Recovery of nutrients from biofuel ash via organic acid-facilitated solid-liquid extraction

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HIGHLIGHTS

- 0.1 M citric acid showed the best recovery of beneficial nutrients from ash.
- 0.1 M citric acid can recover more than 80% of P and Ca from biofuel ash.
- Amounts of leached heavy metals to filtrate were lower that limits of detection.

GRAPHICAL ABSTRACT
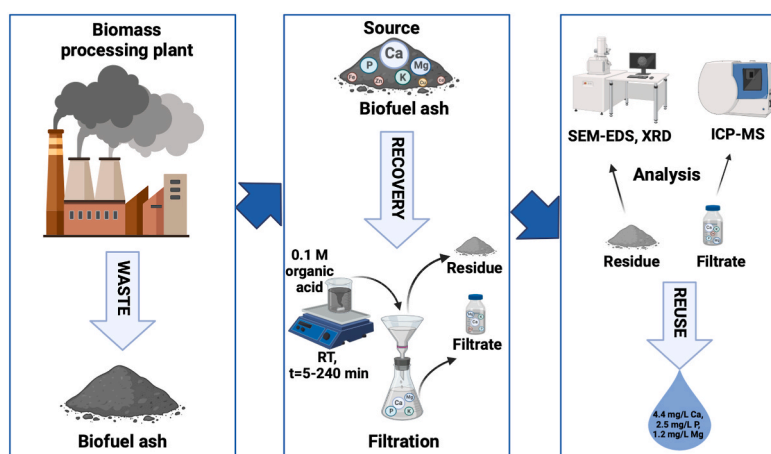
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ABSTRACT

Solid-liquid extraction was investigated to obtain selected major plant nutrients (P, K, Ca, Mg) from biofuel ash using weak organic acids like salicylic acid, citric acid, and oxalic acid as sacrificial leaching agents. In this study, three organic acids were compared to determine the most effective leaching agent for maximizing the P, K, Ca, and Mg extraction from biofuel ash. The findings indicated that 0.1 M citric acid was the most efficient for plant nutrient recovery, with 81.9% of P recovered after 30 min, 82.4% of Ca, 76.8% of Mg, and 47.3% of K. after 120 min. The highest amount of K, with 59.3% was recovered after 180 min of extraction with 0.1 M oxalic acid. However, recovery of P–80.7% was lower, and much lower recovery of Ca–2.3%, and Mg–68.6% after 180 min of extraction with 0.1 M oxalic acid. The leachates were not contaminated with heavy metals, just 0.47 mg/L of Zn, 7.67 mg/L of Al, and 1.99 mg/L of Fe were detected after 180 min of extraction with 0.1 M oxalic acid. The formation of calcium oxalates after extraction with 0.1 M oxalic acid was seen by SEM-EDS. The findings

indicated that to achieve the highest recovery of all beneficial nutrients (P, K, Ca, Mg) different extraction times and different extraction agents are required.

1. Introduction

Worldwide, the amount of generated solid waste is rising (Jebaranjitham et al., 2022). Managing solid waste properly is essential because it greatly influences our environment (Mulya et al., 2022). Effective waste management is still a challenge worldwide (Bello et al., 2022; Ferronato and Torretta, 2019). Sustainable handling and reuse of industrial solid waste is a key objective to recycling resources without supplying harmful substances to humans or the environment (Soni et al., 2022; Tejaswini et al., 2022). Close attention should be paid to the nutrients in waste, which are lost if the waste is not recycled or otherwise utilized (Drapanauskaite et al., 2021; Marcińczyk et al., 2022; Matayeva et al., 2022; Oliveira et al., 2021). Nutrient recovery from waste allows reducing the use of natural resources, which is critical for certain nutrients (Barčauskaite et al., 2020; Xu et al., 2023). As a result, it is crucial to avoid or reduce the amount of solid industrial waste that has been deposited in landfills.

The annual production of biofuel ash is increasing, with nearly 500 million tons produced per year and 70% buried in landfills (Cruz et al., 2019). Since biofuel ash is rich in nutrients, an alternative approach to its utilization is to extract these beneficial elements from waste materials (Ondrasek et al., 2021). There has been a rise in demand for phosphorus over the years due to the coming crisis of phosphate rock because its reserves are limited and will be depleted (Li et al., 2016; Nedelciu et al., 2020). Biofuel ash is rich in phosphorus, and its concentration can vary in a wide range, from 0.2 to 73 g/kg in dry weight (Cruz et al., 2019; Tan and Lagerkvist, 2011). Most phosphate compounds are soluble in acids and can be leached and recovered from ashes or other industrial wastes by using various acids (Fournie et al., 2022; Kalmykova and Karlfeldt Fedje, 2013; Krüger and Adam, 2014; Leng et al., 2019; Ottosen et al., 2013). Biofuel ash is not only rich in phosphorus, but also contains large amounts of potassium, calcium and magnesium, which are important nutrients for plants (Buneviciene et al., 2021). In recent years, there has been a predominant focus among researchers on phosphorus recovery from ash due to the high demand (Belibagli et al., 2022; Fournie et al., 2022; Hu et al., 2023). However, it is essential to recognize the importance of the other nutrients that, when extracted alongside phosphorus, can also be utilized for fertilization purposes. However, recovery and reuse of phosphorus and other beneficial elements from biofuel ash is challenging for various reasons. For instance, when ash is buried in landfill sites, there is a possibility that heavy metals can leach and contaminate the soil and water (Woon and Lo, 2016). Also, it is hard to find one leaching agent that can efficiently extract several nutrients together.

