

Nitric acid-assisted extraction of phosphorus and potassium from phosphorite beneficiation waste and sunflower ash

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ABSTRACT

The sustainable utilization of industrial and agricultural wastes as secondary nutrient resources represents an important strategy for resource conservation and circular-economy development. In this study, a nitric acid-assisted extraction process was investigated for the integrated processing of phosphorite beneficiation waste and sunflower ash to obtain a phosphorus–potassium-containing liquid product. The mineralogical, structural, morphological, surface-textural, elemental, and thermal characteristics of the raw materials were examined using XRD, FTIR, SEM–EDX, BET, and TGA analyses to support interpretation of their composition and dissolution behavior. The effects of phosphorite waste-to-sunflower ash ratio, nitric acid concentration, extraction temperature, reaction time, and solid-to-liquid ratio on phosphorus and potassium transfer into the liquid phase were systematically evaluated using a one-factor-at-a-time approach. The preferred operating conditions within the investigated ranges were identified as a phosphorite waste-to-sunflower ash ratio of 100:40 (w/w), an HNO₃ concentration of 57 wt.%, an extraction temperature of 80 °C, a reaction time of 150 min, and a solid-to-liquid ratio of 1:3 (w/v). Under these conditions, the resulting liquid phase contained up to 17.9 g L^{−1} P₂O₅ and 20.4 g L^{−1} K₂O. The observed trends were consistent with acid-assisted dissolution of phosphorus-bearing phases and comparatively easier transfer of potassium-containing species from sunflower ash. Because the total initial P and K inventories and the residual nutrient contents of the post-extraction solids were not independently quantified, the measured concentrations were interpreted as indicators of liquid-phase extraction performance rather than absolute recovery efficiencies. The proposed approach demonstrates the feasibility of integrated valorization of phosphorite beneficiation waste and sunflower ash within a single nitric acid-assisted extraction route.

Keywords: phosphorite beneficiation waste, sunflower ash, nitric acid-assisted extraction, phosphorus, potassium, waste valorization, circular economy.

INTRODUCTION

Phosphorus (P) and potassium (K) are among the most important macronutrients required for sustainable crop production and global food security. Phosphorus plays a fundamental role in energy transfer, nucleic acid synthesis, photosynthesis, and root development, whereas potassium regulates enzyme activation, osmotic balance, carbohydrate transport, and plant resistance to various biotic and abiotic stresses. The continuous

growth of the global population and the increasing demand for agricultural products have resulted in a significant rise in fertilizer consumption worldwide. Consequently, the sustainable supply of phosphorus- and potassium-containing fertilizers has become a major challenge for modern agriculture [2, 6, 18].

The production of conventional phosphate fertilizers remains strongly dependent on mined phosphate rock [15, 18]. Concerns regarding the long-term sustainability of phosphorus supply

are associated not only with the finite nature and geographical concentration of phosphate resources, but also with variations in ore quality, increasing processing requirements, and the environmental impacts of mining and beneficiation [14, 15, 20]. At the same time, phosphate beneficiation generates substantial quantities of phosphorite residues that may still contain valuable phosphate-bearing phases. Their disposal results in both the loss of potentially recoverable resources and additional environmental burdens, highlighting the need for effective valorization strategies [3, 10, 21].

In parallel, large quantities of agricultural biomass residues are generated worldwide, and their combustion produces mineral-rich ashes containing potentially valuable nutrients. Potassium is particularly important in this context because agricultural residue ashes can contain substantial amounts of readily extractable K-bearing compounds [6, 8]. Sunflower ash is a promising secondary potassium source; previous work has demonstrated that a considerable fraction of its potassium can be released even by mild aqueous leaching [19]. Therefore, valorization of sunflower ash as a nutrient source may provide an alternative to its disposal while contributing to more circular potassium management [6, 19].

The concept of waste valorization and circular nutrient management has received increasing attention as a strategy for reducing waste generation while returning valuable nutrients to productive use [2, 18, 22]. Recent studies have examined phosphorus extraction and recovery from phosphate-processing residues, wastewater-derived materials, and other secondary resources [1, 4, 7, 11, 21, 22], while potassium recovery from biomass ashes has generally been investigated as a separate resource pathway [6, 19]. However, comparatively limited information is available on the combined processing of phosphorus-rich phosphorite beneficiation residues and potassium-rich sunflower ash within a single integrated nutrient-extraction route.

