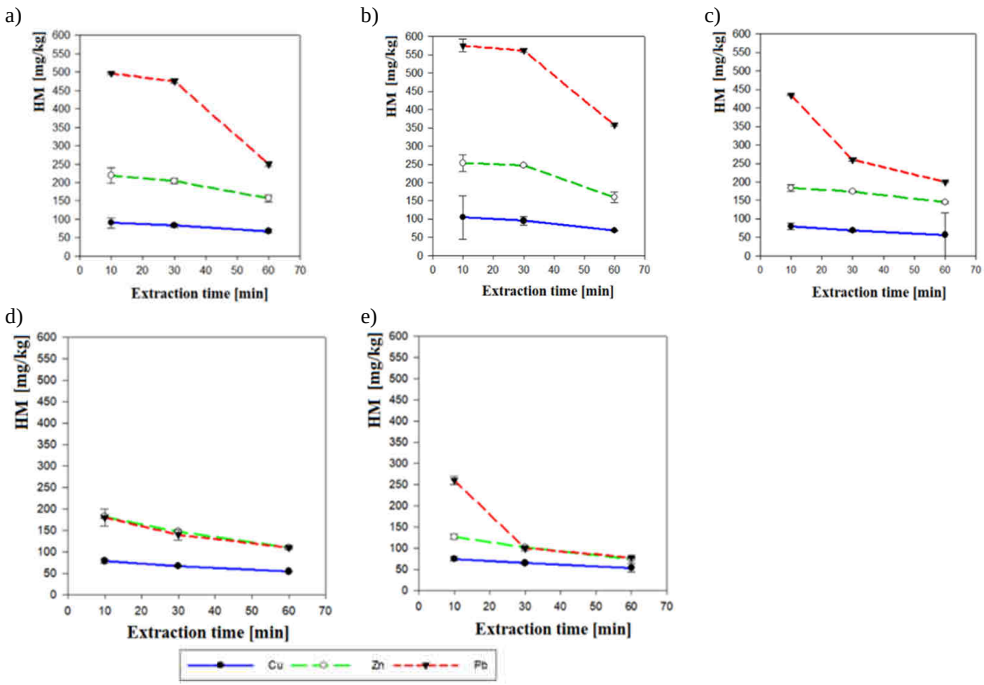

Fig. 1. Remaining concentrations of HM (Zn, Cu, Pb) in the soil depending on extraction time using different concentrations of the combined chelating agents NTA : TA. The tested concentration ratios were: a) 0.1 M : 0.2 M; b) 0.1 M : 0.1 M; c) 0.2 M : 0.2 M; d) 0.2 M : 0.5 M; e) 0.5 M : 0.5 M (pH = 3, t = (20.5 ±2) °C, n = 3, p < 0.05)

The removal of HM from soil using EDTMP and TA was the least effective for Zn and the most effective for Cu. The concentrations of HM and the corresponding extraction efficiencies differed only slightly between the higher concentrations of the combined chelating agents (NTA : TA 0.2 M : 0.5 M and 0.5 M : 0.5 M). However, the lowest concentration of chelating agents resulted in a significantly lower extraction efficiency compared with the higher concentrations of NTA and TA.

The extraction efficiency for the removal of Zn from soil ranged from 46 % to 75.9 %, which may be related to differences in the ability of the chelating agents to bind and mobilise this metal. When EDTMP combined with TA was used for Cu removal, the extraction efficiency at the lowest chelating-agent concentration already exceeded 80 %, with only a slight increase in efficiency as the concentrations of the chelating agents increased (Fig. 2a, e). No data are currently available on the effectiveness of combined chelating agents such as EDTMP with TA and NTA with TA for removing specific HM from soils. Comparative results of these extraction processes using combined acids are presented in Figures 2 and 3. The use of different combined chelating agents reduced HM

concentrations in the soil to the permissible limits set by Council Directive 86/278/EEC [12]. These permissible concentrations were achieved when various NTA and TA concentrations were applied in the experiments and when different extraction times were used.

