

Extraction of zinc and copper from a contaminated soil by using organic acids

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Numerous studies reveal that chemical extraction of heavy metals is one of the most effective soil treatment methods and it is often applied to cleaning polluted areas. Chemical extraction is used as an *ex-situ* approach, so the price is higher compared to the *in-situ* (most of the price consists of plowing, transporting and warehousing of contaminated soil). Despite the higher price, chemical extraction method is not only effective but also fast – >80% of cleaning efficiency can be achieved in a few hours. Although the method is characterized by high efficiency, chemical extraction has not yet been applied for heavy metal contaminated soil treatment in Lithuania. The dependence of chemical extraction efficiency on variable parameters – organic acid type, concentration and temperature are analyzed. The optimum extraction parameters are set by cost-benefit analysis and highest metal removal efficiency. The aim of this work was to optimize the process of zinc and copper removal from contaminated soil using biodegradable organic acids (citric acid, tartaric acid, acetic acid). The calculated sorption capacity of soil for Cu, Zn was 95.5% and 44.8%, respectively. It was found using the X-ray fluorescence spectrometry method that 0.05 M tartaric acid and 0.5 M citric acid are the most effective acids among the tested organic acids (acetic acid, citric acid, tartaric acid) for removal of Cu and Zn from contaminated sand soils; extraction efficiency was up to 86% for removal of Cu and up to 94.7% for removal of Zn (temperature - 20 °C, extraction time - 2 h). The maximum extraction efficiency of Cu (95.1%) and Zn (97.7%) was determined using citric acid (C= 0.5 M, t = 2 h) when the extraction was carried out at 80±2 °C. Studies have shown that, from a cost-effective point of view, the most effective way to clean contaminated with Cu and Zn soil is extraction with 0.05 M tartaric acid. Extraction should be carried out at 20 °C for 2 h. In this case, the highest common unit cost efficiency (~ 86.02%) was achieved at the least cost (temperature, acid concentration).

Keywords: Soil, Extraction, Zinc, Copper, Organic acids, Citric acid, Acetic acid, Tartaric acid.

INTRODUCTION

Heavy metals (HM) are natural components of the soil [1, 2]. The sources of heavy metals are of natural or anthropogenic origin. Under natural conditions soil is supplemented with heavy metals by rock desertification and sedimentation processes. In the natural environment, under the influence of a complex of environmental conditions (humidity, temperature changes, erosion, etc.), rock depression and soil formation processes take centuries; while heavy metals do not locally concentrate in this case, their concentrations in soil remain low.

Anthropogenic pollution with heavy metals is characterized by high concentrations of heavy metals, mostly locally or regionally. Soils are significantly supplemented with heavy metals by human activities: metallurgy, galvanizing industry, mining, transport, waste incineration, fertilizer and pesticide use in agriculture. Heavy metals entering the soil should not always be a problem - stable compounds are not dangerous, but not all heavy metals found in the soil form persistent compounds, it depends on the physical and chemical conditions

of the environment. The amount of heavy metal in the soil depends on the amount of moisture and other parameters [3]. Soil contamination with heavy metals is a topical problem, as the change in physical or chemical properties of soil (in the case of more intensive irrigation, low pH), heavy metals are able to migrate to the environment - to pollute groundwater and to enter and accumulate in plants and living organisms [4]. In ionic states, or when combined with organic compounds, heavy metals can be absorbed by algae, plants, and through the dietary chain can reach the primary and secondary consumers, thus peak heavy metal concentrations accumulate in the tissues of end-users [5,6]. Various components of the living environment often fail to adapt to such sudden changes of environmental pollution - this causes degradation of the ecosystem. The pollution of soils with heavy metals and their compounds raises concern and danger due to the durability of metals, their accumulation in the physical environment and persistence in the living organisms. Heavy metals can enter the human body in several ways, with food or fluids, by direct contact and by inhalation [7]. Due to the toxicity and effects on living

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organisms, lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), copper (Cu), zinc (Zn) and nickel (Ni) are classified by USEPA (United States Environmental Protection Agency) as pollutants that are subject to monitoring of their changes in the environment [4]. Settled heavy metals tend to accumulate in the soil, this geological formation is a good indicator of environment pollution with heavy metals. Soil contamination studies often detect concentrations of heavy metals that exceed the limit values - pollution poses a risk to all ecosystem components, including humans [6, 8, 9].