In the present system, the two waste materials perform complementary functions rather than exhibiting an assumed synergistic extraction effect. Phosphorite beneficiation waste serves primarily as a phosphorus source, and acid treatment is therefore directed mainly toward the dissolution of poorly soluble phosphate-bearing phases [3, 10, 21]. In contrast, sunflower ash serves as a potassium source;

potassium contained in biomass ash is generally more readily extractable, and previous studies have demonstrated effective potassium release from sunflower and other biomass ashes even under mild aqueous extraction conditions [6, 19]. Therefore, the rationale for the integrated use of these materials is to combine two complementary secondary nutrient sources within a single processing route to obtain a phosphorus–potassium-containing liquid product, rather than to enhance the intrinsic solubility of potassium through nitric acid treatment [5, 12].

Nitric acid was selected primarily because of its ability to decompose calcium phosphate-bearing phases and transfer phosphorus into the liquid phase. Recent studies on low-grade and Central Kyzylkum phosphate raw materials have demonstrated the applicability of nitric-acid-based processing for the production of liquid or complex fertilizer intermediates [16, 17]. In the integrated system considered here, potassium from sunflower ash is expected to enter the liquid phase more readily because of the comparatively high solubility of its K-bearing constituents, while nitrate introduced with the extracting reagent may additionally contribute nitrogen to the resulting nutrient-containing liquid phase [6, 16, 19]. Nevertheless, previous nitric-acid studies have predominantly focused on phosphate raw materials, and the combined processing of phosphorite beneficiation waste with sunflower ash remains insufficiently investigated.

The effects of feedstock ratio, nitric acid concentration, extraction temperature, reaction time, and solid-to-liquid ratio on nutrient extraction performance were systematically investigated using the concentrations of P_2O_5 and K_2O released into the liquid phase as comparative process indicators. Because the total initial P and K inventories and the nutrient contents of the post-extraction solid residue were not independently quantified, the present study does not interpret these liquid-phase concentrations as absolute recovery efficiencies. XRD, FTIR, SEM–EDX, BET, and TGA analyses were employed to characterize the mineralogical, structural, and physicochemical properties of the raw materials and to support interpretation of their extraction behavior. The study therefore focuses on evaluating the feasibility and operating conditions of an integrated waste-valorization and nutrient-extraction route rather than establishing a complete nutrient mass balance.

MATERIALS AND METHODS

Raw materials and preparation of sunflower ash

Phosphorite beneficiation waste obtained from the Kyzylkum phosphate processing industry, Uzbekistan, was used as the phosphorus-containing raw material. Prior to extraction, the phosphorite waste was dried at 120 °C to constant mass, ground, and sieved to obtain a particle fraction smaller than 0.25 mm. Sunflower stalks and husks used for ash preparation were collected from the “Zamin” farm located in Fergana district, Fergana region, Uzbekistan. The collected biomass was cleaned to remove adhering soil and other foreign materials, dried, and subsequently incinerated in a TC7L-17 ceramic-fiber muffle furnace (maximum operating temperature: 1700 °C) at 600 °C for 2 h. After incineration, the resulting ash was allowed to cool to room temperature, homogenized, and passed through a 2 mm sieve to remove coarse particles and unburned residues. The prepared sunflower ash was stored in a closed container at room temperature until further use. Analytical-grade nitric acid (HNO₃, 65 wt.%, Farg‘ona Azot JSC, Uzbekistan) was used as the extracting reagent. Nitric acid solutions of the required working

concentrations were prepared by dilution of the stock acid with distilled water. Distilled water was used throughout the extraction experiments and for the preparation of aqueous solutions.

Experimental equipment

Extraction experiments were performed in a cylindrical reactor with an internal diameter of 500 mm, a height of 1000 mm, and a wall thickness of 3 mm, corresponding to an internal volume of approximately 196 L. The reactor was equipped with a paddle-type mechanical stirrer. The overall paddle span was approximately 496 mm, with a clearance of about 2 mm between the paddle tips and the inner reactor wall, and the paddle blade width was 60 mm. The reactor was heated using a tubular electric heating element (TEN), and the reaction temperature was continuously monitored using a Leybold NiCr–Ni thermocouple with an operating range of –50 to +1200 °C. The extraction setup is schematically illustrated in Figure 1.

