Research on the possibility of heavy metals separation from metallurgical wastes using an EDTA extraction and nanofiltration process

Milena Nocoń*, Irena Korus

Silesian University of Technology, Faculty of Environmental Engineering and Energy, Department of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland, email: milena.nocon@polsl.pl

ABSTRACT

Zinc and lead metallurgy generate significant amounts of waste. Among the many types, a large percentage are slags and sediments. Separating heavy metals from wastes using simple processes can become particularly advantageous both because of the possible recovery of valuable components such as heavy metals, but also for environmental reasons. This work presents the results of the extraction process for selected heavy metals from metallurgical wastes (slag from the Short Rotary Kiln, slag from the hazardous waste landfill, and post-neutralization sludge) using ethylenediaminetetraacetic acid disodium salt (Na$_2$EDTA) as a leaching agent. Because heavy metals removal from wastes using an extraction process generates large quantities of post-extraction solutions, the eluates were subjected to nanofiltration to investigate the possibility of metal concentration depending on the varying pH of the process. The metals present in the wastes in the largest amounts, whose removal was studied in the paper, were Pb, Zn, Cu, and Fe in the slag samples and Pb, Zn, and Cd in the post-neutralization sludge. The leaching agent concentration and pH of the extraction process were analyzed in terms of extraction process efficiency. The best efficiency of the leaching process was obtained using a leaching agent solution of 0.15 mol/dm^3 for the slag from the Short Rotary Kiln and 0.075 mol/dm^3 for the other tested samples. For all samples, the highest leaching efficiency was observed at pH = 4, obtaining high removal of Pb (80%), Zn (89%), and Cd (98%), and lower values of separation efficiency of Cu and Fe, not exceeding 30% and 21%, respectively. The use of the nanofiltration process allowed to obtain a high retention rate of metals. The removal efficiency was pH-dependent and the highest retention factor (98%) was obtained at pH = 4 and pH = 10.

Keywords: Heavy metals; Extraction; Nanofiltration; Metallurgical wastes; Zinc and lead metallurgy

1. Introduction

Wastes from the metallurgical industry may be a source of heavy metals such as lead (Pb), zinc (Zn), cadmium (Cd), iron (Fe), copper (Cu), and many others [1,2]. Slags, sludges, suspensions, and dusts are some of the many types of metallurgical waste. Examples of such wastes may include blast furnace slags [3,4], imperial smelting furnace slags [5], sintering, blast furnace or converter sludges [6], and furnace dust [7]. As a source of many heavy metals present in various forms, these materials can be a valuable source of expensive metals. Therefore, the separation of metals by simple, inexpensive, and, above all, effective methods is becoming an important issue. However, the profits for the plants are not the only purpose of separating metals from metallurgical waste. In addition, the continued pursuit of responsible waste management in an environmental sense may be an ancillary aspect. Metals present in mobile forms can, under certain environmental conditions, pass into the environment causing pollution which may create a local problem of contamination, for example, of soils with unwanted metals [1,8]. Thus, the thorough separation of

---

* Corresponding author.

mobile forms of metal compounds from waste is the first of the steps to be taken before waste is sent to the landfill.

One of the most popular methods for heavy metal separation from solid wastes is liquid–solid extraction. For this process, several different types of leaching agents are used. Often used are organic acids [9,10], inorganic acids [11], alkalis [12], or salts [13,14]. Complexing agents are used in the process [15,16] just as often and with satisfactory results for metal removal. The type of agent used, its concentration, and the pH of the process medium are considered key parameters affecting the leachability of heavy metals. It is found, that relatively small changes in pH may result in both increases and decreases in the concentration of leached substances [1]. The dissolution of most minerals, as well as sorption processes, are pH-dependent. In other words, the release of virtually all contaminants that are under control in terms of solubility or sorption is pH-dependent. Cationic components are bound to solid residues on the mineral surface with a certain pH-dependent charge. Thus, the release of cations increases towards low pH values and the release of anions increases towards high pH values [17].

Chelating agents are widely available reagents commonly used in various commercial and industrial applications as ingredients in many products, including detergents, pulp and paper, cosmetics, pharmaceuticals, agrochemicals, and textiles. Na_2EDTA is a widely commonly used leaching agent for heavy metals removal from soil samples [18,19], from industrial and municipal sediments [20] as well as from industrial wastes [21].

Membrane processes are often used for water and wastewater treatment. Among different types of membrane processes, nanofiltration with the use of polymeric membranes demonstrates significant efficiency for heavy metals recovery from liquids [22,23]. The pH of the feed can change the character of membrane surface charge and pore size, dissolved metal species, and thus can affect membrane separation efficiency. The effect of feed pH on the removal of certain heavy metals and permeate flux using nanofiltration membranes has often been studied [24,25].

The work aimed to leach the heavy metals in the liquid–solid extraction process using ethylenediaminetetraacetic acid (EDTA) disodium salt as a leaching agent and concentrate the metals in the obtained solution by nanofiltration process in different feed pH. The effect of EDTA concentration and pH of the leaching agent were studied. The optimal values of these parameters were selected for each type of waste and applied to the extraction process. Obtained extracts under these conditions were subjected to nanofiltration by studying the effect of pH on the retention rate of metals. In the process of slag leaching, metals such as Pb, Zn, Cu, and Fe were analyzed, while Pb, Zn, and Cd were analyzed in the extraction from sludges.

2. Materials and methods

2.1. Sample collection and processing

Slags and sludge from the zinc and lead smelter in Poland were used to investigate the leaching of heavy metals from industrial wastes. Two slag samples were studied: the first was taken directly from the Short Rotary Kiln of the Lead Refining Department (SRK), the second coming from the Short Rotary Kiln but stored for some time at the hazardous waste landfill (SRK HWL) (Fig. 1a and b). The third sample was post-neutralization sludge that came from a metallurgical wastewater treatment plant (SLUDGE) (Fig. 1c). Initially, the slag samples were crushed and grounded in the LJ1 crusher and mill. Then all raw materials were dried at 105°C to a constant mass to determine the moisture content of the samples. All the tested samples were then grounded in the centrifugal ball mill (Retsch S 1000, Katowice, Poland) to the analytical grain with <0.06 mm diameter of the particles, and digested in the microwave-assistance process according to the previously selected procedure by using an aqua regia solution [26]. The digestion process took 8 min at a fixed power of 1,000 W (Milestone MLS 1200 Mega high performance Microwave Digestion Unit, Sorisole, Italy). The predominant metals present in SRK, SRK HWL, and SLUDGE were analyzed in leachates, as well as in solutions after the digestion process using flame atomic absorption spectrometry (AAS) (SpectrAA-880, Varian).