Territories polluted with heavy metals in most European countries, if concentrations of heavy metals are above the permissible limit values, must be cleaned. Soil treatment can be carried out using two principles: *in-situ* and *ex-situ*. Chemical extraction of metals is based on the *ex-situ* principle, therefore its cost is higher than *in-situ* (the major part of price consists of soil excavation, transportation and storage work, the part of chemical reagents is very small). In spite of the higher price, this method of soil treatment is efficient and fast – studies of heavy metal extraction have shown that more than 80% of treatment efficiency can be achieved within a few hours. 88% copper and 86% zinc elimination efficiency after 1 hour contact time at room temperature was reached with sulfuric acid [10]. Application of strong acids for extraction of heavy metals from contaminated soil is not acceptable due to the fact that strong acid reduces the content of organic matter in the soil.

EDTA, nitric acid and hydrochloric acid were used to remove heavy metals from contaminated soils [11]. The efficiency over 70% for lead removal was achieved during extraction of soil with the tested acids - 0.05M EDTA, 1.7% HCl and 10 % HNO₃ using optimized extraction time and acid volumes. Many scientists carried out studies on the extraction of heavy metals from contaminated soils using different chemicals (sulfuric acid, nitric acid, chelators and organic acids – citric acid, PESA, EDTA, EDDS, PDTA, BDTA, IDSA, NTA, HEDTA and EGTA, CDTA, etc. [12-21]. The trivalent heavy metal ions, iron and chromium, were more difficult to be removed than the divalent ions, copper, zinc, nickel, and cadmium. More than 99.9% of heavy metals can be removed from the sludge by treating with 0.5 M sulfuric acid in 2 h [12]. It was found that the extraction of Cr using PESA was more efficient than that using ethylenediaminetetraacetic acid (EDTA) and *S,S*-ethylenediaminedisuccinic acid (EDDS) under similar conditions. The extraction efficiency

reached 58% [14]. The removal efficiencies of Zn, Ni, Cr and Cu reached 53.5%, 40.2%, 35.4% and 13.1%, respectively, using citric acid [15].

The removal efficiencies of Cu, Zn and Pb reached 9.5%, 82.2%, and 87.3%, respectively, at the optimal 0.325 M concentration of nitric acid assisted by ultrasound for 20 min [16]. Zinc and nickel were the heavy metals having the best removal efficiency with citric acid. EDTA gives better results for extraction of copper, cadmium and lead from biosolids [17]. Citric acid was more active than H₂SO₄ for leaching heavy metals (Mo, V, Ni, and Co) from a spent catalyst [18]. The combined application of EDTA and EDDS significantly increased the extraction of heavy metals (especially Pb) from the soil [19]. 0.05 M EDTA and 0.1 M citric acid were tested for the simultaneous extraction Cu, Pb and Zn from an Italian harbour sediment. Best extraction efficiency was achieved using 0.05 M EDTA solution [20]. Soil washing using EDTA and three of its derivatives:

CDTA (trans-1,2-cyclohexanediaminetetraacetic acid), BDTA (benzylidiaminetetraacetic acid), and PDTA (phenyldiaminetetraacetic acid) was tested for extracting Cu²⁺, Zn²⁺, Ni²⁺, Pb²⁺, and Fe³⁺ from a contaminated soil [21]. It was determined that the best extractant was PDTA, worse extractants were EDTA and CDTA. BDTA was the least effective extractant [21]. Removal of Cu, Ni and Pb from soil was achieved using IDSA, NTA, HEDTA and EGTA. Metal extractions ranged between 80 and 97% using IDSA as the best extractant [22]. The extraction of heavy metals from soil can be carried out using EDDS [23]. Different chemicals have been used to remove zinc from the soil: EDTA, NTA, citrates, tartrates, oxalates, and EDTA, citrates, DTPA, sulfides, EDDS – for removal of copper from the soil. A hybrid method involving chelating agents and microorganisms can be applied for removal of heavy metals from electronic waste [24]. Chelating agent GLDA was tested for removal of cadmium, nickel, copper and zinc from industrial sludge [25]. About 89 % cadmium, 82 % nickel, 84 % copper and less than 50 % zinc elimination efficiency was achieved from industrial sludge applying GLDA [25]. Pb removal from contaminated soils applying low molecular weight organic acid (LMWOA) – citric acid (CA), malic acid and nanoscale zero-valent iron (nZVI) were investigated. The maximum Pb removal efficiencies reached 72% for mine soil and 87% for farmland soil after 4 h by the mixed solutions of CA and nZVI, respectively [8].