This study explored the effect of different organic acids (salicylic acid, citric acid, and oxalic acid) on the recovery of beneficial elements from biofuel ash. The leachates were compared with each other for the extraction efficiencies for beneficial nutrients, also the ash residues after leaching were characterized. Thus, the main innovation of this study is to explore the potential for recovering all beneficial nutrients present in biofuel ash simultaneously by using organic acids, which naturally are released from plants/fungi/bacteria to the soil. Additionally, the study evaluates the leaching of heavy and trace metals in this process. To our knowledge, previous studies have not examined the recovery of 4 nutrients (P, K, Ca, Mg) from biofuel ash using weak organic acids. In most of the studies, huge attention is given just to P recovery from biofuel ash, and most of the studies use strong inorganic acids, which leads to the co-leaching of heavy metals from biofuel ash. The objective of this study was to identify an appropriate leaching agent that optimizes the extraction of beneficial elements while minimizing the leaching of heavy metals.

2. Experimental methods

Reagents and solutions. Hydrochloric ($\geq$37%) and nitric ($\geq$65%) acids of analytical grade were obtained from Sigma-Aldrich Corporation (Taufkirchen, Germany). Salicylic acid ($\geq$99%) was obtained from Sigma-Aldrich Corporation (Taufkirchen, Germany), citric ($\geq$99.7%) from Reahem (Slovakia), and oxalic acid of analytical grade was purchased from Eurochemicals (Poland). The standard mixture solution of multiple microelements (Ca, Mg, K, P) in 2% nitric acid was obtained from CPAchem (Bulgaria). Deionized water was prepared using Thermo Scientific (Fremont, CA, USA) distillation apparatus.

Biofuel ash. Biofuel ash used in the experiments was obtained from the biomass processing plant. 500 g of biofuel ash was sieved using a Retsch AS 200 sieve shaker. The vibration frequency was 60 s^{-1}, and the Retsch sieve shaker was allowed to start and stop after 10 min. After the Retsch sieve shaking was completed, the sample amount left on the sieve was taken and weighted using an analytical balance (Shimadzu AW/AX/ AY). The detailed composition of the biofuel ash particle size is given in Fig. S1. It was found that the main fraction consisting of biofuel ash was 63 μm, which was used for further research presented in this study.

Biofuel ash leaching experiments. Approximately 0.2 g of biofuel ash (⌀ 0.063 mm) was soaked with 100 ml of deionized water (H_2O), 100 ml 0.1 M salicylic acid (SA), 100 ml 0.1 M citric acid (CA) or 100 ml 0.1 M oxalic acid (OxA) respectively and mixed using magnetic stirrer for 5, 10, 20, 30, 60, 120, 180 and 240 min at ambient temperature, after each duration the biofuel ash was filtrated. The concentration of macronutrients was measured in the biofuel ash residue and filtrate.

Inductively coupled plasma with mass spectrometer (ICP-MS) detector measurements. The concentration of the main plant macronutrients (Ca, K, Mg, P) in the leachate and biofuel ash residues after constant mixing was determined using ICP-MS (ThermoFisher Scientific, USA). Inductively coupled plasma mass spectrometry was conducted in standard (STD) operation mode. Samples were introduced using an autosampler with ASXpress™ rapid uptake module (Cetac ASX-520, Teledyne Technologies Inc., Omaha, NE, USA) through a PEEK nebulizer (Burgener Mira Mist, Mississauga, Burgener Research Inc., Mississauga, Canada). The quantities of analyzed elements (Ca, K, P, Mg) were determined using an external multi-element calibration curve within the 20–1000 μg/L range.

Biofuel ash X-ray diffraction (XRD) analysis. The crystal structure of the samples was examined using the X-ray diffraction (XRD) method with a Bruker D8 diffractometer (40 kV, 40 mA). The goniometer was working in the θ–θ modification. Measurements were conducted at a 2θ angle within a scan range of 10–70°, employing Cu cathode Kα radiation ($\lambda = 0.15406$ nm) in 0.01° increments and a Lynx eye position-sensitive detector.

Scanning electron microscopy (SEM). The surface morphology of raw and processed biofuel ash was analyzed using a scanning electron microscope (SEM, Hitachi S–3400N) equipped with a secondary electron detector at an accelerating voltage of 3 kV. Elemental mapping of the samples was conducted using energy-dispersive X-ray spectroscopy (EDS, Bruker Quad 5040).

X-ray photoelectron spectroscopy (XPS). The upper surface layer chemistry analysis was done using an X-ray photoelectron spectroscope (XPS, PHI 5000 Versaprobe). Monochromated 1486.6 eV Al radiation, 12.5 W beam power, and 100 μm beam size were used during the measurement.