2.2. Solid–liquid extraction for potential recovery of selected heavy metals

Two sets of extraction experiments were carried out – first with the different Na_2EDTA solution concentrations and second with various pH (all tested in triplicate) and the effectiveness of metal recovery was evaluated. A simple solid–liquid
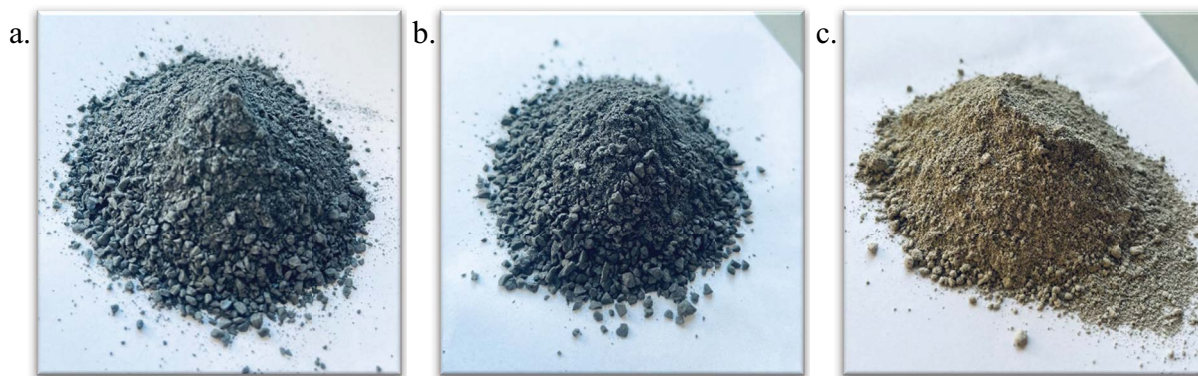

Fig. 1. Tested samples (a) SRK, (b) SRK HWL, and (c) SLUDGES.

batch extraction method was used. This method is commonly used in the metal extraction from solids [27,28]. The extraction test was conducted in the 100 cm³ glass bottles with wide necks containing 0.5 ± 0.0237 g of the samples, and a specific volume of the leaching agent (50 cm³) was added. For samples with varying pH, values were corrected with HNO_3 (Merck, Warszawa, Poland) and NaOH (POCH S.A., Gliwice, Poland). The extraction mixtures were placed on an orbital shaker (OHAUS) and shaken for 21 h at a speed of 250 rpm. After a mixing time, the suspension was filtered through the 0.45 μm cellulose acetate membranes, and metal content was defined by using AAS. The other process parameters were: 1/100 solid/liquid ratio, temperature = 25°C, 1-stage process.

2.2.1. Na₂EDTA concentration leaching test

For the leaching tests, Na_2EDTA was used, in varying concentrations. This agent is often used in various leaching tests [15,29,30]. To analyze the effect of leaching agent concentration on extraction efficiency, metal extraction was carried out using varying concentrations of Na_2EDTA solution: 0, 10, 50, 75, 100 and 150 mmol/dm³ without pH adjustment.

2.2.2. Effect of pH leaching test

In order to analyze the effect of pH on leaching efficiency, metal extraction of each sample for the leaching agent concentration selected in the earlier step was carried out. The leaching agent concentrations used were: 150 mmol/dm³ for SRK and 75 mmol/dm³ for SRK HWL and SLUDGE samples. The analysis was conducted for 5 pH values of the mixture: 4, 5, 7, 9, 11.

2.3. Sequential extraction before and after leaching tests

Sequential extraction of selected metals in all tested materials were carried out using a modified three-stage sequential extraction procedure (BCR – Community Bureau of Reference, European Commission) [31]. The leaching process for each metal fraction in the 1st, 2nd, and 3rd stages was carried out in centrifuge tubes placed on an Ohaus Orbital Shaker (250 rpm, 16 h). Separation from the liquid was then carried out using an MPW-380 centrifuge (3,000 rpm, 20 min). The sample residue between extraction steps was washed by adding 20 cm³ of demineralized water. The residue from the third step was subjected to microwave-assisted digestion with aqua regia solution, maintaining a constant power of 1,000 W for 8 min. The resulting solutions were then analyzed for Zn, Pb, Cu, and Fe concentrations for the SRK and SRK HWL samples and the SLUDGE sample for Pb, Zn, and Cd using AAS. The total sum of the four metals (Pb, Zn, Cu, and Fe) in each fraction was adjusted to 100% based on the relative proportions for each metal. The extraction was carried out twice: first on a separate raw sample of the test materials before the leaching processes, and later on the residue of each sample after the leaching process under the selected optimal process parameters. The process was carried out to compare the effect of extraction on the mobility of metals in the materials under study.

2.4. Nanofiltration process

Thin-film composite polyamide membrane from SUEZ S.A., Paris, France was used in the test. The membrane was soaked in distilled water for 3 h, then conditioned at a pressure range of 10–20 bar to stabilize the flux. The average permeability of pure water was then determined at pressure of 14 bar (A = 1.54 [L/(m²/h·bar)]). Filtration was carried out using a laboratory stirred cell, made of steel and working in the dead-end mode, presented in Fig. 2. Feed solution consisted of mixtures obtained during extraction. Before the process, the pH was corrected using NaOH (POCH S.A., Gliwice, Poland) or HNO_3 (Merck, Warszawa, Poland) solutions, and these values were 2, 4, 6, 8, and 10. 200 cm³ of the feed with the corrected pH was poured into the system, which was
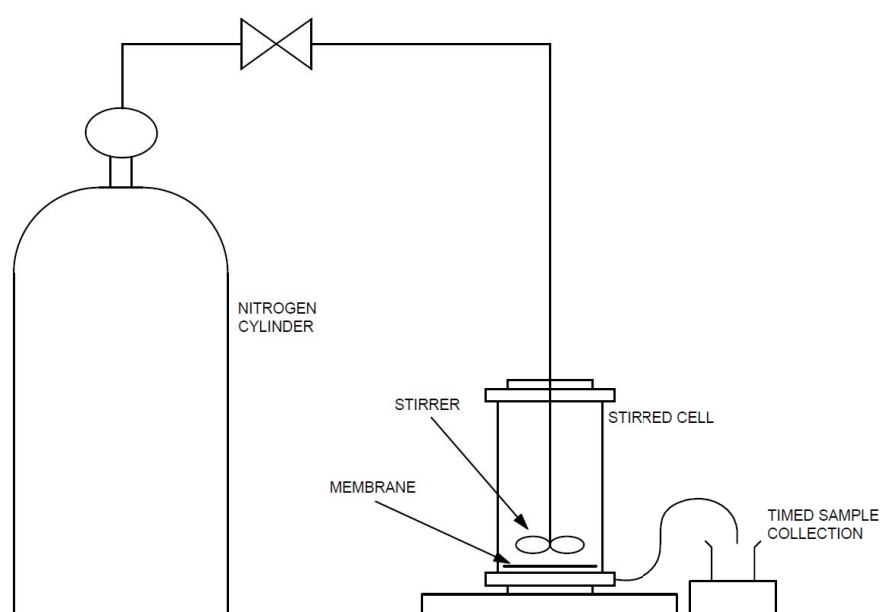

Fig. 2. Schematic diagram of the dead-end nanofiltration system.

operated at 14 bar. 15 cm³ of permeate was collected to avoid concentrating the solution. The metal content of the permeate was then analyzed using AAS. The process was carried out at room temperature. The metals in question retention coefficient were calculated based on Eq. (1):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p and C_f mean the solute concentration in the permeate and feed solution, respectively.