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Low molecular weight organic acids such as acetic acid, oxalic acid and citric acid could be used for removal of heavy metals from polluted soil [26]. During chemical extraction of heavy metals from the contaminated soil it is important to remove both forms of metals - mobile and immobile. The extraction of metals from soil with organic ligands depends on the competition between the metal-binding functional groups from the sludge structure and the organic chelator [15]. Physical and chemical extraction reaction conditions can be changed for increasing of effectiveness of contaminated soil treatment.

The aim of this work was to optimize the process of zinc and copper removal from contaminated soil using biodegradable organic acids.

METHODOLOGY

Scheme of experiment:

1. Sampling of soil.
2. Determination of soil type and pH before pollution.
3. Determination of total carbon quantity in soil.
4. Contamination of soil with aqueous solutions of zinc and copper nitrates.
5. Determination of zinc and copper concentrations in contaminated soil samples and pH determination.



Fig. 1. Soil sampling points

Samples were taken with a steel rack at a depth of 10 cm, and about 650 g of soil were taken from each point. The total mass of soil was about 10 kg. The collected samples were placed in the same container to form a composite sample. Soil was transported to the laboratory, dried at 38 °C temperature for 24 h, sieved through 3 sieves - 2 mm, 0.25 mm and 0.125 mm for determination of soil type. Soil fraction with a size smaller than 2

6. Extraction of heavy metals from soils applying organic acids.

7. Determination of the effect of temperature and acid concentration unit efficiency on the removal of copper and zinc.

All reagents used in the research were of analytical reagent grade, deionized water meets the requirements of LST EN ISO 3696: 1996 standard.

Instruments used in the study:

X-ray fluorescence spectrometer Niton XL2;
TOC Analyzer Shimadzu TOC V;
Elution shaker C. Gerhardt GmbH and Co.KG - Rotoshake RS12;
Mettler Toledo pH meter;
Electric chopper-homogenizer;
Radwag AS60/220 laboratory balance.

Collection of soil samples

Soil samples were taken from an unbuffered, natural area - in the meadow near the coniferous forest in the territory of Ukmergė town. The nearest industrial or energetic company was more than 2 km away from the sampling point. The chosen area is near to the Bugeniai village (coordinates X-546828, Y-612062). The sample locations are arranged in a grid of 20 meters (120 meters from the road and 100 meters from the nearest building) (see Fig. 1).

mm was selected for pH determination and pollution with the investigated heavy metal salts (nitrates).

Determination of soil type, pH and metals concentrations before pollution

The type of soils that are predominant in the territory of Lithuania was chosen for the study. According to standards EN ISO 14688-1:2002 and

EN ISO 14688-2:2004 was determined as sand soil type.

pH of the soil was determined according to standard LST ISO 10390: 2005. 20 g of analysed soil was mixed with 100 ml of 0.1 M KCl solution, shaken for 1 h with the Elution shaker C. Gerhardt GmbH and Co.KG - Rotoshake RS12 and filtered through a 0.45 µm filter. pH of the separated suspension was measured with a Mettler Toledo pH meter; pH of the suspension was 7.9. Deionised water (5 l) of was mixed with 3 kg of soil. The soil was stirred for 30 min with an electric grout mixer, after which the soil was filtered through a 0.45 µm filter. The filtered soil was dried at 38 °C for 24 h. Five samples of 30 g of soil were collected and background concentrations of heavy metals (Cu and Zn) were measured with the X-ray fluorescence spectrometer Niton XL2. Concentration of copper was 15.45±3 mg/kg, concentration of zinc was 42.22±2 mg/kg.

Determination of total carbon quantity in soil

Quantity of total carbon in soil was 2.5-3.0 %. It was determined using the TOC Analyzer Shimadzu TOC V.

Pollution of soil with aqueous solutions of zinc and copper nitrates

Limit values for metals in soil according to Lithuanian hygiene norm HN 60:2015 are these: 75 mg/kg (Cu) and 300 mg/kg (Zn). Salts of the investigated heavy metals were dissolved in 600 ml of deionised water (2.85 g Cu(NO₃)₂×3H₂O and 13.5 g Zn(NO₃)₂×6H₂O). Ratio of solution: soil was 2:1 (v:w).