3. Results and discussion

3.1. Biofuel ash characterization

The chemical composition of used biofuel ash is shown in Table 1. It can be seen that ash contained major (>1%), minor (1–0.1%), and trace (<0.1%) elements, according to their elemental concentrations. The major nutrients in biofuel ash were Ca (4.8%), K (2.8%), and Al (1.4%). Other nutrients, such as Mg, P, and Fe, were detected in minor concentrations. The amounts of beneficial elements in ash indicate that it can be a promising secondary source for K, Ca, Mg, and P. Microelements, such as Cu, Zn, and Ni, were also detected in the ashes with traces of Cr and Pb. Similar results of ash chemical composition were reported in the literature (Vassilev et al., 2010).

3.2. The effect of extraction time and solvent type on beneficial nutrients leaching

The single-stage leaching process involves a single step where the biofuel ash (L_0) is contacted with a weak organic acid solvent (V_2) (Varzakas and Tzia, 2014) (Fig. 1).
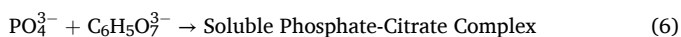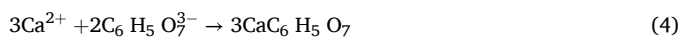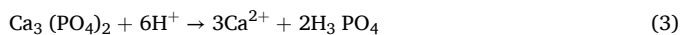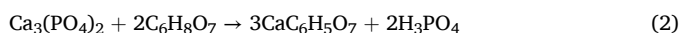
The overall mass balance equation is:

$$L_0 + V_2 = L_1 + V_1 = M \tag{1}$$

The nutrient leaching data using different leaching agents are shown in Fig. 2. The P recovery from biofuel ash using different leaching agents is shown in Fig. 2 (A). The lowest P recovery was obtained after 5 min treatment with deionized water, which was only 1.5%, while 98.5% of P remained in the solid phase. The maximum extraction of P – 11.4% from ash after using deionized water was determined after 120 min. However, extending the leaching time to 180 min or 240 min did not increase P recovery. P is likely incorporated in biofuel ash particles, which are insoluble in water and require a lower pH of solution to dissolve them. The pH of the solution with deionized water was alkaline (pH > 10) throughout the extraction time (Fig. 3). This aligned with previous studies of P recovery from sewage sludge ash, which showed very low P recovery using water as a leaching agent (Ottosen et al., 2013).

Weak organic acids were further utilized in this work to extract P due to their complexing (chelating) ability to extract metal ions while also resulting in a local pH decrease (Alnimer et al., 2023; Ping et al., 2020).

The general reaction for the dissolution of a phosphate compound (such as calcium phosphate) in citric acid can be represented by the following reaction:

$$Ca_3(PO_4)_2 + 2C_6H_8O_7 \rightarrow 3CaC_6H_5O_7 + 2H_3PO_4 \tag{2}$$

$$Ca_3(PO_4)_2 + 6H^+ \rightarrow 3Ca^{2+} + 2H_3PO_4 \tag{3}$$

$$3Ca^{2+} + 2C_6H_5O_7^{3-} \rightarrow 3CaC_6H_5O_7 \tag{4}$$

$$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-} \tag{5}$$

$$PO_4^{3-} + C_6H_5O_7^{3-} \rightarrow \text{Soluble Phosphate-Citrate Complex} \tag{6}$$
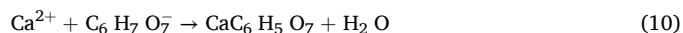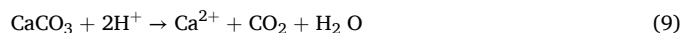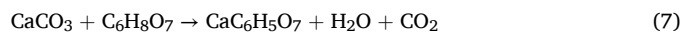
The largest amount of P (81.9%) was found to be released into the filtrate after extracting the biofuel ash with citric acid for 30 min. Also, very similar P recovery results (80.7%) in the filtrate were obtained after using oxalic acid. However, the extraction time was six times longer compared to citric acid. Fang et al. (2018) studies with incinerated sewage sludge ash and higher concentration organic acids (0.2 M citric

acid and 0.2 M oxalic acid) showed that >90% of P can be recovered using oxalic acid and about 80% by citric acid. Another research study on incinerated sewage sludge ash found that oxalic acid performed better than sulfuric acid in P recovery when the incineration temperature was 600–850 °C (Liang et al., 2019).

The K recovery from biofuel ash using different leaching agents is shown in Fig. 2 (B). Around 8% of K was recovered from biofuel ash using deionized water, regardless of the duration of the extraction. It shows that a small amount of K in ash is released as water-soluble salts (such as KCl). Using the extraction with salicylic acid, the maximum recovery of K was obtained after 60 min and 240 min at 34.1% and 36.7%, respectively. Citric acid increased the recovery of K to more than 40% after 120 min. However, the highest recovery of K from biofuel ash was determined using oxalic acid at 59.3% after 180 min. Recent studies showed that the most cost-effective K extraction from fly ash is extraction with water (Ma et al., 2023). Nevertheless, this extraction method is more suitable for ashes in which most of the K is in water-soluble compounds. Wang et al. (2017) also found that 86.4% of K from ash leaches to the filtrate during water extraction.

The Ca recovery from biofuel ash using different leaching agents is shown in Fig. 2 (C). The highest Ca recovery was obtained after 120 min with citric acid. The recovery attained 82.4% of the Ca in the filtrate, and just 17.6% of Ca remained in the solid phase.