3. Results and discussion

3.1. Characterization of the samples

The total content of metals such as Pb, Zn, Cu, and Fe in the two slags studied was significant, but higher in the slag from the waste landfill than in the slag taken from production, however, the distribution of individual metals was significantly different. More extensive characterization was carried out for all samples before [32]. The metal content in the samples was arranged in the following orders: Fe > Zn > Pb > Cu (SRK slag), Fe > Pb > Cu > Zn (SRK HWL slag), and Pb > Cd > Zn (SLUDGE). Both slags analyzed contained the highest iron content for the SRK and SRK HWL samples, with significantly less zinc, lead, and copper. The content of the main metals was spread slightly differently in the sludge sample. Here the highest content is lead and cadmium. The lowest amount represents zinc.

3.2. Concentration of the leaching agent

Single extraction showed different behavior of metals during the leaching process with EDTA solutions. The differences in metal removal efficiency depended on both the type of metal considered and the type of samples subjected to leaching but also the amount (concentration) of the leaching agent. Fig. 3 shows the dependence of the amount of metals leached from the samples on the concentration of the Na₂EDTA solution used for extraction. The removal of four metals: Pb, Zn, Cu, and Fe for SRK and SRK HWL samples and Pb, Zn, and Cd for SLUDGE sample increased with increasing EDTA disodium salt concentration with the range 0–150 mmol/dm³. The highest metal removal efficiency was observed for the concentrations 150 mmol/dm³ for SRK samples and 75 mmol/dm³ for SRK HWL and SLUDGES samples when the higher concentrations of the leaching agent reached a constant level. For these conditions, Pb removal reached 97.75%, 93.7%, and 82.0%, and Zn removal was 34.4%, 30.3%, and 89.19% for SRK, SRK HWL and SLUDGES samples, respectively. Cu and Fe removal was assessed only in the slag samples and indicated the removal efficiency of Cu - 20.5% and 52.1%, Fe - 21.53% and 9.9% for SRK and SRK HWL, respectively. Cd was removed in 98% of the SLUDGE sample. The total removal of Pb, Zn, Cu, and Fe was 33.9% for SRK sample and 34% for SRK HWL sample. For SLUDGE, Pb, Zn, and Cd were extracted in 90.7%.

EDTA can form coordinated chemical bonds with divalent cations and form complexes, then it facilitates the solubilization from the solid to the leaching solution. Quite a big difference in the efficiency of the removal for all of the metals can be caused by the competitive character of the metals [29]. This effect is visible in the case of lead. While the effectiveness of the lead removal reached almost 100%, the leaching efficiency of the other metals did not exceed the 38% in the SRK and 60% in the SRK HWL samples. While at increasingly higher concentrations of the leaching agent, the recovery of lead minimally decreased, a gentle increase in the extraction efficiency of the other metals could be observed (Zn, Cu, and Fe). This effect was not observed in the SLUDGE samples. The situation in which lead leaches much better compared to the other metals tested was often found in the literature [19,33,34]. However, different results can be found in the literature, according to which lead is leached to a small extend compared to other metals from other industrial and municipal wastes [35,36]. Despite the different values of the constant of formation of metal complexes with EDTA (Table 2), these values do not fully explain the observed differences. The mobility of metals present in the waste matter was likely the factor that played a more important role in determining the leaching behavior. Pb in the SRK and SRK HWL samples is present in mobile form in greater amounts among the other metals tested, which is reflected in its fastest and highest elution. In the SLUDGE sample, it was Zn and Cd that were present in mobile form to the greatest extent compared to Pb resulting in higher elution efficiencies for both metals in comparison to Pb, which nevertheless also showed high elution efficiency. This indicates that metal leaching can depend on many factors, but it is the mobility of the metal that may be critical.

3.3. pH of the leaching agent

The pH of the solution is an important factor in determining the effectiveness of heavy metal extraction using chelates. It can affect the retention of metals in the solid sample, as well as the ability of the chelating agent to extract metals by various mechanisms.