Experimental design

The extraction experiments were designed according to a one-factor-at-a-time (OFAT) approach, in which one process parameter was

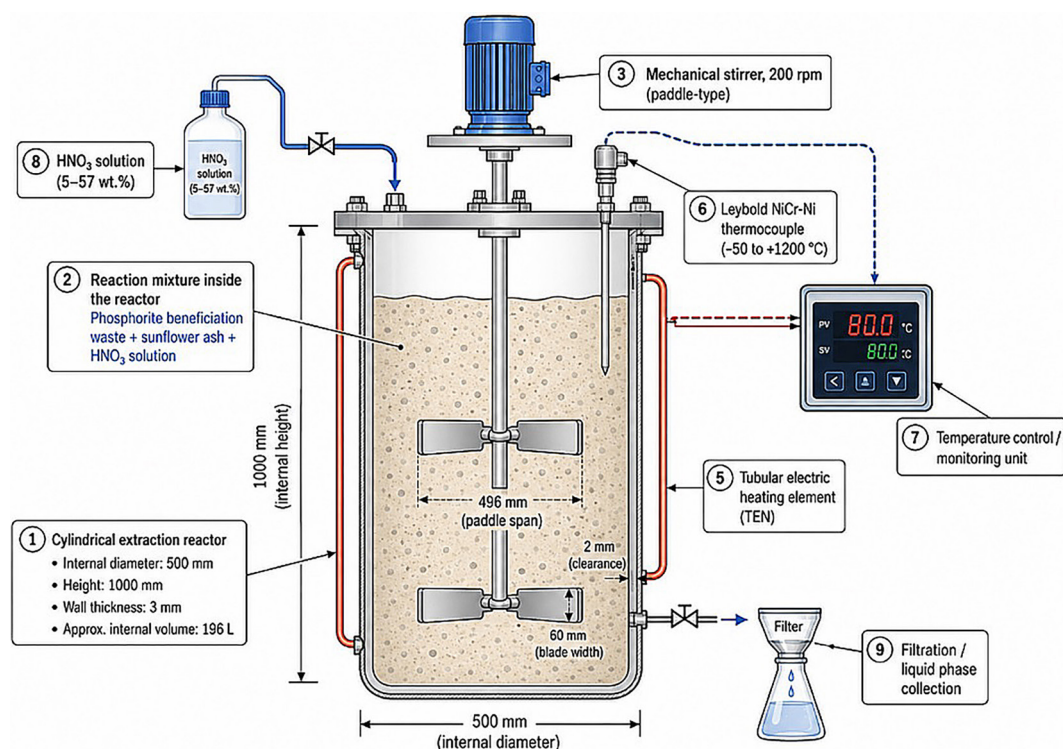


Figure 1. Schematic representation of the nitric acid-assisted extraction setup

varied within a predefined range while the remaining experimental conditions were maintained at the values specified for the corresponding experimental series. The investigated factors were the phosphorite beneficiation waste-to-sunflower ash mass ratio, nitric acid concentration, extraction temperature, extraction time, and solid-to-liquid ratio. The concentrations of P_2O_5 and K_2O in the separated liquid phase were used as comparative response variables for evaluating the effect of each process parameter.

The investigated levels were as follows:

1. Phosphorite beneficiation waste-to-sunflower ash ratio (w/w): 100:10, 100:20, 100:30, 100:40, 100:50, 100:52, 100:54, 100:58, and 100:60;
2. HNO_3 concentration: 5, 10, 15, 20, 30, 40, 50, and 57 wt.%;
3. Extraction temperature: 40, 50, 60, 70, 80, and 90 °C;
4. Extraction time: 30, 60, 90, 120, and 150 min;
5. Solid-to-liquid ratio (w/v): 1:2, 1:3, 1:4, 1:5, and 1:6.

For each experimental run, the reaction mixture was mechanically stirred at 200 rpm. After completion of the extraction, the suspension was filtered and the concentrations of P_2O_5 and K_2O in the separated liquid phase were determined using the analytical procedures described below.

Preparation of extraction mixtures

Phosphorite beneficiation waste and sunflower ash were mixed at the following mass ratios (phosphorite waste: sunflower ash, w/w): 100:10, 100:20, 100:30, 100:40, 100:50, 100:52, 100:54, 100:58, and 100:60. These compositions were selected to evaluate the effect of increasing sunflower ash addition on the phosphorus–potassium composition of the resulting liquid phase. The more closely spaced ratios in the higher-ash region were additionally examined to assess changes in potassium concentration in greater detail. Among the investigated compositions, the 100:40 (w/w) ratio provided a comparatively balanced liquid-phase P_2O_5 and K_2O composition and was therefore selected for the subsequent extraction experiments.

Nitric acid-assisted extraction procedure

The prepared phosphorite beneficiation waste–sunflower ash mixtures were introduced into the reactor and contacted with nitric acid solution

under mechanical stirring at 200 rpm. The experimental series were conducted sequentially according to the one-factor-at-a-time (OFAT).