The dissolution of metals carbonate (e.g., $CaCO_3$, K_2CO_3, $MgCO_3$) in citric acid ($C_6H_8O_7$) is a typical acid-base reaction where the weak organic acid (e.g., citric acid) reacts with the base (e.g., $CaCO_3$, K_2CO_3, $MgCO_3$) as, a result, metal citrate, carbon dioxide, and water are produced (7–10).

$$CaCO_3 + C_6H_8O_7 \rightarrow CaC_6H_5O_7 + H_2O + CO_2 \tag{7}$$

$$C_6H_8O_7 \rightarrow C_6H_7O_7^- + H^+ \tag{8}$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \tag{9}$$

$$Ca^{2+} + C_6H_7O_7^- \rightarrow CaC_6H_5O_7 + H_2O \tag{10}$$

Salicylic acid is the second-best leaching agent for Ca recovery from biofuel ash. In similar results to those obtained with citric acid experiments, more than 40% of Ca leached out to the filtrate using salicylic acid after 5 min of extraction. The highest recovery of Ca using salicylic acid is obtained at 73.7% after 240 min. This was also influenced by the pH of the solution. The best pH for the Ca recovery is around 3–3.5, and a similar pH of the solution was obtained using citric and salicylic acids (Fig. 3). The worst extraction of Ca from biofuel ash was achieved using oxalic acid. The recovery was about 2%, and the extraction time had no significant influence on the Ca extraction from solid to filtrate. Using oxalic acid to recover Ca from biofuel ash will likely result in insoluble calcium oxalates, which later precipitate. Also, to leach calcium ions, the pH of the solution needs to be from 2 to 3 (Cohen, 2009). Using oxalic acid for all the extraction time, the pH of the solution was lower than 2 (Fig. 3). Recent studies also discovered similar findings (Jang et al., 2022).

The Mg recovery from biofuel ash using various leaching agents is shown in Fig. 2(D). The highest Mg recovery of 76.8% was obtained after 120 min with citric acid treatment. Just about 7% of Mg was recovered from biofuel ash by treating it with deionized water for 120 min, and it was the highest recovery of Mg using the deionized water. The highest recovery of Mg using salicylic acid is obtained after 60 min and 240 min at 61.6% and 63.3%, respectively. The Mg recovery from biofuel ash

Table 1
Chemical composition of the sieved biofuel ash in dry material.

	Total Ca, %	Total Mg, %	Total K, %	Total P, %	Total Fe, %	Total Al, %	Total Cu, mg/kg	Total Zn, mg/kg	Total Ni, mg/kg	Total Cr, mg/kg	Total Pb, mg/kg
Biofuel ash	4.8 ± 0.08	0.9 ± 0.00	2.8 ± 0.03	0.5 ± 0.01	0.6 ± 0.00	1.4 ± 0.02	24.3 ± 1.70	118 ± 0.50	15.5 ± 1.10	19.7 ± 1.38	2.8 ± 0.09
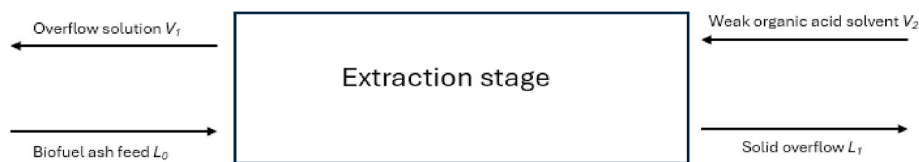
Fig. 1. Single-stage solid -liquid extraction.

(A)

(B)

(C)