Determination of zinc and copper concentrations in polluted soil samples and pH determination

Before the soil extraction tests were carried out, the condition was raised: in the contaminated soil the concentrations of Cu and Zn should be at least 2 times higher than set in the Lithuanian Hygiene Norm HN 60:2015. After contamination with heavy metals, the soil and solution were mixed with the Elution shaker C. Gerhardt GmbH and Co.KG - Rotoshake RS12 for 2 h. After mixing, the soil was filtered through a 0.45 µm filter. The filtered soil was dried at 38 °C for 24 h. The values of heavy metals in the polluted soil were determined with the X-ray fluorescence spectrometer Niton XL2. Concentration of copper in the polluted soil was 9.54 times and concentration of zinc in polluted soil was 4.47 times higher than the limit values presented in the Lithuanian Hygiene Norm HN 60:2015, it means that raised condition was achieved. After contamination of soil with heavy metals salts pH decreased to 3.9.

Extraction of heavy metals from soils applying organic acids

The research was based on Wang's proposed methodology [15], which used the best-case method in metal extraction studies. The method is based on the fact that the optimal solution to the problem is determined using less resources: all possible variants are not examined, some of them disappear at the initial stage of the study, for example, if the dependence of the extraction efficiency on a single variable parameter, e.g., acid concentration, is investigated, after studies with 3 variables the most effective option found in the next step is the best-defined option (see Table 1).

Table 1. Extraction study using the best-case method.

Acid	Acid concentration [M]	Temperature [°C]
Tartaric acid, Acetic acid, Citric acid	0.05, 0.1, 0.2, 0.35, 0.5	20, 40, 60, 80

The effects of the three variables on the effectiveness were investigated in extraction studies. The main variable was the extractant (organic acid), secondary variables - acid concentration [M] and temperature [°C]. Three organic acids were used in the experiments: tartaric acid, acetic acid and citric acid. The following acid concentrations were used in the studies: 0.05 M, 0.1 M, 0.2 M, 0.35 M and 0.5 M [12,15]. After determination of two optimal organic acids, experiments were carried out with selected concentrations of acids, variable – temperature.

According to the literature review, the maximum extraction efficiency is achieved within the first 2 hours, so the extraction tests were carried out from 0.5 to 24 h (0.5, 2, 8, 24 h). Based on the primary extraction results, the extraction efficiency is practically constant after 2 h; therefore the selected extraction time was 2 h.

Optimal extraction conditions and parameters were found during experiments.

Determination of the effect of temperature and acid concentration unit efficiency on the removal of copper and zinc

The unit efficiency calculation was used for evaluation of efficiency of acid concentration unit and temperature unit. This indicator shows what performance could be achieved with a part of a particular parameter. In this case the obtained efficiency is divided by a certain parameter, the highest value equals 100%, and all other calculations are carried out according to the principle of proportionality. This method is effective for comparing completely different parameters (different acid concentrations, temperatures) if their values are known. This parameter also helps researchers to achieve the best result with the lowest cost. For example with X acid of 0.5 M concentration it was achieved 80% extraction efficiency and with Y acid 0.01 M - 60% efficiency. The highest value is equal to 100%, in

this case unit efficiency of Y acid is 100%, and X acid unit efficiency is just 2.6%. In the analysed case it is better to use Y acid if the cost of acid concentration is estimated. The maximum efficiency is achieved with X acid and reaches 80%. Efficiency of acid unit is higher for Y acid, but overall efficiency is only 60%.

RESULTS AND DISCUSSION

Cu and Zn salts (nitrates) were used for artificial contamination of soil with the investigated heavy metals. The concentration of the metals in the soil was determined by X-ray fluorescence spectrometry. According to the measured concentration of metals in the artificially contaminated soils, the amount of metals absorbed by the soil was calculated. The results of soil absorption capacity are presented in Table 2.

Table 2. The absorption capacity of heavy metals in the test soil and other parameters

Metal	Metal concentration in soil, mg/kg	Limit value according to HN 60:2015	Soil absorption efficiency,%	Exceeding the limit value, times
Cu	715.23	75	95.49	9.54
Zn	1341.03	300	44.85	4.47

It shows that the main condition for soil contamination was achieved - all metal concentrations exceeded the limit value set in the Lithuanian Hygiene Norm HN 60:2015 more than 2 times. Soil mostly effectively absorbed copper - soil absorption efficiency was more than 95%, soil absorption efficiency for zinc was near 45% (Table 2). The investigated soil was homogeneous - the distribution of the metal concentration in different soil samples around the mean value was $\pm 3.6\%$ for Cu and $\pm 5.7\%$ for Zn, accordingly. The homogeneous distribution of metal concentrations in soils is important for extraction studies, as it leads to lower errors of research results.