In the preliminary feedstock-ratio screening, the phosphorite beneficiation waste-to-sunflower ash ratio was varied from 100:10 to 100:60 (w/w), while the HNO_3 concentration, extraction temperature, extraction time, and solid-to-liquid ratio were maintained at 57 wt.%, 70 °C, 120 min, and 1:3 (w/v), respectively. Based on the resulting liquid-phase P_2O_5 and K_2O concentrations, 100:40 (w/w) was selected as the working feedstock composition for the subsequent experimental series.

Using the selected 100:40 (w/w) composition, the effect of nitric acid concentration was investigated at 5, 10, 15, 20, 30, 40, 50, and 57 wt.% HNO_3 , while the temperature, extraction time, and solid-to-liquid ratio were maintained at 70 °C, 120 min, and 1:3 (w/v), respectively. The highest measured nutrient concentrations within the investigated acid-concentration range were obtained at 57 wt.% HNO_3 , which was therefore used in the subsequent experimental series.

The effect of extraction temperature was then investigated at 40, 50, 60, 70, 80, and 90 °C, using a feedstock ratio of 100:40 (w/w), 57 wt.% HNO_3 , an extraction time of 120 min, and a solid-to-liquid ratio of 1:3 (w/v). Based on the combined P_2O_5 and K_2O response, 80 °C was selected as the working temperature for the following experiments.

Extraction time was subsequently varied at 30, 60, 90, 120, and 150 min, while the feedstock ratio, HNO_3 concentration, temperature, and solid-to-liquid ratio were maintained at 100:40 (w/w), 57 wt.%, 80 °C, and 1:3 (w/v), respectively. The highest measured nutrient concentrations within the investigated time range were obtained at 150 min, which was therefore used in the final solid-to-liquid-ratio experiments.

Finally, the effect of the solid-to-liquid ratio was systematically evaluated at 1:2, 1:3, 1:4, 1:5, and 1:6 (w/v) under a feedstock ratio of 100:40 (w/w), an HNO_3 concentration of 57 wt.%, an extraction temperature of 80 °C, an extraction time of 150 min, and a stirring speed of 200 rpm. Although 1:3 (w/v) had been used as a preliminary working ratio in the preceding experimental series, its selection was subsequently evaluated within this dedicated solid-to-liquid-ratio experiment.

After completion of each extraction run, the resulting suspension was filtered and the separated liquid phase was collected for chemical analysis. Phosphorus was determined

spectrophotometrically using the vanadomolybdate yellow method at 420 nm with a Shimadzu UV-2600i spectrophotometer and was expressed as P_2O_5 . Potassium was determined using an FP8800 flame photometer and was expressed as K_2O . The final pH of each liquid extract was measured using a PH-4502C pH meter and was recorded as a monitored response parameter rather than as an independently controlled experimental variable.

The total bulk phosphorus and potassium contents of the initial solid feedstocks were not independently quantified. Therefore, the measured liquid-phase P_2O_5 and K_2O concentrations were used as comparative indicators of nutrient extraction performance rather than for calculation of absolute phosphorus and potassium recovery efficiencies.

Characterization techniques

The raw materials were characterized using complementary analytical techniques. Mineralogical characteristics were evaluated by X-ray diffraction (XRD) through qualitative identification of crystalline phases. Structural and chemical-bond characteristics were examined by Fourier-transform infrared spectroscopy (FTIR) based on the identification of principal functional groups and characteristic bonds. Morphological characteristics were investigated by scanning electron microscopy (SEM), while energy-dispersive X-ray spectroscopy (EDX) was used to determine the local elemental composition. Physicochemical characteristics were evaluated by Brunauer–Emmett–Teller (BET) analysis for specific surface area and pore properties and by thermogravimetric analysis (TGA) for thermal behavior and stability.

Statistical analysis

All extraction experiments were performed in triplicate ($n = 3$), and the results are expressed as mean $\pm$ standard deviation (SD). For each independently investigated process factor, including phosphorite beneficiation waste-to-sunflower ash ratio, nitric acid concentration, extraction temperature, extraction time, and solid-to-liquid ratio, statistical differences among the experimental levels were evaluated using one-way analysis of variance (one-way ANOVA). When ANOVA indicated a statistically significant effect, Tukey's honestly significant difference (HSD) post-hoc test was applied for pairwise comparisons. Differences were considered statistically significant at p

< 0.05 . One-way ANOVA and Tukey's HSD post-hoc tests were performed using OriginPro 2024. The same software was used for graphical processing, while Microsoft Excel was used only for preliminary data organization and calculations.