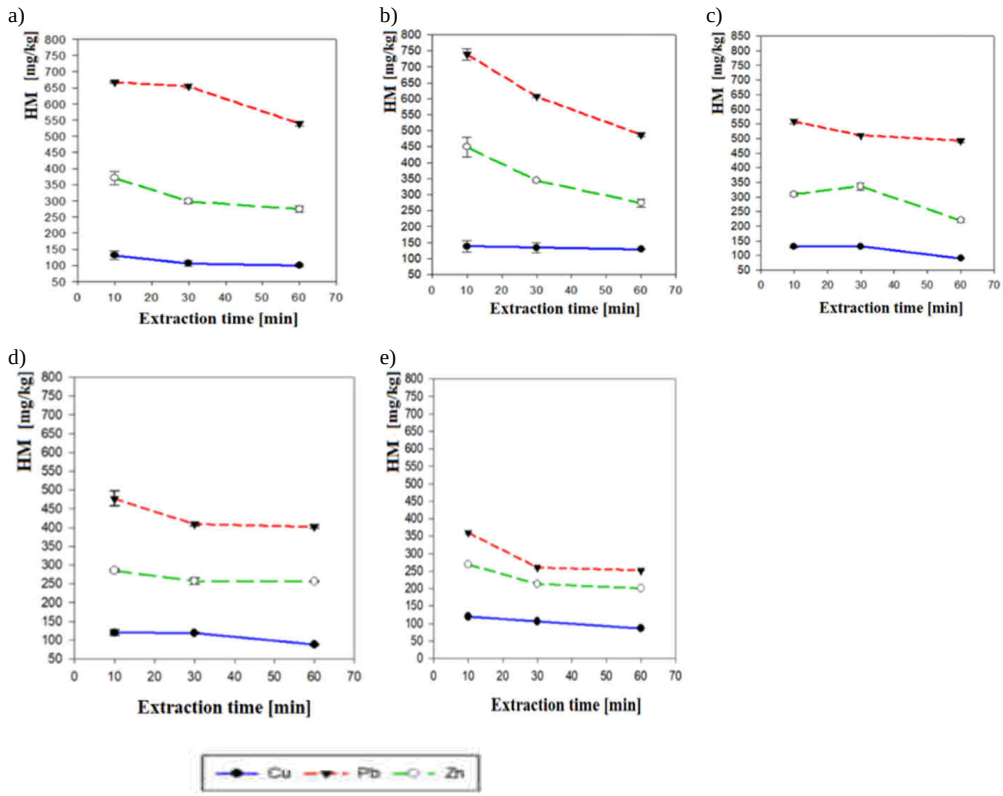

Fig. 2. Remained concentrations of HM (Zn, Cu, Pb) in the soil dependence on extraction times using different concentrations of the combined chelating agents EDTMP: TA: a) 0.1 M : 0.2 M; b) 0.1 M : 0.1 M; c) 0.2 M : 0.2 M; d) 0.2 M : 0.5 M; e) 0.5 M : 0.5 M (pH = 3, t = (20.5 ± 2) °C, n = 3, p < 0.05)

Applying a 10-minute extraction, the most effective removal of Cu to permissible concentration limits was achieved with 0.5 M NTA and TA, reducing Cu from 712.5 mg/kg to 75 mg/kg. Zn was also effectively removed using 0.2 M NTA and TA, with Zn concentrations reduced from 840 mg/kg to 127 mg/kg (Fig. 2).

The Zn concentration in the soil was reduced to permissible limits even at the lowest NTA and TA concentration (0.1 M), and this was achieved with the shortest extraction time. When EDTMP combined with TA was used, Zn concentrations reached permissible limits only at higher chelating-agent concentrations of 0.2 M and 0.5 M, with Zn decreasing from 840 mg/kg to 286 mg/kg. Pb concentrations in the soil decreased steadily as the concentrations of the chelating agents increased.

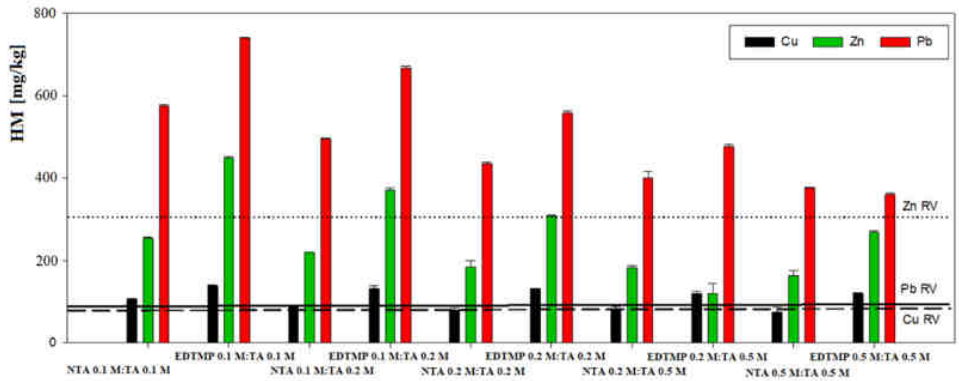

Fig. 3. Changes in HM (Cu, Zn, Pb) concentrations in soil using different concentrations of the combined chelating agents during a 10-minute extraction (pH = 3, t = (20.5 ± 2) °C, n = 3, p < 0.05)