When the pH in 0.075 and 0.15 mol/dm³ Na₂EDTA solution is lower than 4, Na₂EDTA becomes less dissolvable. Naturally, improving the solubility and mobility of Na₂EDTA at the right pH during extraction will promote the formation of stable and soluble complexes with heavy metals. The effect of pH on metal removal efficiency is shown in Fig. 4. For the SRK sample, the best efficiency of the metals removal was observed by using Na₂EDTA solution with a pH = 4. In such a case, a leaching efficiency was as follows: Pb - 100%, Zn - 48%, Cu - 26%, and Fe - 32%. For this sample, the greatest effect of the pH used was seen for Zn and Fe, and leaching efficiencies in solution at pH = 11 were Zn - 11% and Fe - 2%. For Pb and Cu, this effect was not strongly evident and their separation effectiveness remained relatively constant for each solution pH. The removal of Zn and Fe showed a high dependence on the pH of the solution in the SRK HWL sample, and so, for a solution with pH = 4, the removal efficiency of these metals was Zn - 47% and Fe - 10% and at pH = 11: Zn - 9% and Fe - 1%. As in the case of the SRK sample, the removal of lead and copper showed no significant dependence on the pH of the solution. For the SLUDGE sample, the removal of metals such as Pb, Cd, and Zn was not highly dependent on pH for all the tested pH ranges.
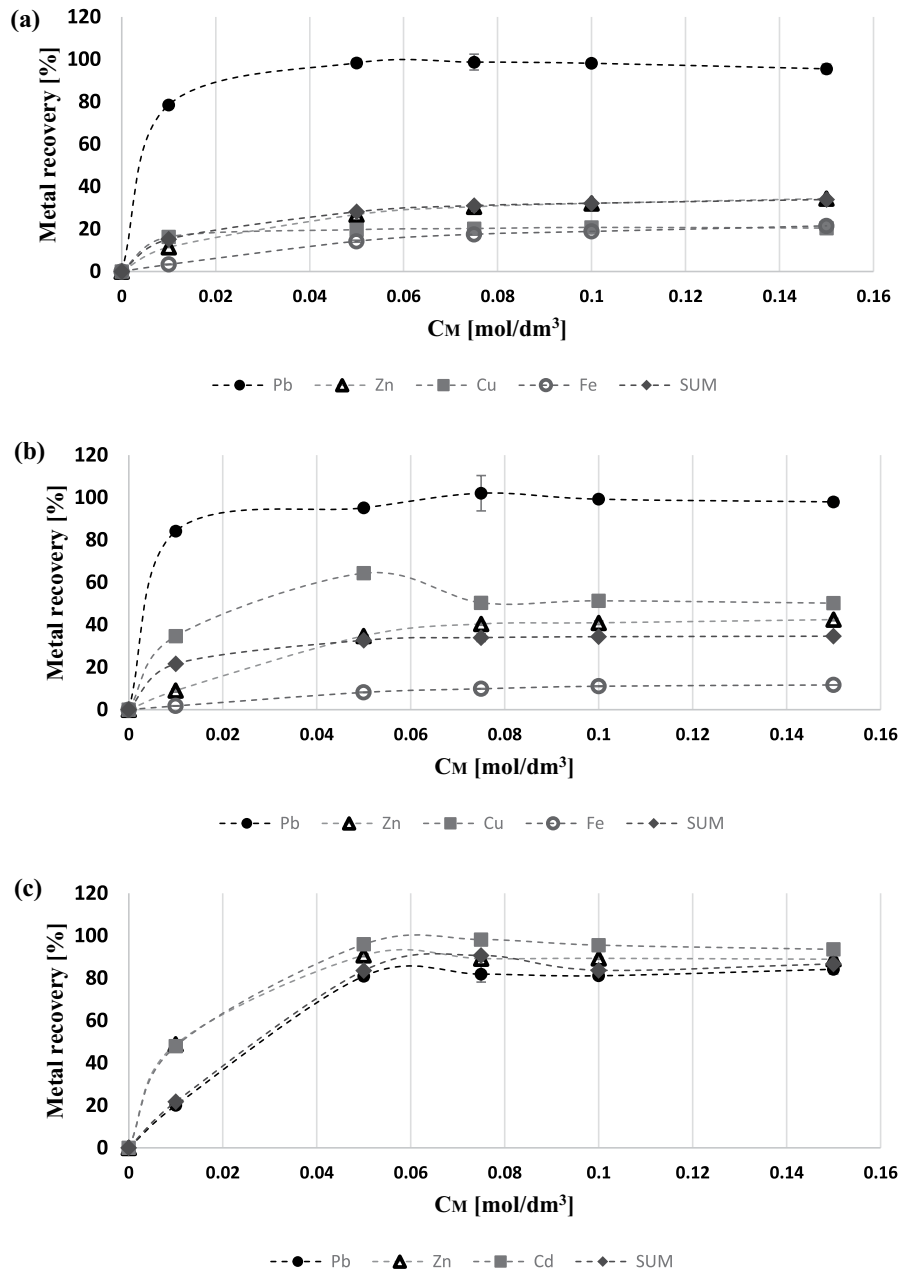
Fig. 3. Metals recovery dependence on the Na₂EDTA concentration for (a) SRK, (b) SRK HWL, and (c) SLUDGES samples.

Overall, for the slag samples, it can be concluded that for the total metals, the use of the lowest pH (pH = 4) gave the best removal effect - 44% and 33% for the SRK and SRK HWL samples, respectively. The metal leaching efficiency decreased with increasing applied pH, and for the highest pH (pH = 11), the efficiency was - 17% and 27% for the SRK and SRK HWL samples, respectively. A similar phenomenon was observed in the results of other studies where EDTA was used as a leaching agent for heavy metal separation [15,38].

3.4. Sequential extraction analysis

BCR sequential extraction analysis enabled the separation four fractions of metals: acid-soluble (F1), bound to iron and manganese oxides (also known as reducible) (F2), oxidizable (F3) and residual (F4). The acid-soluble fraction of heavy metals is the most mobile form, which shows a tendency to be bioavailable. The availability of the other fractions (F2 and F3) are diverse and depend on the conditions. Fraction F2 also called "potentially available" may be released into the environment in the reducing conditions, but slower than the F1. F3 can also be considered potentially mobile however, this faction will only be available under oxidizing conditions [39,40]. In contrast, the residual fraction (F4) is an immobile and biologically inaccessible fraction that is strongly bound to the mineral matrix. Sequential extraction and evaluation of the mobility of individual metals was carried out for all samples before leachability tests.
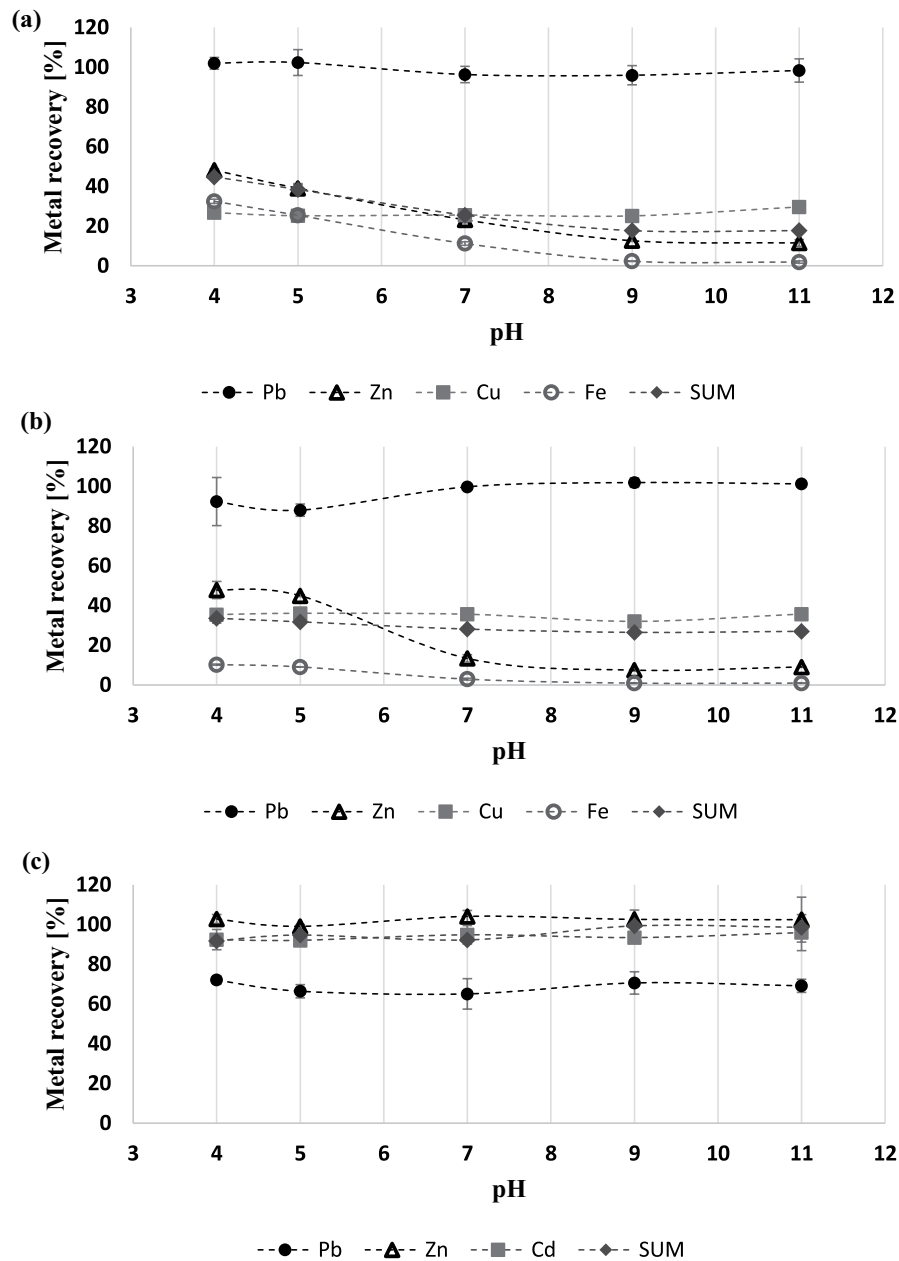
Fig. 4. Metals recovery dependence on the pH of the leaching agent for (a) SRK, (b) SRK HWL, and (c) SLUDGES samples.