RESULTS

Qualitative X-Ray diffraction analysis of phosphorite waste and sunflower ash

The crystalline phases present in the phosphorite beneficiation waste and sunflower ash were identified by X-ray diffraction, and the corresponding patterns are shown in Figure 2. The phosphorite waste exhibited reflections attributable mainly to apatite, calcite, and quartz, whereas the sunflower ash showed potassium-bearing crystalline phases together with calcite, quartz, and anhydrite [8, 15]. These results qualitatively confirm the presence of phosphorus-bearing phases in the phosphorite waste and potassium-containing phases in the sunflower ash and therefore support interpretation of their behavior during nitric acid-assisted extraction. No quantitative phase analysis, such as Rietveld refinement, was performed; consequently, the XRD results were used only for qualitative phase identification and were not used to calculate nutrient recovery or establish a quantitative mass balance.

Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of phosphorite beneficiation waste and sunflower ash are presented in Figure 3. Both materials exhibited broad absorption bands at $3400\text{--}3450\text{ cm}^{-1}$, assigned to O–H stretching vibrations of hydroxyl groups and adsorbed water, together with bands in the $1600\text{--}1650\text{ cm}^{-1}$ region corresponding to H–O–H bending vibrations of molecular water. The intense absorption region between 1000 and 1100 cm^{-1} was associated with phosphate and Si–O stretching vibrations. In the phosphorite waste, the prominent band near 1040 cm^{-1} was attributed mainly to phosphate-related stretching vibrations, whereas the bands around 875 and 712 cm^{-1} were associated with carbonate and quartz-related Si–O vibrations, respectively [8, 15].

In the sunflower ash, the strong band near 1035 cm^{-1} was assigned predominantly to Si–O

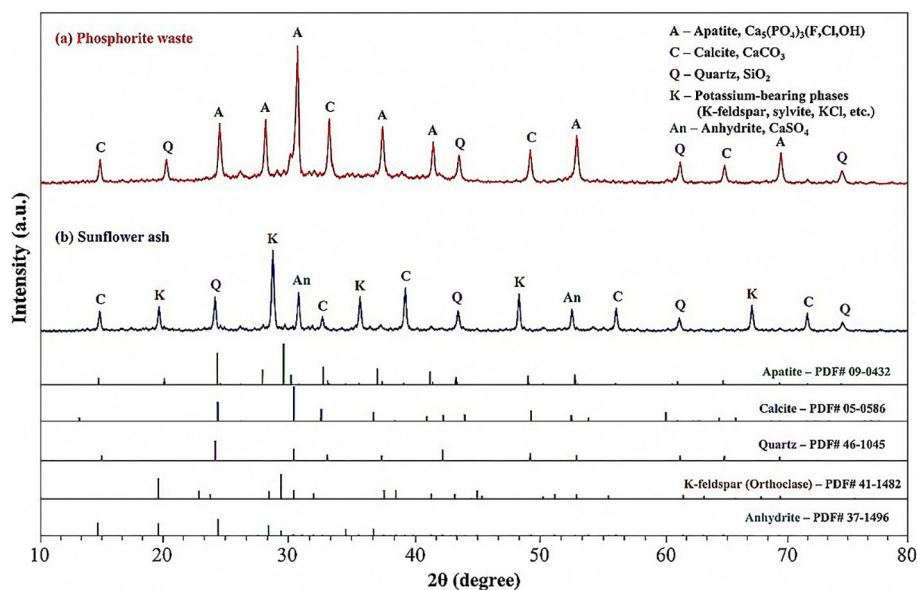


Figure 2. X-ray diffraction patterns of phosphorite beneficiation waste and sunflower ash, showing the principal crystalline phases identified in the two feedstocks

stretching, while the bands in the 780–800, 870–880, and 690–720 cm^{-1} regions were attributed to sulfate, carbonate, and quartz-related Si–O vibrations, respectively. These FTIR observations qualitatively support the mineral-phase assignments obtained from XRD and were used to assist interpretation of the chemical characteristics of the raw materials rather than for quantitative evaluation of nutrient extraction [8, 15].

BET surface area and porosity analysis

The textural properties of phosphorite beneficiation waste and sunflower ash were evaluated by nitrogen adsorption–desorption analysis, and the corresponding isotherms, pore-size distributions, and BET plots are presented in Figure 4.

Both materials exhibited Type IV adsorption–desorption isotherms with H3-type hysteresis loops, indicating predominantly mesoporous structures [8].