Dependence of Cu extraction efficiency on acid type and concentration

45 units of contaminated soil (10 g) were used for determining the effect of acid type and concentration on heavy metals extraction efficiency. The extraction time and temperature were constants (2 h, 20 \pm 2 °C). Three different organic acids (tartaric, acetic, citric) and 5 different concentrations (0.05 M, 0.1 M, 0.2 M, 0.35 M, 0.5 M) were used for extraction.

After extraction with organic acids soil pH was in the range from 1.9 to 3.7 depending on acid type and concentration – with tartaric acid (1.9-2.5), with citric acid (2.1-2.5), with acetic acid (2.8-3.7). Dependence of residual Cu concentration in soil on extractant type and concentration is presented in fig. 2.

Figure 2 shows that copper from the contaminated soil was most effectively eliminated by tartaric acid. With all concentrations of tartaric acid, the copper removal efficiency remained similar – it increased with increasing of tartaric acid concentration from 80% to 86.0%.

Citric acid was also effective in removing copper from soil, but at low concentrations (0.05 M and 0.1 M), it was not as effective as tartaric acid. Extraction efficiency was in the range from 67.7% to 85.4 %.

Acetic acid was the least effective on the extraction of copper from contaminated soil. Applying this acid the efficiency of copper extraction ranged from 34.2% to 69% with increasing acetic acid concentration.

Deionised water reduced copper concentration in the control contaminated soil sample by only

14.5%. It can be argued that copper forms solid insoluble complexes with soil particles and is difficult to be removed if the medium is not acidified.

Dependence of Zn extraction efficiency on acid type and concentration

Dependence of residual Zn concentration in soil on extractant origin and concentration is presented in fig. 3.

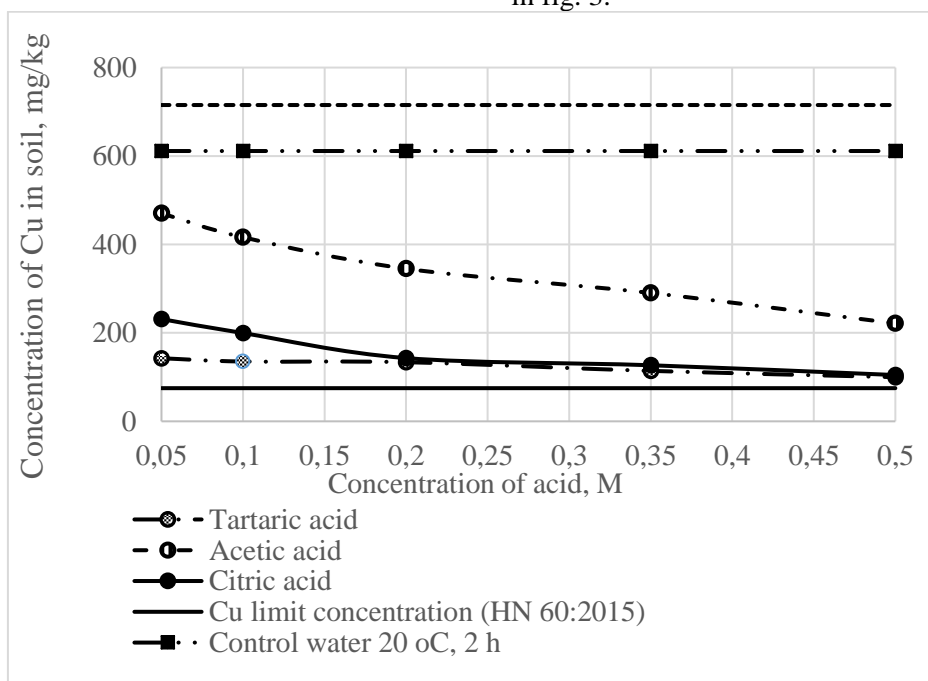


Fig. 2. Dependence of residual Cu concentration in soil on extractant type and concentration, temperature 20 °C± 2 °C, extraction time 2 h.