(D)
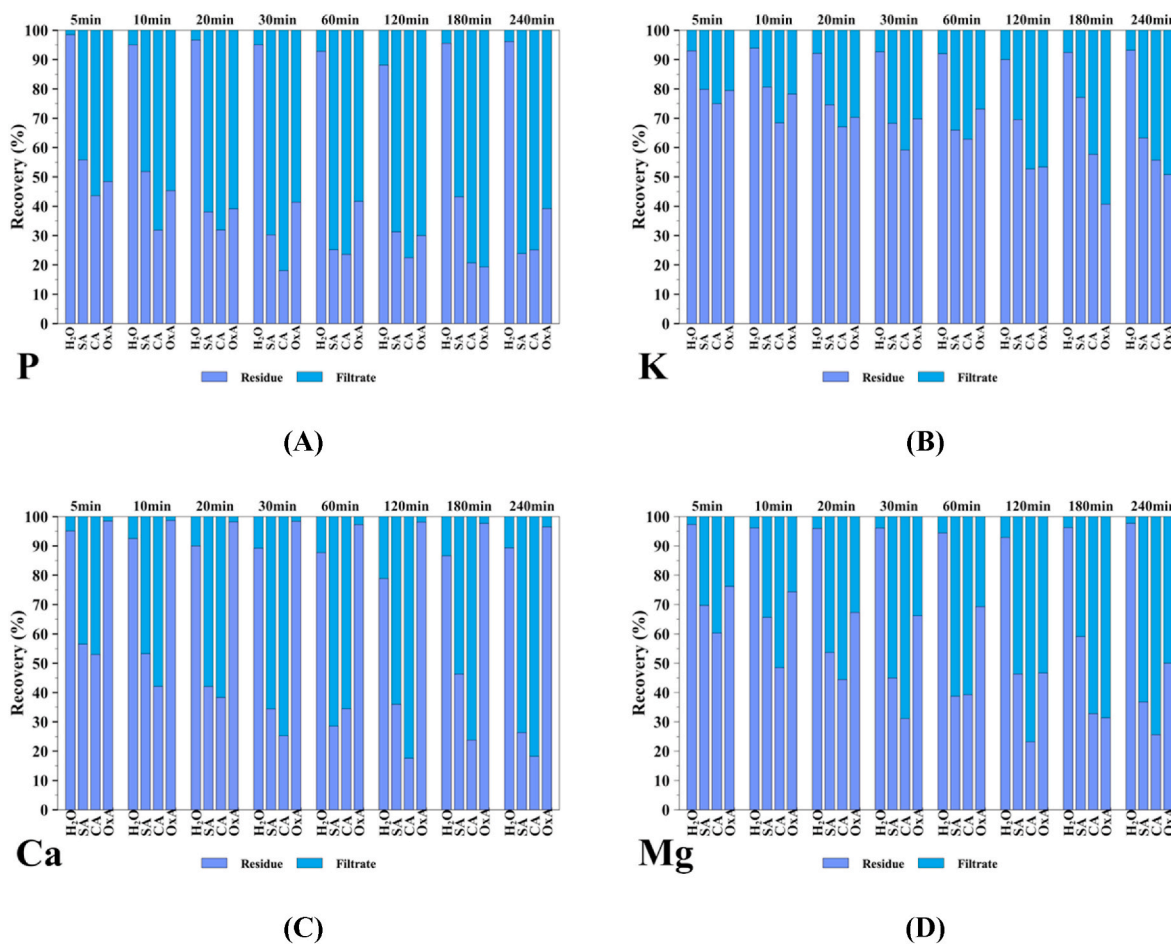
Fig. 2. Recovery of **(A)** P, **(B)** K, **(C)** Ca, **(D)** Mg from biofuel ash after extraction with different leaching agents. Note: *H₂O* deionized water, *SA* 0.1 M salicylic acid, *CA* 0.1 M citric acid, *OxA* 0.1 M oxalic acid.

shows the same pattern as Ca. This shows the Mg co-dissolution with Ca. It is likely that Mg is incorporated in biofuel ash in the same compounds as Ca.

The changes in the pH of leaching solutions during the extraction time are shown in Fig. 3. The most alkaline leachate was obtained by washing the biofuel ash with deionized water. The highest difference in pH values before and after leaching was obtained, ranging from 6.39 before washing and to 10.23 after washing. The high pH values were caused by the following reaction (Morel and Hering, 1993):

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{11}$$

When organic acids were used to extract beneficial nutrients from biofuel ash, the pH of initial solutions was very low – 1.35 oxalic acid, 1.90 – salicylic acid, and 1.95 – citric acid. Only the pH of citric and salicylic acid extraction solutions slightly increased to 3.35 and 3.15, respectively, at the end of extraction.