Cu and Zn were efficiently removed from the polluted soil at NTA and TA concentrations of 0.1 M and 0.2 M when the extraction time was 30 minutes (Fig. 4), with HM concentrations decreasing steadily as the concentrations of the chelating agents increased. Pb was also effectively removed from the polluted soil, reaching concentrations as low as 100 mg/kg, compared with an initial Pb concentration of 1624 mg/kg. The combined chelating agents EDTMP and TA at concentrations of 0.1 M and 0.2 M were effective in removing Zn; however, increasing the concentration of one of the chelating agents (EDTMP or TA at 0.2 M) did not result in a uniform reduction of HM concentrations.

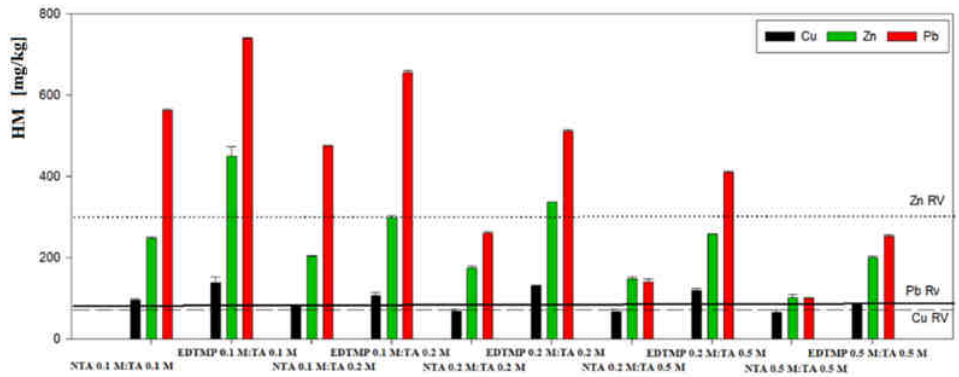

Fig. 4. Changes in HM (Cu, Zn, Pb) concentrations in soil using different concentrations of the combined chelating agents during a 30-minute extraction (pH = 3, t = (20.5 ± 2) °C, n = 3, p < 0.05)

The highest removal efficiency of HM from the soil was achieved with an extraction time of 60 min. Cu was efficiently reduced to 68 mg/kg and Zn to 159.5 mg/kg even at the lowest NTA and TA concentration (0.1 M) (Fig. 4). These results indicate that extending the extraction time substantially enhances HM removal, particularly when lower chelating-agent concentrations are used.

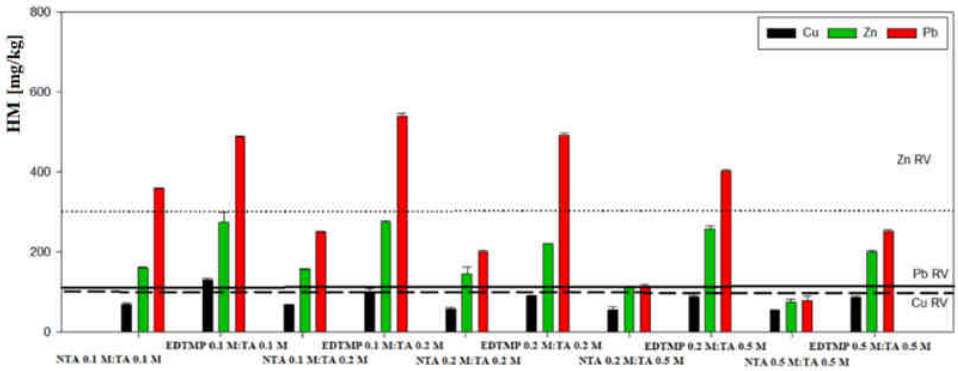

Fig. 5. Changes in HM (Cu, Zn, Pb) concentration in soil using different concentrations of the combined chelating agents, 60 min extraction time (pH = 3, t = (20.5 ± 2) °C, n = 3, p < 0.05)

Zn was efficiently reduced to permissible limits - down to 273.5 mg/kg - when the lowest EDTMP and TA concentration was used. The highest concentration of NTA and TA (0.5 M) effectively removed Pb to 78 mg/kg, but this level of Pb reduction was not achieved when EDTMP and TA were applied. This difference can be explained by the fact that Pb is one of the most strongly immobilised heavy metals in light, sandy soils with low organic matter content [49].