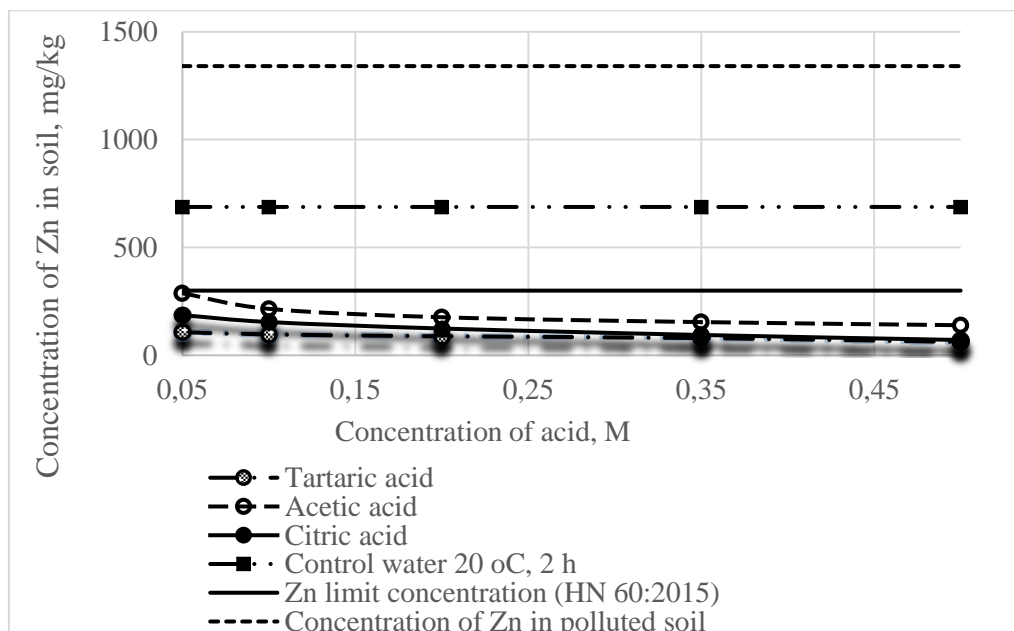


Fig. 3. Dependence of residual Zn concentration in soil on extractant type and concentration, temperature 20 °C± 2 °C, extraction time 2 h.

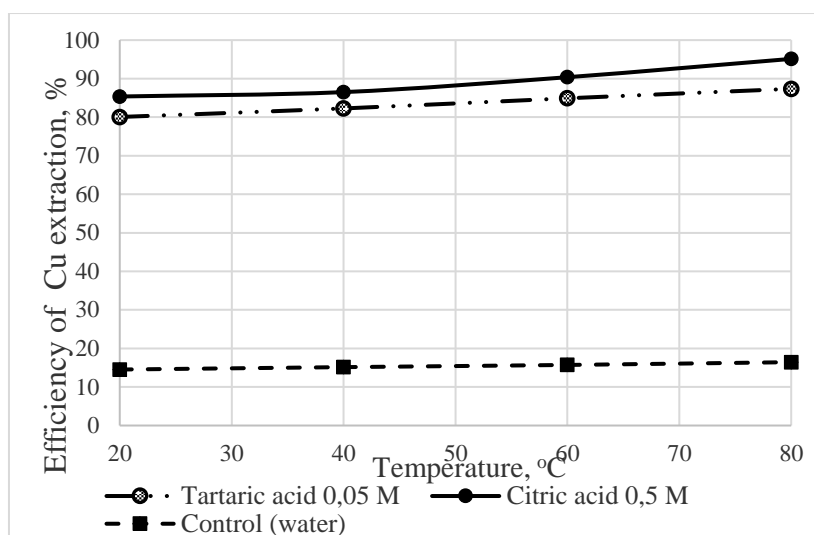


Fig. 4. Dependence of Cu extraction efficiency on the soil temperature, extraction time 2 h.

All three investigated organic acids were very effective for extraction of zinc from contaminated soil (fig. 3). The most effective extractant for removal of zinc from contaminated soils (like in case of copper) was tartaric acid.

With all investigated concentrations of tartaric acid copper removal efficiency was similar - it increased with increasing tartaric acid concentration from 92% to 95.4%.

Citric acid was also effective in removing zinc, but slightly less compared to tartaric acid. The effectiveness of citric acid with increasing acid concentration ranged from 86.1% to 94.7%.

Acetic acid proved to be the least effective. With this acid zinc removal efficiency increased from 78.6% to 89.6% with increasing acid concentration.

Deionised water reduced zinc concentration in the control contaminated soil sample by 48.7%, therefore, in the case of soil contamination with zinc, the primary soil treatment method (taking into account the extent of exceeding the limit value) may be a method of soil washing with water.