Then, for comparison purposes, the same analysis was performed for the sample residue after leaching in the following conditions:

- SRK: 150 mmol/dm³ Na₂EDTA, pH = 4, *t* = 25°C, 1-stage process, S/L = 1/100, 200 min,
- SRK HWL: 75 mmol/dm³ Na₂EDTA, pH = 4, *t* = 25°C, 1-stage process, S/L = 1/100, 200 min,
- SLUDGE: 75 mmol/dm³ Na₂EDTA, pH = 4, *t* = 25°C, 1-stage process, S/L = 1/100, 200 min.

The results of the sequential extraction before and after the extraction process are shown in Fig. 5. A significant difference in the content of individual fractions between slag and sludge samples is apparent. In general, the lead for the slag samples in the raw material before extraction was mostly present in F1, that is, in the most mobile fraction (80%). After extraction, the share of this lead fraction decreased significantly (to about 20%–30%). Naturally, as the percentage of F1 decreases, the contents of the other fractions (F2, F3, F4) increase while the proportions among the forms F2, F3, F4 stay the same. This is clear evidence that extraction with Na₂EDTA solution leaches mainly the most mobile form of the lead. For the other metals, the proportion of the residual form in the raw slag material accounted for almost 50% in each case. The decrease in the most mobile form content as a result of leaching was evident only in the case of Zn and was no more than 15%. In some cases, even a slight increase
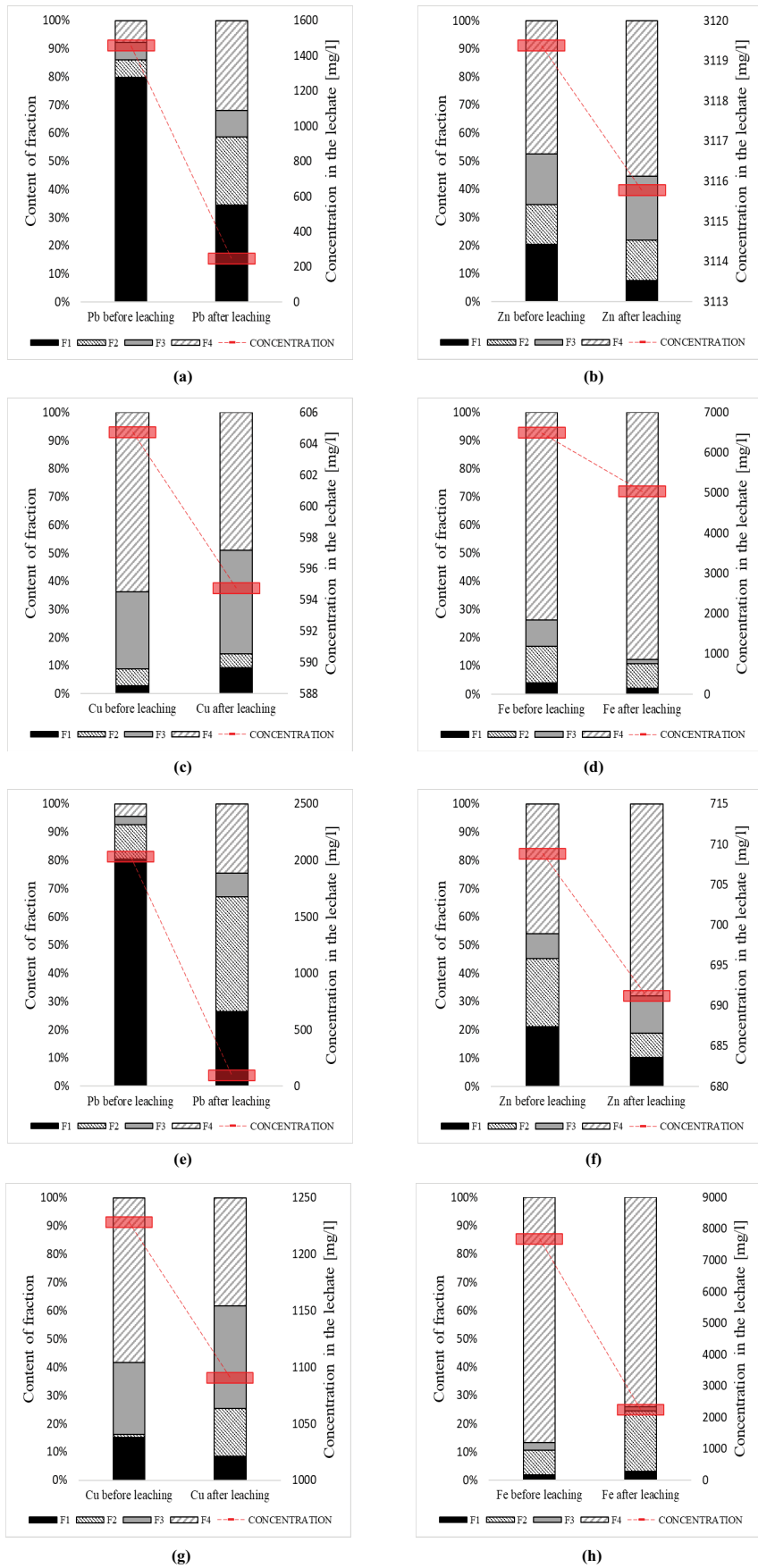
(a)

(b)

(c)

(d)