Experimental studies on HM extraction from contaminated soil using combined chelating agents showed that, in order to reduce the concentrations of all HM (Cu, Zn, and Pb) to the limits set by the Council Directive 86/278/EEC [12], the most effective option was the combination of NTA and TA with a 60-minute extraction time. Under these conditions, Cu and Zn concentrations were reduced even when the lowest chelating-agent concentration (0.1 M) was used, while Pb required a higher concentration of NTA and TA (0.5 M) to reach permissible levels.

Comparative analysis of the extraction efficiency using combined chelating agents (EDTMP and TA, NTA and TA) and organic chelating agents of synthetic origin (NTA and EDTMP)

Comparison of HM removal efficiencies using combined and synthetic organic chelating agents. For the 10-minute extraction time, only slight differences in HM removal efficiency were observed between the combined chelating agents and the synthetic-only organic chelating agents. When using the combined NTA and TA chelating agents, Cu removal efficiencies ranged from 70.3 % to 91.1 % (Fig. 3).

As mentioned above, EDTMP is a chelating agent with limited solubility in water, and its chelating properties are sensitive to pH values and surface-binding mechanisms. The addition of TA further lowers the pH of the solution, which leads to a steady decrease in the efficiency of EDTMP. This effect may also be influenced by the chemical properties of the soil. Under these conditions, the removal efficiency for HM (Cu, Zn, and Pb) increased proportionally, reaching 90.9 %, 87.7 %, and 93 %, respectively (Fig. 4).

Nevertheless, the extraction efficiency remained significantly lower when EDTMP and TA were used together. The removal efficiency of Cu reached 87.9 % with EDTMP and TA, and similar Cu removal efficiencies were obtained across different EDTMP and TA

concentrations and extraction times. In comparison, Cu removal was slightly higher when using NTA 0.5 M and TA 0.5 M (93.3 %) than when using NTA alone (92.2 %) at an extraction time of 60 min (Fig. 5).

Pb was also efficiently removed from the soil under the same conditions. Using NTA 0.5 M and TA 0.5 M with a 60-minute extraction time resulted in a Pb removal efficiency of 95.2 %, whereas applying NTA 0.5 M alone for the same duration yielded a lower efficiency of 87.1 % (Fig. 5). It was also observed that when EDTMP and combined EDTMP-based chelating agents were used, the efficiency of this chelating system decreased as the extraction time increased. At an extraction time of 10 minutes, EDTMP showed higher effectiveness in binding HM compared with longer extraction times, a trend that has also been reported in previous research studies.

The variation in extraction efficiency for the different chelating agents is expressed as the following series: for the combined chelating agents NTA and TA (0.5 M : 0.5 M), Pb > Cu > Zn, and for EDTMP and TA (0.5 M: 0.5 M), Cu > Pb > Zn. For the synthetic-origin chelating agents used individually, the efficiency series was NTA: Cu > Zn > Pb, and EDTMP: Cu > Pb > Zn. These patterns reflect the differing complexation strengths, solubility characteristics, and metal-binding preferences of each chelating system.

Comparable efficiencies in removing selected heavy metals (Cu, Pb, and Zn) from soil have been observed in other studies. Using ammonium tartrate, researchers achieved extraction efficiencies of 88 % for Pb, 97 % for Cu, and 98 % for Zn [50].

All three chelating systems can influence soil quality, particularly through heavy-metal mobilisation and their effects on microbial processes. Addressing the remaining knowledge gaps will require innovative research approaches and a stronger focus on sustainable alternatives [51-53].

In sandy loam soils, the in-situ extraction of heavy metals can be limited by several interacting physical, geochemical, technical, and environmental factors. The high permeability and low sorption capacity of these soils allow both metals and acidic extraction solutions to migrate rapidly to deeper layers, making it difficult to control the treatment zone and increasing the risk of groundwater contamination. A key geochemical limitation is the low buffering capacity: pH shifts occur quickly, mobilising not only heavy metals but also essential nutrients, which can negatively affect soil fertility. From a technical and economic perspective, effective solution-collection systems must be installed and multiple washing cycles applied, which increases operational complexity and costs, especially at larger scales. Environmentally, the main concerns are the potential for secondary pollution and the risk of damaging soil structure and ecological functions.