The phosphorite beneficiation waste exhibited a higher BET specific surface area ($18.67 \text{ m}^2 \text{ g}^{-1}$) than sunflower ash ($7.42 \text{ m}^2 \text{ g}^{-1}$). Its total pore volume was also higher, reaching $0.064 \text{ cm}^3 \text{ g}^{-1}$ compared with $0.031 \text{ cm}^3 \text{ g}^{-1}$ for sunflower ash. The corresponding average pore diameters were 13.8 and 16.7 nm, respectively. The micropore volumes were $0.010 \text{ cm}^3 \text{ g}^{-1}$ for phosphorite waste and $0.004 \text{ cm}^3 \text{ g}^{-1}$ for sunflower ash, whereas the mesopore volumes were 0.054 and $0.027 \text{ cm}^3 \text{ g}^{-1}$, respectively.

The BJH pore-size distributions further indicated that the pore structures of both materials

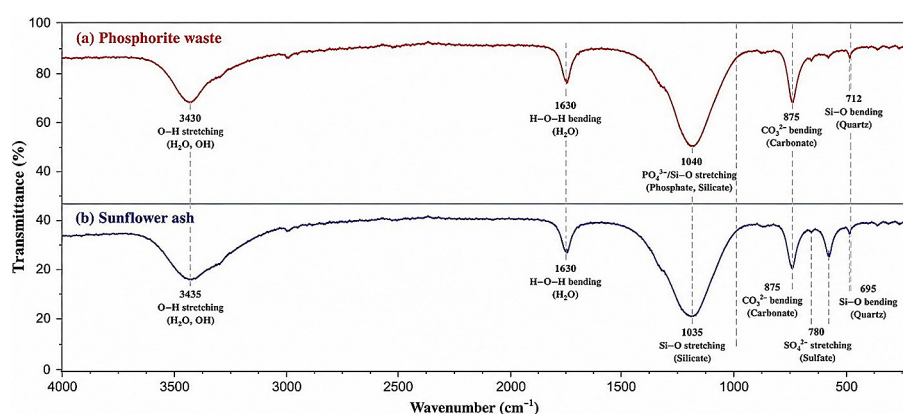


Figure 3. FTIR spectra of phosphorite beneficiation waste and sunflower ash showing the principal absorption bands associated with hydroxyl, phosphate, carbonate, sulfate, and silicate-related groups

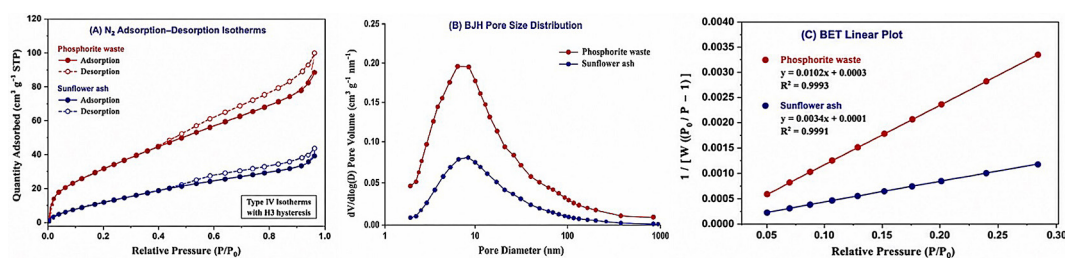


Figure 4. Nitrogen adsorption–desorption characterization of phosphorite beneficiation waste and sunflower ash: (A) adsorption–desorption isotherms, (B) BJH pore-size distributions, and (C) BET linear plots

were dominated by mesopores, mainly within the approximately 5–50 nm range. The comparatively higher surface area and pore volume of the phosphorite waste suggest greater accessible solid–liquid interfacial area during nitric acid treatment. These textural characteristics may facilitate penetration of the extracting solution into the solid matrix and thereby support interpretation of the observed dissolution behavior. However, the BET parameters were used only as physico-chemical descriptors of the raw materials and not as quantitative indicators of nutrient recovery efficiency [3, 10, 21].

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDX)

The surface morphology and local elemental composition of the phosphorite beneficiation waste were examined by SEM–EDX, and the results are presented in Figure 5. The SEM micrograph (Figure 5A) reveals irregularly shaped and angular particles with a heterogeneous surface morphology. Rough surfaces, microcracks, and locally porous regions are visible in several particles. Such morphological features may increase the accessibility of the solid surface to the extracting solution and therefore assist interpretation of the dissolution behavior observed during nitric acid treatment [3, 10, 21].