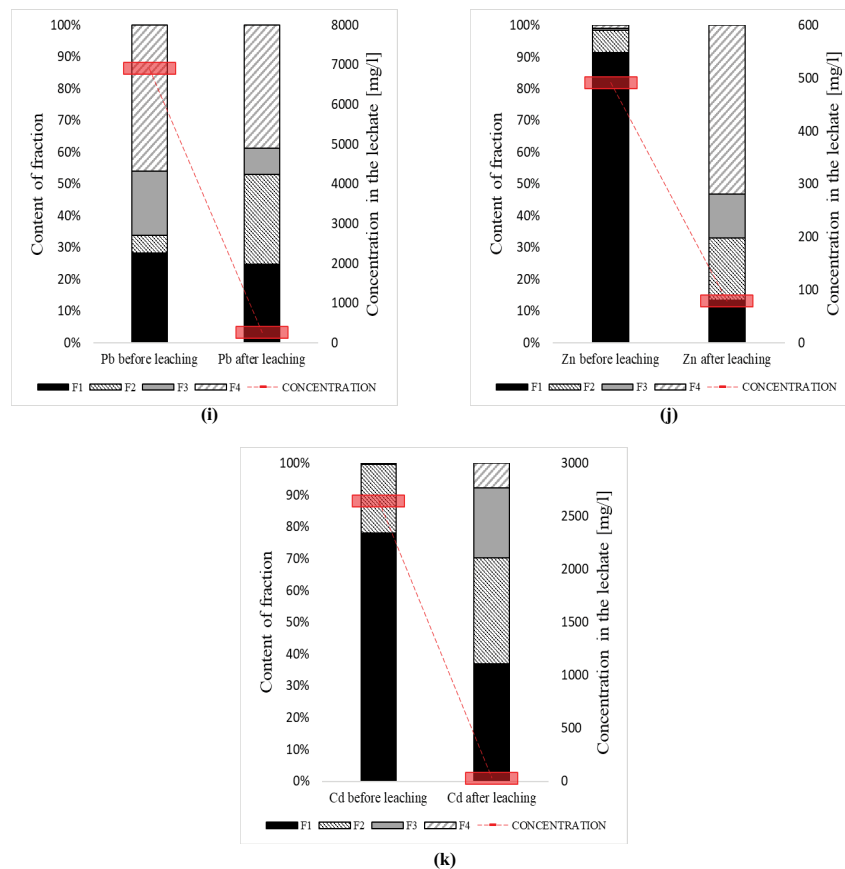(e)

(f)

(g)

(h)

Fig. 5 (Continued)

Fig. 5. Content of individual metal fraction (leachable by BCR method) in samples before and after EDTA extraction and concentration of total metals in the leachates (additional *y*-axis): (a) Pb, (b) Zn, (c) Cu, (d) Fe for SRK sample, (e) Pb, (f) Zn, (g) Cu, (h) Fe for SRK HWL sample, (i) Pb, (j) Zn, and (k) Cd for SLUDGE sample.

in the content of the most mobile fraction was observed after the leaching process (Cu in the SRK sample or Fe in the SRK HWL sample) with a simultaneous decrease in the content of the residual fraction. This could mean that in these cases mainly other metal fractions (F2, F3 or F4) leached out.

For the SLUDGES material, some of the metals (Zn and Cd), were present in the most mobile form (90% and 78%, respectively) with a very low content of F3 and F4 forms. After the leaching process, a significant decrease in the most mobile form content was noted (78% for Zn and 43% for Cd). At the same time, the proportions of the other F2, F3, and F4 fractions increased significantly. This situation may mean that in the case of Zn and Cd, only the most mobile form of these metals was almost completely leached. In the case of lead, which takes almost 30% of the most mobile form before leaching, the extraction process only slightly decreases the share of this fraction (F1) with a decrease in the content of the F3 and F4 fractions and an increase in F2. This could indicate simultaneous leaching of the most mobile form (F1) and organic form (F3) of this metal during the extraction process with Na_2EDTA solution.

3.5. Nanofiltration process

Fig. 6 shows the retention of Pb, Zn, Cu and Fe at various pH values. Heavy metals retention during the nanofiltration processes are strongly influenced by pH. In an acidic environment, the high concentration of H^+ ions present in the solution results in progressive neutralization of the negative active centers on the membrane surface. The influence of the membrane charge on the cations and anions retention is therefore significantly limited [41]. For all tested samples high metals retention was observed in the feed solution with pH = 4. In all cases, in the feed solution with pH = 5 metals retention slightly decreases and then, at a higher pH values, increase in retention coefficient was noticeable. In the slags samples the greatest effect of pH on retention rates was observed for Fe. For both slags, the highest retention factor for this metal oscillated around 98% for pH = 10. Nanofiltration is an effective method to further concentrate the metals in the extracts after EDTA leaching and the retention coefficients obtained for all metals give a very high result.

Al-Rashdi et al. [23] during investigating the effect of feed pH on metal retention factors also reported similar phenomenon in case of Cu(II) and As(III). For these metals, metals retention coefficients decreased at the pH of the feed solution higher that 4–5 and then increased significantly at pH = 10. For Pb(II) ions, the influence of pH was not widely visible and retention factors reached maximum for pH = 4 of the feed. Ballet et al. [25] also showed similar phenomenon for Cd ions, where retention of cadmium salts in the pH ~ 5 reached the minimum.
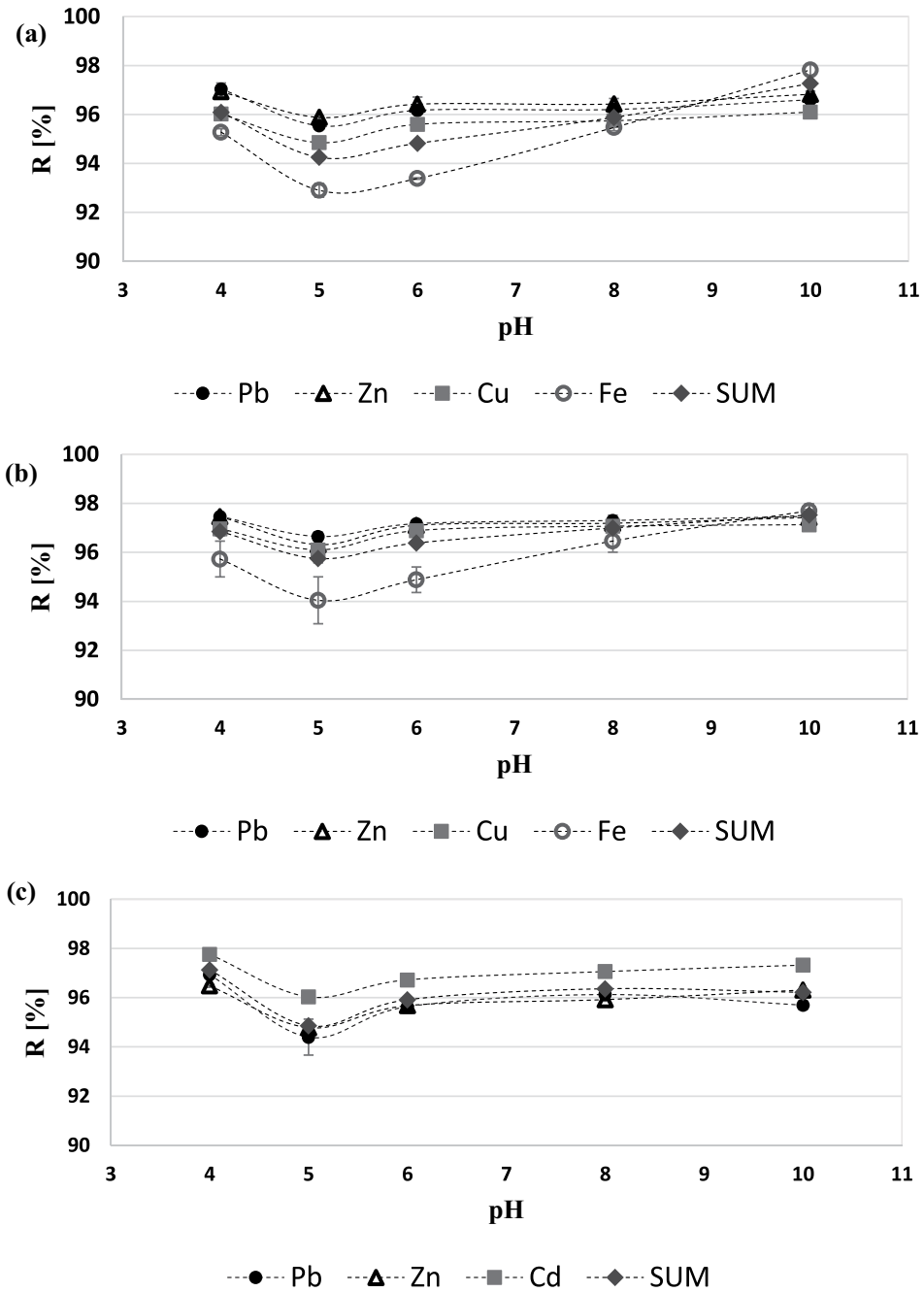
Fig. 6. Retention coefficient as a function of the feed pH for (a) SRK, (b) SRK HWL, and (c) SLUDGE samples.