Organic acids - tartaric acid (TA), methylene diphosphonic acid (EDTMP), and nitrilotriacetic acid (NTA) - mobilise Pb, Cu, and Zn in sandy loam soils primarily through surface complexation and the disruption of metal-colloid bonds under acidic conditions (pH ≈ 3). In this soil type, the low clay and organic matter content results in weaker metal sorption, making complex formation with carboxylate and phosphonate groups the dominant extraction mechanism. EDTMP, with its multiple phosphonate groups, forms particularly stable complexes and therefore mobilises Pb and Cu more efficiently than TA or NTA, especially at higher concentrations (0.2 M - 0.5 M).

The high permeability of sandy loam promotes the downward migration of acidic solutions and mobilised metals, which under field conditions could pose a risk to groundwater quality. Acidification to pH = 3 reduces the soil's buffering capacity and enhances the leaching of base cations (Ca, Mg, K), potentially weakening soil structure and

long-term fertility. Although these processes are controlled in laboratory settings, transferring them to natural environments would require additional hydraulic control and protective measures.

The efficiency of extraction is also influenced by metal speciation: Pb is commonly associated with oxides and carbonates, Cu with organic matter, and Zn with weaker sorption sites, resulting in distinct mobilisation behaviours both kinetically and thermodynamically. In acidic media, strong proton competition for sorption sites accelerates metal desorption and promotes complex formation with organic acids. In sandy loam soils, diffusional limitations are minimal, meaning that extraction is governed mainly by chemical interactions rather than mass-transfer constraints.

The results after 10 and 30 minutes help clarify the dynamics of the extraction process, but the most practically relevant outcome is represented by the concentrations measured after 60 minutes. To illustrate this more clearly, all extraction efficiencies for the 60-minute treatments are shown in Figure 6. Each point represents a tested pair of chelating-agent doses (i_1 molarity on the *x*-axis, i_2 molarity on the *y*-axis), and the labels indicate the mean removal efficiency for Cu, Pb, and Zn at each dose combination.

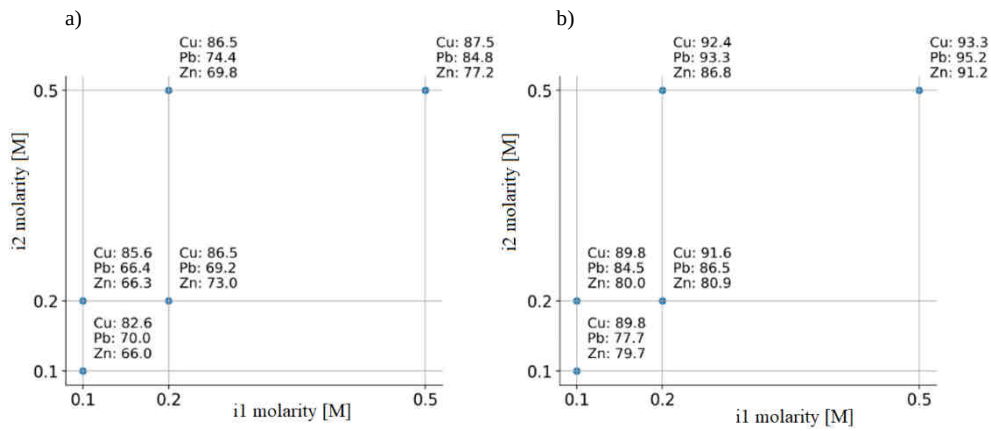

Fig. 6. Combined dose maps of extraction efficiency [%] at 60 min: a) EDTMP (i_1) + TA (i_2) and b) NTA (i_1) + TA (i_2) (pH = 3, t = (20.5 ± 2) °C, n = 3, p < 0.05)

The analysis of the results from the perspective of mathematical modelling shows several noteworthy patterns, even though the current study focuses on general tendencies in the effects of chelating-agent use and therefore includes only a limited number of time-point measurements. Despite this limitation, the existing data already reveal distinct behaviours. In Figures 1a-c, different extraction patterns can be observed: in Figure 1c, the concentration decreases more or less steadily, whereas in Figures 1a and 1b the process appears to be inhibited at the beginning. Modelling attempts for related processes have been reported in the literature [54-56], but the present case may differ due to soil-specific properties such as porosity or chemical composition, which may introduce additional chemical reactions.

From the current results, the most interesting behaviour is seen in Figure 2c (zinc). This is the only case in which the concentration after 30 minutes is noticeably higher than at the beginning of the experiment. Such a temporary increase suggests a potentially important

research gap and indicates that more detailed modelling could provide valuable insights into the mechanisms governing this behaviour.