3.3. Characterization of leached biofuel ash residues

The pXRD (Fig. 4) and SEM-EDS analysis (Fig. 5) were carried out before and after nutrient extraction with different leaching agents to investigate morphological changes of biofuel ash and to identify compounds formed during the treatment. Interpretation of the obtained data was carried out by comparing the experimental data with reference XRD patterns of possible compounds from RRUFF database (SiO₂ (Levien et al., 1980), AlPO₄ (Muraoka and Kihara, 1997), Ca(OH)₂ (Desgranges et al., 1993), CaCO₃ (Markgraf and R.J., 1985), Al₆Si₂O₁₃ (Lenz et al., 2019), Fe₂H₅KO₁₁P₂ (Lindberg, 1957), KAlSi₂O₆ (Pea Cor, 1968), Fe₂O₃ (Pauling and Hendricks, 1925), Ca(C₂O₄)*2H₂O (Echigo and Kimata, 2010), CaSiO₃ (Essene, 1974). The obtained data showed that the dominant phase in the untreated and treated biofuel ash was quartz (SiO₂). Additionally, in all the samples, small quantities of berlinite (AlPO₄), portlandite (Ca(OH)₂), calcite (CaCO₃), mullite (Al₆Si₂O₁₃), and hematite (Fe₂O₃) were found. After the biofuel ash treatment with 0.1 M of oxalic acid, small quantities of weddellite (Ca(C₂O₄)*2H₂O) and wollastonite (CaSiO₃) were observed. Weddellite belongs to the
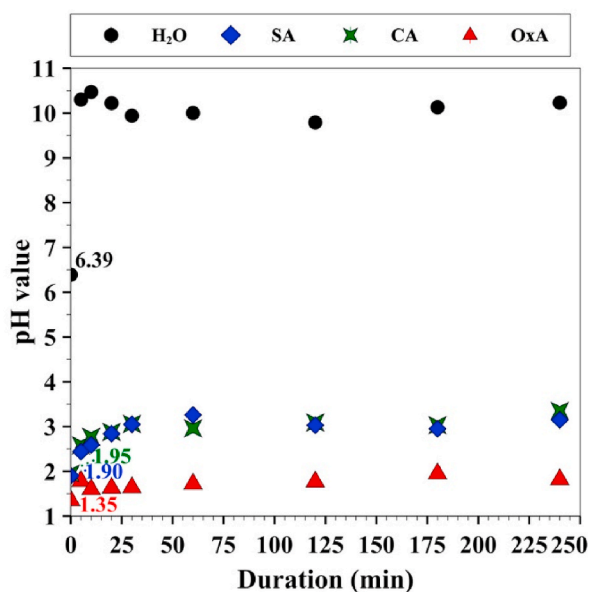
Fig. 3. The changes of leachates pH using different leaching agents during the extraction time. Note: H_2O deionized water, *SA* 0.1 M salicylic acid, *CA* 0.1 M citric acid, *OxA* 0.1 M oxalic acid.
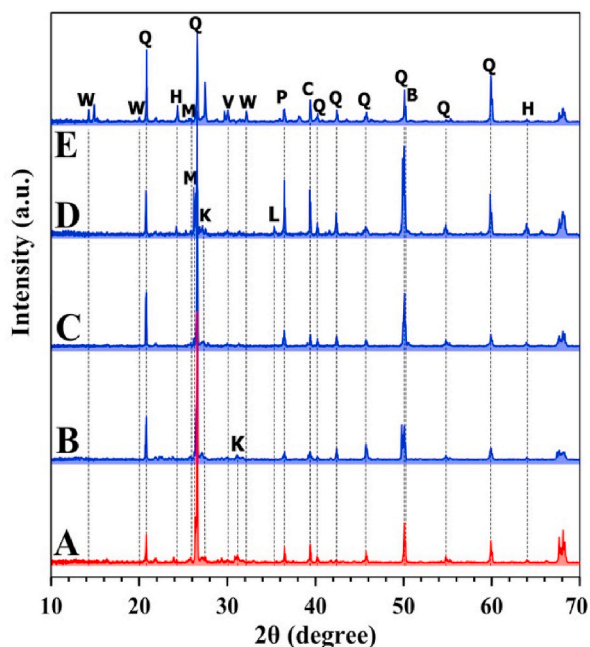

Fig. 4. pXRD patterns of untreated biofuel ash (**A**) and biofuel ash residue after 4 h treatment with deionized water (**B**), 0.1 M salicylic acid (**C**), 0.1 M citric acid (**D**), 0.1 M oxalic acid (**E**).

organic oxalate minerals group, which showed the formation of calcium oxalates and later precipitate. Leucophosphite ($Fe_2H_5KO_{11}P_2$) was also detected in the ash treated with 0.1 M citric acid. Untreated ash and treated with deionized water were accompanied by small quantities of leucite ($KAlSi_2O_6$). No crystalline peaks of microelements and heavy metals were detected, likely due to their low concentration in the

crystal.

Scanning Electron Images together with corresponding elemental maps obtained with Energy Dispersive Spectroscopy (Fig. 5) showed that biofuel ash treated with different leaching agents had a more porous structure compared to untreated biofuel ash samples (Fig. 5 (A)). The larger particles were observed in untreated ash samples. The post-extraction ash particles (Fig. 5(B–E)) had a smaller and more irregular shape. The morphology of these treated and untreated biofuel ash particles was in line with previous findings (Donatello, 2009; Ottosen et al., 2013).

From SEM-EDS elemental mapping, it was observed that beneficial elements (Ca, Mg, K, P) are evenly distributed all over the particle surface in all samples. After the extraction with organic acids (Fig. 5 (C-E)), it is seen that P distribution on the particle surface is decreasing compared to the untreated sample and ash sample treated with deionized water. These results confirm recovery results after treatment with different leaching agents. However, Ca distribution on the particle surface after the extraction with 0.1 M oxalic acid increased compared to ash residues after washing with 0.1 M salicylic acid or 0.1 M citric acid. This indicates that calcium oxalates may have formed after washing the ash with oxalic acid. SEM-EDS maps (Fig. 5) approve our findings obtained by ICP-MS that the best leaching agent for K recovery was oxalic acid. It was observed that the recovery of K after a 4-h treatment increased in the following order according to SEM-EDS results: OxA > SA > CA > H_2O. Meanwhile, according to ICP-MS results, the order was Ox > CA > SA > H_2O. The specificity of the measurement techniques used determined the differences. By using ICP-MS, samples were digested and quantitatively determined to target analytes, while SEM-EDS is a non-destructive detection method that enables the qualitative surface analysis and morphological changes in the samples (DeTata et al., 2023; Wilschefski and Baxter, 2019). No visual changes in Mg content were observed by SEM-EDS (Fig. 5). Previously performed studies declare that plants' nutrient recovery from ash depends on leaching agent pH (Cohen, 2009). It was determined that pH 0 - ~2.2 was the best for K recovery from sewage sludge ash, and an increase of pH to 5 decreased the recovery more than four times (Cohen, 2009). Previously mentioned findings would explain the results obtained in this study that OxA was the most promising leaching agent distinguished from others by its lowest pH.

The surface chemical composition of the untreated and treated biofuel ash was investigated by XPS analysis. The elemental composition of untreated and treated biofuel ash obtained with XPS is shown in Table 2. The wide scan spectrum of untreated and treated biofuel ash is shown in Fig. 6.