Table 1
Physico-chemical parameters of analyzed sewage sludge

Total metal content	Value		
	SRK	SRK HWL	SLUDGE
Pb, mg/g	61.8 ± 1.33	98.6 ± 3.41	497.3 ± 34.33
Zn, mg/g	132.0 ± 1.53	27.7 ± 0.34	19.8 ± 0.35
Cu, mg/g	23.1 ± 0.61	49.4 ± 0.67	–
Fe, mg/g	286.1 ± 22.26	348.8 ± 12.43	–
Cd, mg/g	–	–	138.3 ± 12.31

Table 2
Formation constants ($\log K$) for 1:1 metal-EDTA complexes at ionic strength 0.01 M [37]

Pb	18.0
Zn	16.5
Cu	18.78
Fe(III)	25.1
Cd	16.5

4. Conclusions

Na$_2$EDTA extraction of Pb, Zn, Cu, Fe and Cd from three samples was studied by using a single batch leaching experiment. Na$_2$EDTA turned out to be an effective leaching agent for heavy metals removal from the tested samples. Based on the obtained results, it was shown that metal extraction efficiency was the most visible for Pb > Zn > Cu > Fe for the SRK sample, Pb > Cu > Zn > Fe for SRK HWL and Cd > Zn > Pb for SLUDGE samples. The leaching performance of metals is influenced by several factors: concentration of the leaching agent, as well as its pH, the type and origin of the sample, the type of metal under study, and its form of occurrence in the materials in terms of mobility. The best extraction efficiency was obtained by using a 150 mmol/dm^3 Na$_2$EDTA solution for the metal leaching from SRK sample, and 75 mmol/dm^3 for the metal leaching from SRK HWL and SLUDGES samples. In the different pH of the solution, the influence of this parameter was obvious on the metal leaching efficiency for the slag's samples. The acidic conditions increase the mobility of heavy metals. When the pH value was 4, the summary extraction efficiency was 44% for SRK and 33% for SRK HWL. For the sludge sample, pH was not a variable affecting the efficiency of metals extraction. Sequential extraction carried out before and after the leaching process showed that for metals that were available in significant amounts in materials in the most mobile form, leaching with a Na$_2$EDTA solution allowed the metal to leach largely from this form. Other fractions were not so readily available.

Using a nanofiltration process to concentrate the metals in the eluents gave very good results. Metals retention for all three samples did not descend below 93% in any cases. Varying pH yielded different retention rates, but they were within a wide range of efficiencies (93%–98%) and still gave high retention of all metals tested. This means that running a nanofiltration process for concentrating metallurgical waste extraction solutions yields high retention rates of metals over a wide range of feed pH.

Acknowledgements

References

[1] A. Król, K. Mizerna, M. Bożym, An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag, J. Hazard. Mater., 384 (2020) 121502, doi: 10.1016/j.jhazmat.2019.121502.

[2] T.T.T. Dung, A. Golreihan, E. Vassilieva, N.K. Phung, V. Cappuyns, R. Swennen, Insights into solid phase characteristics and release of heavy metals and arsenic from industrial sludge *via* combined chemical, mineralogical, and microanalysis, Environ. Sci. Pollut. Res., 22 (2015) 2205–2218.

[3] T. Wang, L. Yang, F. Rao, K. Jiang, C. Byrynnai, Effect of chitosan on the mechanical properties and acid resistance of metakaolin-blast furnance slag-based geopolymers, Environ. Sci. Pollut. Res. Int., 16 (2023) 47025–47037.

[4] B.F. Belov, A.Ya. Babanin, Nanostructural analysis and adsorption capacity of blast-furnace slags, Metallurgist, 66 (2022) 445–450.

[5] N.-H. Yin, Y. Sivry, F. Guyot, P.N.L. Lens, E.D. van Hullebusch, Evaluation on chemical stability of lead blast furnace (LBF) and imperial smelting furnace (ISF) slags, J. Environ. Manage., 180 (2016) 310–323.

[6] M. Alwaeli, J. Golaszewski, A. Pizon, A. Andrzejewska, P. Szwan, K. Ceglarz, W. Buchta, T. Jachnik, J. Zlotos, Metallurgical sludge as sand replacement and constituent of crushed concrete aggregate, IOP Conf. Ser.: Mater. Sci. Eng., 603 (2019) 032087, doi: 10.1088/1757-899X/603/3/032087.

[7] A.V. Maiorova, T.V. Kulikova, A.B. Shubin, Extraction of zinc and arsenic from metallurgical furnace dust, JOM, 73 (2021) 3588–3596.

[8] S. Różański, Fractionation of selected heavy metals in agricultural soils, Ecol. Chem. Eng. S, 20 (2013) 117–125.

[9] S.-K. Seo, C.-M. Kwon, F.S. Kim, C.-J. Lee, Experiment and kinetic modeling for leaching of blast furnace slag using ligand, J. CO$_2$ Util., 27 (2018) 188–195.