NTA and EDTA are not readily biodegradable, which leads to environmental persistence and increases the risk of ecotoxicity. Tartaric-acid-based compounds may offer better biodegradability, although available data remain limited. Both NTA and EDTA form highly stable metal complexes - an advantage in industrial applications but a concern when released into the environment. Tartaric acid also forms stable complexes, yet their environmental impact is likely less severe due to the potential for biodegradation.

NTA + TA mixture performs more effectively than the other tested chelating agents because TA acts as a mildly dissociating organic acid that forms weak complexes with metal ions and disrupts their attachment to soil surfaces, thereby increasing the mobility of Zn, Cu, and Pb into the soil solution. At the same time, NTA forms thermodynamically more stable and highly soluble complexes with these mobilised metal ions, preventing them from re-adsorbing onto mineral or organic soil fractions. Through this sequential "mobilisation + stabilisation" mechanism, NTA and TA operate synergistically, which explains why their combination outperforms both individual chelators and mixtures containing EDTMP, the latter often binding too strongly to soil surfaces and reducing overall extraction efficiency.

Limitation of application

The studies were carried out under controlled laboratory conditions (fixed temperature, a single soil type, constant acidic pH, artificial contamination), and these factors should be considered limitations of the experiment. Such controlled settings allow for a precise assessment of the effects of organic acids on heavy-metal extraction, but they do not reflect the natural heterogeneity of soils or the variability of environmental conditions.

In real field (in situ) conditions, temperature, moisture, soil composition, buffering capacity, and pH fluctuate in both space and time, which may lead to extraction efficiencies that differ from laboratory results. Moreover, different soil types vary in cation-exchange capacity, organic-matter content, and mineralogical composition, all of which can significantly influence metal mobility and the effectiveness of organic acids. As a result, extraction efficiencies determined in the laboratory may be either overestimated or underestimated when the method is applied in practice.

Conclusion

1. The most suitable chelating agents under the conditions of this experiment were the combined chelating agents NTA and TA with an extraction time of 60 minutes. Cu and Zn concentrations were reduced to permissible limits even when using the lowest NTA and TA concentration (0.1 M), while the 0.5 M dose and 60-minute extraction time resulted in the lowest concentrations of Cu, Zn, and Pb in the soil - 48 mg/kg, 74 mg/kg, and 78 mg/kg, respectively - and the highest extraction efficiencies of 93.3 %, 91.1 %, and 95.2 %, respectively.
2. The combined chelating agents NTA and TA demonstrated higher extraction efficiencies than the synthetic organic chelating agent NTA alone across different extraction times. The variation in extraction efficiency for the combined chelating agents follows the series: NTA and TA (0.5 M : 0.5 M): Pb > Cu > Zn; EDTMP and

TA (0.5 M : 0.5 M): Cu > Pb > Zn. For synthetic chelating agents used individually, the efficiency series was: NTA: Cu > Zn > Pb; EDTMP: Cu > Pb > Zn.