Dependence of Cu extraction efficiency on temperature

The efficiency of extraction also depends on the temperature of the solution. Contaminated soil samples (10 g) were used to determine the efficiency of extraction with temperature. In the study of extraction efficiency with temperature, the most effective first-stage acids and their concentrations were used - 0.05 M tartaric acid and 0.5 M citric acid.

Extraction with both mentioned acids was carried out at different temperatures – 20 °C, 40 °C, 60 °C and 80 °C. After extraction soil samples were dried and analyzed using XRF spectrometer. The

obtained data on the concentrations of Cu remaining in the soil samples after rinsing are presented in Fig. 4.

Increasing the temperature from $20 \pm 2^\circ\text{C}$ to $80 \pm 2^\circ\text{C}$ resulted in a slight increase in the removal efficiency of copper from the soil using 0.05 M tartaric acid - only by 7.3%. The maximum removal efficiency was 87.4% at $80 \pm 2^\circ\text{C}$.

The use of 0.5 M citric acid at higher temperature increased the efficiency of copper removal by 9.7%. The maximum copper removal efficiency with citric acid was achieved at a temperature of $80 \pm 2^\circ\text{C}$ and reached 95.1%.

Removal of copper on applying deionised water increased from 14.5% to 16.4% on increasing temperature (Fig. 4). Increasing of temperature had no significant effect on the effectiveness of copper removal from contaminated soil using organic acids.

Dependence of Zn extraction efficiency on temperature

The obtained data on the concentrations of Zn remaining in the soil samples after rinsing are presented in Fig. 5.

With an increase in temperature from $20 \pm 2^\circ\text{C}$ to $80 \pm 2^\circ\text{C}$, the removal of zinc from the contaminated soil with the use of 0.05 M tartaric acid slightly increased as for copper - only by 4% (Fig. 4). The maximum removal efficiency was 96% at $80 \pm 2^\circ\text{C}$.

Using 0.5 M citric acid a slight increase in zinc elimination efficiency was noted with increasing temperature by just 3%. The maximum zinc removal efficiency applying citric acid was achieved at a temperature of $80 \pm 2^\circ\text{C}$ and was 97.7%.

The efficiency of zinc removal from the the control sample of soil with deionised water with increasing temperature increased from 48.7% to 50.6% (Fig. 5).

Increasing of temperature had no significant effect on the efficiency of zinc removal from contaminated soil using organic acids.

It is very important to estimate which acid is more effective for the removal of the selected metals. The most effective was 0.5 M citric acid for extraction of zinc and copper from contaminated soil, but with 0.05 M tartaric acid comparable metal removal efficiency was achieved, 10 times lower tartaric acid concentration being effective enough.

Determination of temperature and acid concentration unit efficiency on removal of copper and zinc

The efficiency of acid concentration and temperature units on copper and zinc common extraction efficiency is presented in fig. 6.

The results of extraction efficiency according to acid concentration unit and temperature unit are quite different, because the tartaric acid concentration is 10 times lower (lower costs) but extraction efficiency is similar to that with 0.5 M citric acid.

In this case the maximum rational efficiency was achieved with 0.05 M tartaric acid at the lowest temperature - 20 ° C (higher cost does not compensate for the benefit of metals removal and it is seen from the above presented results that the temperature does not significantly affect the efficiency of Cu and Zn removal from contaminated soil).

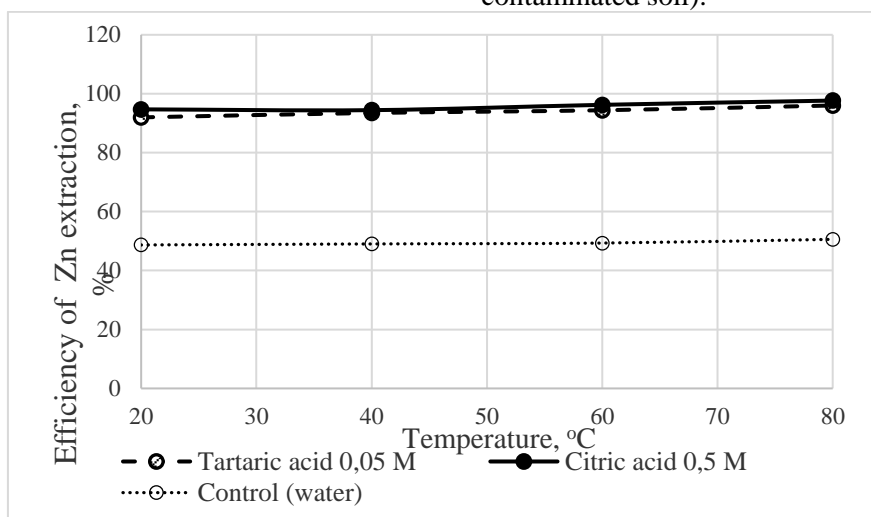


Fig. 5. Dependence of Zn extraction efficiency from the soil on temperature, extraction time 2 h.