[10] X. Wang, J. Chen, X. Yan, X. Wang, J. Zhang, J. Huang, J. Zhao, Heavy metal chemical extraction from industrial and municipal mixed sludge by ultrasound-assisted citric acid, J. Ind. Eng. Chem., 27 (2015) 368–372.

[11] C.-Y. Kuo, C.-H. Wu, S.-L. Lo, Removal of copper from industrial sludge by traditional and microwave acid extraction, J. Hazard. Mater., 120 (2005) 249–256.

[12] U.S. Mohanty, L. Rintala, P. Halli, P. Taskinen, M. Lundström, Hydrometallurgical approach for leaching of metals from copper rich side stream originating from base metal production, Metals, 40 (2018) 8, doi: 10.3390/met8010040.

[13] R.K. Nadirov, L.I. Syzdykova, A.K. Zhussupova, M.T. Usserbaev, Recovery of value metals from copper smelter slag by ammonium chloride treatment, Int. J. Miner. Process., 124 (2013) 145–149.

[14] Z. Ye, S. Hong, C. He, Y. Zhang, Y. Wang, H. Zhu, H. Hou, Evaluation of different factors on metal leaching from nickel tailings using generalized additive model (GAM), Ecotoxicol. Environ. Saf., 236 (2022) 113488, doi: 10.1016/j.ecoenv.2022.113488.

[15] Z. Ding, Q. Wang, X. Hu, Extraction of heavy metals from water-stable soil aggregates using EDTA, Procedia Environ. Sci., 18 (2013) 679–685.

[16] T. Van Gerven, H.C., K. Imbrechts, K. Hindrix, C. Vandecasteele, Extraction of heavy metals from municipal solid waste incinerator (MSWI) bottom ash with organic solutions, J. Hazard. Mater., 140 (2007) 376–381.

[17] H.A. Van Der Sloot, D.S. Kosson, Leaching Assessment Methodologies for Disposal and Use of Bauxite Residues, Research Report for the International Aluminium Institute (IAI), London, UK, 2010.

[18] A.H. Khalil, S.S. Alquzweeni, H.M. Modhloom, Removal of copper ions from contaminated soil by enhanced soil washing, Int. J. Environ. Res., 4 (2015) 1141–1146.

[19] B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Leaching of heavy metals from contaminated soils using EDTA, Environ. Pollut., 113 (2001) 111–120.

[20] A. Polettini, R. Pomi, E. Rolle, D. Ceremigna, L. De Propris, M. Gabellini, A. Tornato, A kinetic study of chelant-assisted remediation of contaminated dredged sediment, J. Hazard. Mater., 137 (2006) 1458–1465.

[21] B. Karwowska, Optimization of metals ions extraction from industrial wastewater sludge with chelating agents, Arch. Environ. Prot., 4 (2012) 15–21.

[22] J. Zheng, X. Zhang, G. Li, G. Fei, P. Jin, Y. Liu, C. Wouters, G. Meir, Y. Li, B. Van der Bruggen, Selective removal of heavy metals from saline water by nanofiltration, Desalination, 525 (2022) 115380, doi: 10.1016/j.desal.2021.115380.

[23] B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal, Removal of heavy metal ions by nanofiltration, Desalination, 315 (2013) 2–17.

[24] L.B. Chaudhari, Z.V.P. Murthy, Treatment of landfill leachates by nanofiltration, J. Environ. Manage., 91 (2010) 1209–1217.

[25] G.T. Ballet, L. Gzara, A. Hafiane, M. Dhahbi, Transport coefficients and cadmium salt rejection in nanofiltration membrane, Desalination, 167 (2004) 369–376.

[26] M. Kruk, Comparison of Digestion Methods of Slag Samples From Zinc and Lead Industry to Identify the Content of Selected Metals, Edukacja a wyzwania nauki i technologii, G. Wiciak, K. Szykowska, Eds., Łódź, 2022 (in Polish).

[27] L.J. Wei, O.T. Haan, T.C.S. Yaw, L.C. Abdullah, M.A. Razak, T. Cionita, A. Toudehdehghan, Heavy metal recovery from electric arc furnace steel slag by using hydrochloric acid leaching, E3S Web Conf., 34 (2018) 02007, doi: 10.1051/e3sconf/20183402007.

[28] K. Lewińska, A. Karczewska, M. Siepak, B. Gałka, M. Stysz, C. Kaźmierowski, Recovery and leachability of antimony from mine- and shooting range soils, J. Elementol., 22 (2017) 79–90.

[29] Q. Liu, S.-y. Yang, Y.-m. Chen, J. He, H.-t. Xue, Selective recovery of lead from zinc oxide dust with alkaline Na_2EDTA solution, Trans. Nonferrous Met. Soc. China, 24 (2014) 1179–1186.

[30] R. Qiu, Z. Zou, Z. Zhao, W. Zhang, T. Zhang, H. Dong, X. Wei, Removal of trace and major metals by soil washing with Na_2EDTA and oxalate, J. Soils Sediments, 10 (2010) 45–53.

[31] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, Ph. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit., 1 (1999) 57–61.

[32] M. Nocoń, I. Korus, K. Loska, Quantitative and qualitative analysis of slags from zinc and lead metallurgy, Arch. Environ. Prot., 49 (2023) 26–37.

[33] P.K. Andrew Hong, C. Li, S.K. Banerji, T. Regmi, Extraction, recovery, and biostability of EDTA for remediation of heavy metal-contaminated soil, J. Soil Contam., 8 (1999) 81–103.

[34] N. Finzgar, D. Lestan, The two-phase leaching of Pb, Zn and Cd contaminated soil using EDTA and electrochemical treatment of the washing solution, Chemosphere, 73 (2008) 1484–1491.

[35] P. Hu, B. Yang, C. Dong, L. Chen, X. Cao, J. Zhao, L. Wu, Y. Luo, P. Christie, Assessment of EDTA heap leaching of an agricultural soil highly contaminated with heavy metals, Chemosphere, 117 (2014) 532–537.

[36] L. Hauser, S. Tandy, R. Schulin, B. Nowack, Column extraction of heavy metals from soils using the biodegradable chelating agent EDDS, Environ. Sci. Technol., 39 (2005) 6819–6824.

[37] A.E. Martell, R.M. Smith, R.J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46, MD, Gaithersburg, 2001.

[38] H.A. Elliott, G.A. Brown, Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils, Water Air Soil Pollut., 45 (1989) 361–369.

[39] A. Sungur, M. Soylak, H. Ozcan, Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability, Chem. Speciation Bioavailability, 26 (2014) 219–230.

[40] A.J. Zimmerman, D.C. Weindorf, Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures, Int. J. Anal. Chem., 2010 (2010) 387803, doi: 10.1155/2010/387803.

[41] M. Bodzek, Application of membrane techniques for the removal of micropollutants from water and wastewater, Copernican Letters, 6 (2015) 24–33.