References

[1] Moliszewska E, Bida I, Matik K, Ślusarczyk A, Pawliczek D, Havryliuk O, et al. Arch Environ Prot. 2025;51:83-91. DOI: 10.24425/aep.2025.153752.
[2] Łyszczarz S, Błońska E, Lasota J. Arch Environ Prot. 2020;46:69-79. DOI: 10.24425/aep.2020.134537.
[3] Zhang Y, Lu X, Deng S, Zhu T, Yu B. Arch Environ Prot. 2024;50:56-71. DOI: 10.24425/aep.2024.149432.
[4] Bolińska MI, Siemieniuk A. Rocz Ochr Środ. 2022;24:41-53. DOI: 10.54740/ros.2022.004.
[5] Dmochowska A, Majder-Lopatka M, Salamonowicz Z, Piechota-Polanczyk A, Polanczyk A. Rocz Ochr Środ. 2021;23:94-105. DOI: 10.54740/ros.2021.006.
[6] Malinowski R, Meller E, Sammel A, Malinowska K, Lisowska S. Rocz Ochr Środ. 2018;20:430-50. DOI: 10.5601/jelem.2022.27.1.2275.
[7] Malić N, Ilić P, Kurilić SM. Ecol Chem Eng S. 2025;32:27-41. DOI: 10.2478/eces-2025-0002.
[8] Jin X, Tong X, Hua S, Xu Y. Ecol Chem Eng S. 2024;31:155-75. DOI: 10.2478/eces-2024-0011.
[9] Bandurska K, Krupa P, Berdowska A, Jatulewicz I, Zawierucha I. Ecol Chem Eng S. 2021;28:277-86. DOI: 10.2478/eces-2021-0020.
[10] Mikhalovsky S, Voytko A, Demchenko V, Demchenko P. Chem J Mold. 2021;16:9-27. DOI: 10.19261/cjm.2021.852.
[11] Abd-Alla MH, Morsy FM, El Enany AWE, Ohyama T. Int Biodeterior Biodegradation. 2012;67:48-55. DOI: 10.1016/j.ibiod.2011.10.008.
[12] Council Directive 86/278/EEC of 12 June 1986. On the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Available from: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31986L0278.
[13] Masindi V. Rijeka: Intech Open. 2018. DOI: 10.5772/intechopen.76082.
[14] Mir AR, Pichtel J, Hayat S. Biometals. 2021;34:737-59. DOI: 10.1007/s10534-021-00306-z.
[15] Natasha N, Shahid M, Bibi I, Iqbal J, Khalid S, Murtaza B, et al. Sci Total Environ. 2022;808:152024. DOI: 10.1016/j.scitotenv.2021.152024.
[16] Aslam M, Aslam A, Sheraz M, Ali B, Ulhassan Z, Najeeb U, et al. Front Plant Sci. 2021;11: 587785. DOI: 10.3389/fpls.2020.587785.
[17] Gluhar S, Kaurin A, Lestan D. Chemosphere. 2020;257:127226. DOI: 10. 1016/j.chemosphere.2020.127226.
[18] Deng T, Zhang B, Li F, Jin L. Chemosphere. 2017;168:450-6. DOI: 10.1016/j.chemosphere.2016.09.152.
[19] Qiao J, Sun H, Luo X, Zhang W, Mathews S, Yin X. Chemosphere. 2017;167:422-8. DOI: 10.1016/j.chemosphere.2016.10.034.
[20] Schmidt CK, Brauch HJ. Env Chem. 2006:211-234. DOI: 10.1007/698_5_019.
[21] Schmidt CK, Brauch HJ. Environ Toxicol Int J. 2004;19:620-37. DOI: 10.1002/tox.20071.
[22] Tounsi N, Dupont L, Mohamadou A, Aplincourt M, Plantier-Royon R, Massicot F, et al. Actual Chim. 2006;293:12-4. Available from: https://new.societechimiquedefrance.fr/numero/n293-janvier-2006.
[23] Mathur JN, Thakur P, Dodge CJ, Francis AJ, Choppin GR. Inorg Chem. 2006;45:8026-35. DOI: 10.1021/ic052166c.
[24] Ke X, Zhang FJ, Zhou Y, Zhang HJ, Guo GL, Tian Y. Chemosphere. 2020;255:126690. DOI: 10.1016/j.chemosphere.2020.126690.
[25] Albrecht M, Dehn S, Raabe G, Fröhlich R. Chem Commun. 2005;45:5690-2. DOI: 10.1039/b509147k.
[26] Alman-Abad ZS, Pirkharrati H, Asadzadeh F, Maleki-Kakelar M. Ads Sci Technol. 2020;38:79-93. DOI: 10.1177/0263617420916592.
[27] Wang Z, Li B, Sun Y, Yang W. J Mar Sci Eng. 2022;10:636. DOI: 10.3390/jmse10050636.
[28] Cheng S, Lin Q, Wang Y, Luo H, Huang Z, Fu H, et al. Arab J Chem. 2020;13:5160-70. DOI: 10.1016/j.arabjc.2020.02.015.
[29] Wang G, Zhang S, Zhong Q, Peijnenburg WJGM, Vijver MG. J Clean Prod. 2018;197:479-90. DOI: 10.1016/j.jclepro.2018.06.225.
[30] Feng Z, Ji S, Ping J, Cui D. TrAC Trends Anal Chem. 2021;143:116402. DOI: 10.1016/j.trac.2021.116402.
[31] Naghipour D, Gharibi H, Taghavi K, Jaafari J. J Environ Chem Eng. 2016;4:3512-8. DOI: 10.1016/j.jece.2016.07.034.
[32] Yang ZH, Dong CD, Chen CW, Sheu YT, Kao CM. Environ Sci Pollut Res Int. 2018;25:5231-42. DOI: 10.1007/s11356-017-9235-7.
[33] Zhai X, Li Z, Huang B, Luo N, Huang M, Zhang Q, et al. Sci Total Environ. 2018;635:92-9. DOI: 10.1016/j.scitotenv.2018.04.119.