The XPS results showed that the primary components near the surface region in untreated ash were O (56.7%), C (22.3%), Ca (10.3%), and Si (5.1%). Also, in smaller quantities, S (2.8%), Mg (1.8%), P (1.0%), K (0.4%) and Al (0.1%). The results of surface analysis of the treated biofuel ash by XPS showed that the same main elements, such as O (57.0–59.2%) and C (16.4–17.9%), are in major quantities, together with Si (15.9–22.9%). However, much less Ca (0.5–0.6 %) is found on the surface in the biofuel ash treated with 0.1 M citric acid and 0.1 M salicylic acid compared to 3.2% and 5.4% in the biofuel ash treated with deionized water and 0.1 M oxalic acid, respectively. These XPS results align with our Ca recovery results (Fig. 2(C)).

3.4. The effect of extraction time and solvent type on heavy metals leaching

The trace elements (Zn, Fe, Al) leaching data using different leaching agents are shown in Fig. 7. Also, Table 1 shows the total concentrations of Zn, Fe, Al, Cu, Pb, Cr, Ni, and Cd in untreated biofuel ash for reference. For Cu, Cd, Cr, Ni, and Pb, the data is not shown in Fig. 7 due to the very low concentration (< lower than limit of detection) of the selected elements. The highest concentration of Zn (0.47 mg/L) leached into the solution after 120 min after using oxalic acid. Furthermore, a similar
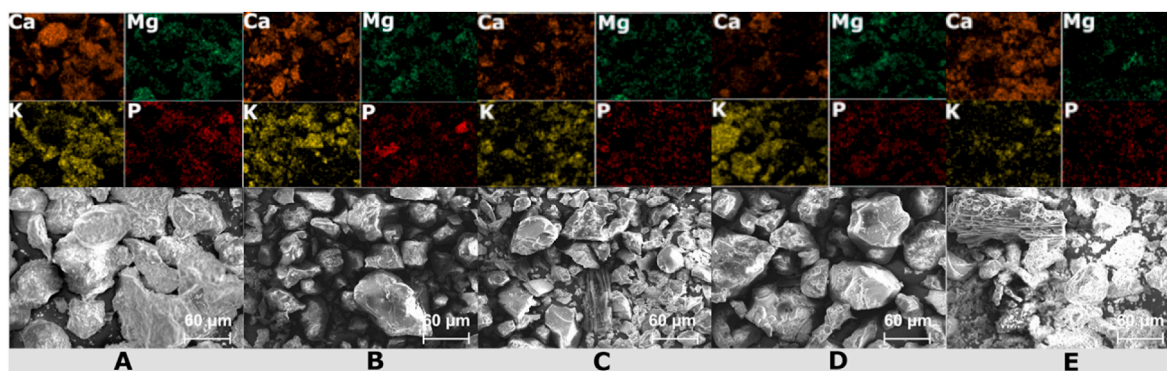
Fig. 5. Scanning Electron (SEM) images and Energy Dispersive Spectroscopy (EDS) maps of untreated biofuel ash **(A)** and biofuel ash residue after 4 h of extraction with deionized water **(B)**, 0.1 M salicylic acid **(C)**, 0.1 M citric acid **(D)**, 0.1 M oxalic acid **(E)**.

Table 2
Elemental composition of samples obtained with XPS.

Sample name	O	C	Si	Al	Ca	K	Mg	P	S
A	56.7	22.3	5.1	0.1	10.3	0.4	1.8	1.0	2.4
B	58.6	16.9	15.9	2.8	3.2	2.0	0.6	–	–
C	57.4	17.7	22.9	0.3	0.6	0.1	0.2	0.7	–
D	59.2	16.4	20.5	2.0	0.5	1.2	0.3	–	–
E	57.0	17.9	18.4	0.4	5.4	0.5	0.2	0.3	–

Note: untreated biofuel ash **(A)**, biofuel ash residue after 4 h of treatment with deionized water **(B)**, 0.1 M salicylic acid **(C)**, 0.1 M citric acid **(D)**, and 0.1 M oxalic acid **(E)**.
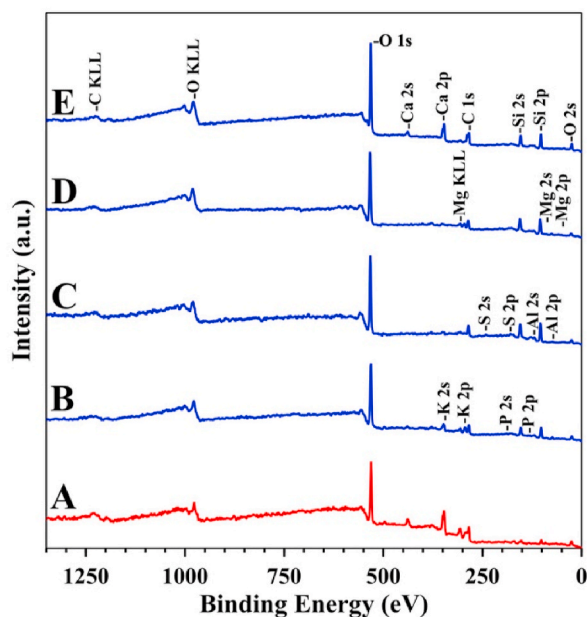

Fig. 6. XPS survey spectrums of untreated biofuel ash **(A)** and biofuel ash residue after 4 h treatment with deionized water **(B)**, 0.1 M salicylic acid **(C)**, 0.1 M citric acid **(D)**, 0.1 M oxalic acid **(E)**.