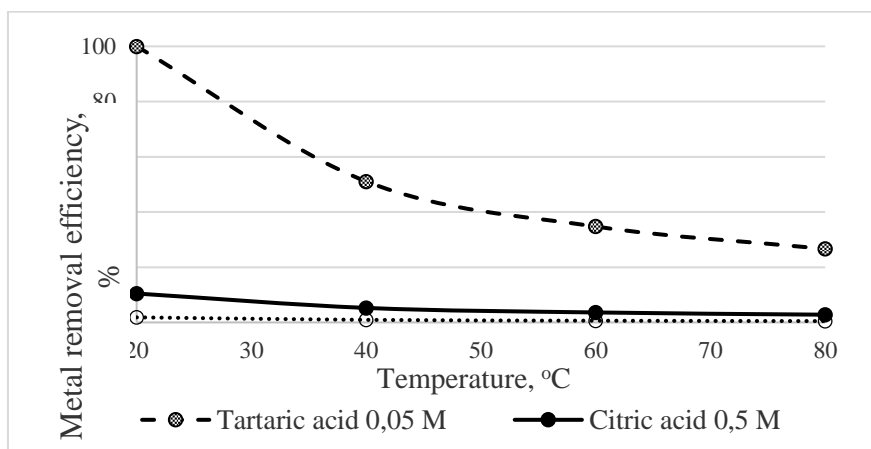


Fig. 6. Efficiency of temperature and concentration unit, % on removal of copper and zinc, extraction time 2 h

The obtained results of the study are ambiguous and should be evaluated depending on the objectives of the application:

Condition 1 – if evaluation is carried out according to the highest metal removal efficiency - in this case 0.5 M citric acid and 80 °C temperature should be used.

Condition 2 - if evaluation is carried out according to the practical application possibilities (in terms of unit temperature and unit efficiency) - in this case it is best to use 0.05 M tartaric acid and $20 \pm 2^\circ\text{C}$ temperature.

Better extraction efficiency was achieved for zinc removal from polluted soil compared to copper using citric acid as extractant. Similar results were obtained by other scientists - the removal efficiencies of Zn and Cu reached 53.5% and 13.1% using citric acid [15]; zinc was the heavy metal having better removal efficiency from biosolid with citric acid, compared to copper [17].

It can be concluded that tartaric acid offers similar extraction efficiency as citric acid. Similar results were obtained by other scientists - citrate removed 80 to 99.9% of all metals (Cd, Pb, Cu and Zn) within 24 h at pH from 2.3 to 7.5. Tartarate removed 84 to 99.9% of all metals from soil within 24 h at pH from 2.1 to 6.7 [27].

It can be concluded that acetic acid is the worst extractant among the tested organic acids.

The efficiency of heavy metals extraction from polluted soil depends on extraction time, type of heavy metals (soluble or not soluble in water), type of organic acid and its concentration, process temperature, quantity of organic carbon and other parameters. Low molecular organic acids such as tartaric and citric are better chelating agents compared to acetic acid and can be applied for removal of heavy metals from soil. These organic acids are environment-friendly and can be decomposed by bacteria.

CONCLUSIONS

1. It has been found using X-ray fluorescence spectrometry that 0.05 M tartaric acid and 0.5 M citric acid are the most effective acids among the tested organic acids (acetic acid, citric acid, tartaric acid) for removal of Cu and Zn from contaminated sand soils; extraction efficiency was up to 86% for Cu removal and up to 94.7% for Zn removal (temperature - 20 °C, extraction time - 2 h).

2. The maximum extraction efficiency of Cu (95.1%) and Zn (97.7%) was found using citric acid (C= 0.5 M, t = 2 h) when the extraction was carried out at $80 \pm 2^\circ\text{C}$.

3. Studies have shown that, from a cost-effective point of view, the most effective way to clean contaminated with Cu and Zn soil is the extraction with 0.05 M tartaric acid. Extraction should be carried out at 20° C for 2 h. In this case, the highest common unit cost efficiency (~ 86.02%) was achieved at the least cost (temperature, acid concentration).

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