[34] Long QB, Zhao HB, Qiu TS, Wu H, Yan HS, Qiu S. Colloids Surf A: Physicochem Eng Aspects. 2025;138247. DOI: 10.1016/j.colsurfa.2025.138247.
[35] Li R, Wang B, Zhao Y, Zhang N, Zhao X, Gao Z, et al. J Environ Chem Eng. 2025;118926. DOI: 10.1016/j.jece.2025.118926.
[36] Li J, Fan J, Sun J, Wang Z, Lv K, Qu Y, et al. SPE J. 2025;30(12):7347-63. DOI: 10.2118/231144-PA.
[37] Li J, Ji YX, Ni XX, Lv KH, Huang XB, Sun JS. Petroleum Sci. 2024;21(3):1980-91. DOI: 10.1016/j.petsci.2024.01.021.
[38] Wu D, Liu J, Sun J, Wang R, Liu J, Wang Y, et al. Fuel. 2026;407:137314. DOI: 10.1016/j.fuel.2025.137314.
[39] Shi L, Li A, Xu Y, Yang H, Yang G. Microchim Acta. 2025;192(5):307. DOI: 10.1007/s00604-025-07157-2.
[40] Shi Y, Jiao Z, Wang J, Wang Z, Chu C, Guo Y, et al. Plant Biotechnol J. 2025;23(8):3164-76. DOI: 10.1111/pbi.70132.
[41] Kashkarov EB, Abdulmenova AV, Krotkevich DG, Syrtanov MS., Paushkina KK., Nassyrbayev A, et al. Ceram Int. 2025. DOI: 10.1016/j.ceramint.2025.06.270.
[42] ISO 10381-3:2001. Soil quality - Sampling - Part 3: Guidance on safety. Available from: https://www.intertekinform.com/en-gb/standards/iso-10381-3-2001-611409_saig_iso_iso_1402214.
[43] ISO 10390:2021. Soil, treated biowaste and sludge - Determination of pH. Available from: https://www.intertekinform.com/en-gb/standards/iso-10390-2021-588283_saig_iso_iso_2964571.
[44] ISO 14688-1:2017. Geotechnical investigation and testing - Identification and classification of soil - Part 1: Identification and description. Available from: https://www.intertekinform.com/en-gb/standards/iso-14688-1-2017-591091_saig_iso_iso_2622740.
[45] Freitas EV, Nascimento C. J Soils Sediments. 2017;17:1272-8. DOI: 10. 1007/s11368-015-1350-9.
[46] ISO 17892-4:2016**.** Geotechnical investigation and testing - Laboratory testing of soil - Part 4: Determination of particle size distribution. Available from: https://www.intertekinform.com/en-gb/standards/iso-17892-4-2016-606906_saig_iso_iso_1391168.
[47] Yan D, Guo Z, Xiao X, Peng C, He Y, Yang A, et al. J Environ Manage. 2021;296:113174. DOI: 10.1016/j.jenvman.2021.113174.
[48] Adewumi AJ, Ogundele OD. Sust Environ. 2024;10:2293239. DOI: 10.1080/27658511.2023.2293239.
[49] Nishimura S, Yonemura S, Minamikawa K, Yagi K. J Geophys Res Biogeosci. 2015;120:63-76. DOI: 10.1002/2014JG002746.
[50] Wasay SA, Barrington SF, Tokunaga S. Environ Tech. 1998;19:369-79. DOI: 10.1080/09593331908616692.
[51] Pikuła D, Stępień W. Agronomy. 2021;11:878. DOI: 10.3390/agronomy11050878.
[52] Riedel R, Krahl K, Buder K, Böllmann J, Braun B, Martienssen M. J Microbiol Methods. 2023;212: 106793. DOI: 10.1016/j.mimet.2023.106793.
[53] Baek NH, Clesceri NL. Water Res. 1986;20:345-9. DOI: 10.1016/0043-1354(86)90082-5.
[54] Ponizovsky AA, Mironenko EV, Studenikina TA. Commun Soil Sci Plant Anal. 1999;30:21-30. DOI: 10.1080/00103629909370181.
[55] Zhang W, Tsang DCW. Chemosphere. 2013;91:1281-8. DOI: 10.1016/j.chemosphere.2013.02.034.
[56] Di Palma L, Verdone N. Chem Eng Trans. 2012;28:193-8. DOI: 10.3303/CET1228033.