The EDX analysis of the selected region (Figure 5B) indicated O, Ca, P, and Si as the predominant detected elements, with corresponding semi-quantitative contents of 49.20, 23.60, 17.10, and 4.40 wt.%, respectively. Minor amounts of Al, Mg, Fe, and K were also detected. The simultaneous occurrence of Ca and P is consistent with the presence of calcium phosphate-bearing phases identified qualitatively by XRD, whereas Si is consistent with the occurrence of silicate/quartz-containing phases. Importantly, the EDX values represent the local elemental composition

of the analyzed area and should not be interpreted as the bulk phosphorus or potassium contents of the initial feedstock. Accordingly, these results were used only to support interpretation of the raw-material characteristics and possible extraction behavior and were not used for calculation of absolute nutrient recovery efficiency [15].

Thermogravimetric analysis (TGA)

The thermal behavior of phosphorite beneficiation waste and sunflower ash was evaluated by thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses, as shown in Figure 6. Both materials exhibited multistage mass-loss behavior. The initial mass loss below approximately 150 °C was attributed mainly to the removal of physically adsorbed water. Between 150 and 400 °C, additional mass loss was associated with dehydroxylation and the decomposition of residual organic matter, with sunflower ash showing a somewhat greater change in this region.

The most pronounced thermal transformation occurred between approximately 400 and 800 °C, where the DTG curves exhibited decomposition features around 600–700 °C. These changes are consistent with the thermal decomposition of carbonate-containing phases, including calcite-related constituents identified by XRD [8, 15]. Above 800 °C, only minor additional mass changes were observed. At the end of the thermal treatment, phosphorite waste retained approximately 77% of its initial mass, whereas sunflower ash retained approximately 55%. These results indicate the higher proportion of thermally stable mineral constituents in the phosphorite waste. The TGA–DTG results were used to support interpretation of the physicochemical characteristics of the raw materials and were not used as quantitative indicators of phosphorus or potassium extraction efficiency.

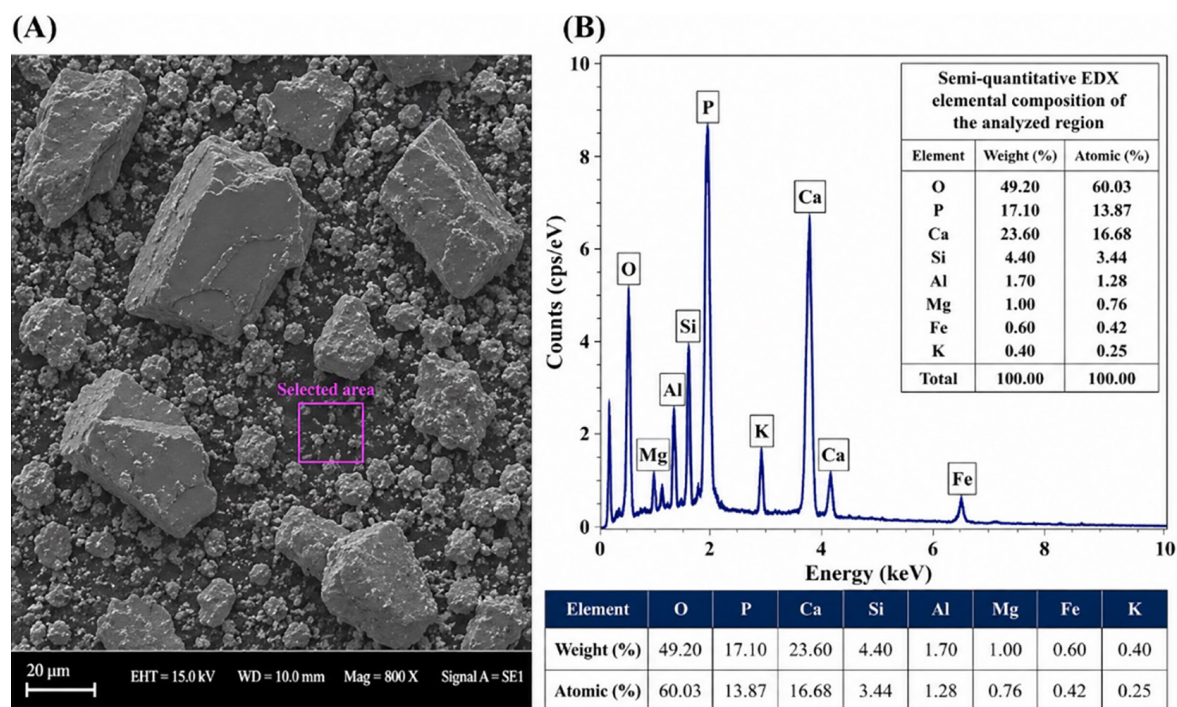


Figure 5. SEM–EDX characterization of phosphorite beneficiation waste: (A) SEM micrograph showing the heterogeneous particle morphology and (B) EDX spectrum and semi-quantitative elemental composition of the selected analysis region