Fig. 7. Concentration of trace elements at different times in leachate from biofuel ash using various leachants. Note: *H₂O* deionized water, *SA* 0.1 M salicylic acid, *CA* 0.1 M citric acid, *OxA* 0.1 M oxalic acid.

for 180 min. The extraction time significantly impacted Al leaching, with the leached Al concentration increasing as the extraction time increased.

It should be noted that for heavy metals release, pH and the type of acid have a significant effect (Ajorloo et al., 2022; Luo et al., 2019). Studies have shown that the highest concentration of Zn leaches from fly ashes when the pH is below 5. When the solution pH is alkaline (7.5–11.5), Zn precipitates as $Zn(OH)_2$ (Zhipeng et al., 2015). These findings explain why Zn was not detected after the extraction with deionized water. Additionally, the CaO content in ashes significantly influences the leachability of heavy metals; higher CaO content increases the acid-neutralizing capacity, thereby reducing the leachability of heavy metals (Yue et al., 2019). Organic acids, such as acetic and oxalic acid, are less effective at extracting heavy metals than mineral acids (Karlfeldt Fedje et al., 2010). However, citric acid is an exception from organic acids and is quite effective in leaching heavy metals (Wang et al., 2018).

4. Conclusions

Biofuel ash has a significant potential for beneficial nutrient recovery. This study evaluated the effectiveness of three weak organic acids and deionized water for the recovery of beneficial nutrients, such as P, K,

amount of Zn (0.46 mg/L) leached to the solution after treatment with citric acid for 180 min. When salicylic acid was used for the extraction, the Zn concentration at all times leached similarly about 0.38 mg/L. It is noteworthy that after the extraction with deionized water, Zn concentration in leachate was lower than the limit of detection. However, very small amounts of Fe and Al were leached into the solution after the extraction with deionized water. The highest concentration of Fe (2.94 mg/L) was leached into the solution after extraction with salicylic acid
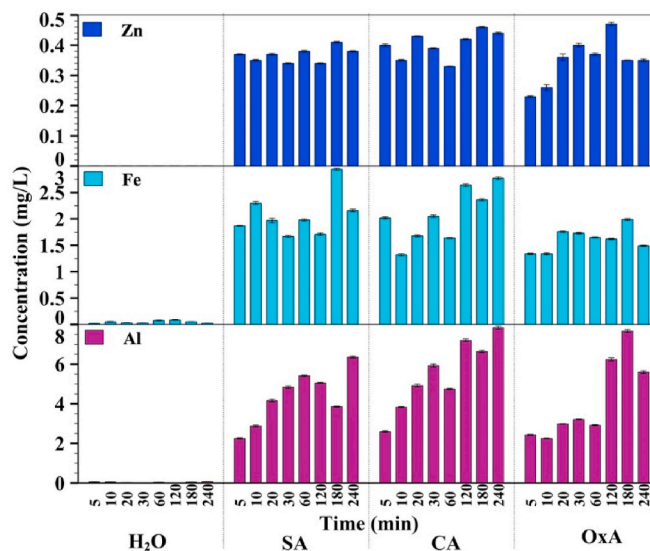
Ca, and Mg, from biofuel ash through acid leaching over time. The main findings of this study are, that 0.1 M citric acid was selected as the optimum beneficial nutrients (P, K, Ca, Mg) leachant. The optimized leaching conditions were: extraction time 30 min for P, 120 min for K, Ca, and Mg, acid concentration – 0.1 M, liquid to solid ratio – 500:1. The concentration of nutrients in obtained leachates were: P – 2.5 mg/L, K – 2.0 mg/L, Ca – 4.4 mg/L, Mg – 1.2 mg/L. The second best leaching agent for extracting beneficial nutrients from biofuel ash was 0.1 M oxalic acid for recovery of P and K and 0.1 M salicylic acid for recovery of Ca and Mg. XRD analysis of treated biofuel ash with 0.1 M oxalic acid showed the formation of calcium oxalates, which led to lower calcium recovery. SEM-EDS and XPS analysis of treated biofuel ash showed the decrease of main nutrients in particle surface after treatments. This study indicates that weak organic acids are suitable for the recovery of beneficial nutrients from biofuel ash and also capable of extracting more than 80% of P after 30 min of extraction, more than 80% of Ca after 120 min, and more than 70% of Mg after 120 min. The lowest recovery using weak organic acids as leaching agents was observed for K.

CRediT authorship contribution statement

Donata Drapanauskaitė: Writing – original draft, Visualization. **Karolina Barčauskaitė:** Writing – review & editing, Visualization, Methodology. **Kristina Bunevičienė:** Investigation, Formal analysis. **Marius Urbonavičius:** Investigation, Formal analysis. **Šarūnas Varnagiris:** Investigation, Formal analysis. **Jonas Baltrusaitis:** Writing – review & editing, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.142945.

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