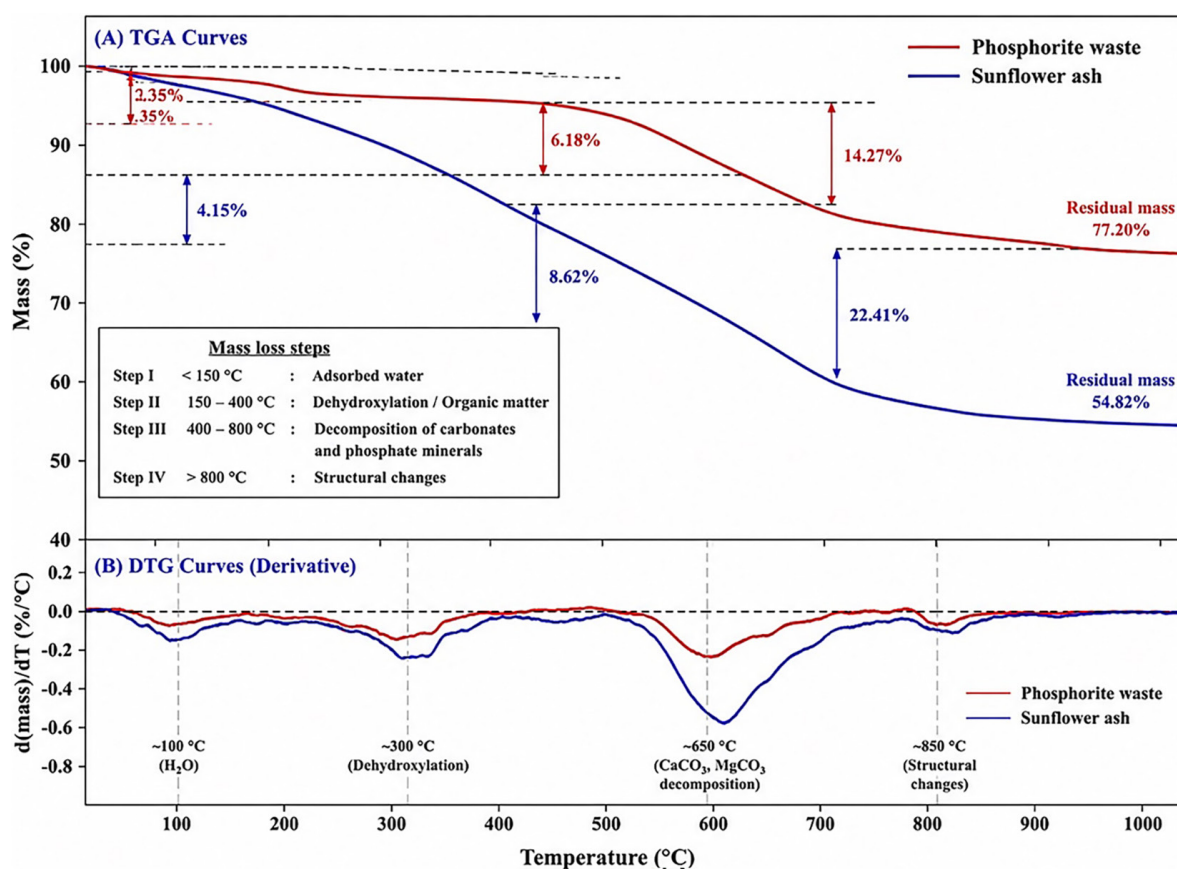


Figure 6. Thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of phosphorite beneficiation waste and sunflower ash: (A) mass change with temperature and (B) derivative mass-loss profiles

Effect of phosphorite waste-to-sunflower ash ratio on liquid-phase P_2O_5 and K_2O concentrations

The effect of the phosphorite beneficiation waste-to-sunflower ash mass ratio on the nutrient composition of the liquid phase was investigated at ratios of 100:10, 100:20, 100:30, 100:40, 100:50, 100:52, 100:54, 100:58, and 100:60 (w/w). During the feedstock-ratio screening experiments, the HNO_3 concentration was fixed at 57 wt.%, while the extraction temperature, reaction time, solid-to-liquid ratio, and stirring speed were maintained at 70 °C, 120 min, 1:3 (w/v), and 200 rpm, respectively. The results are presented as mean $\pm$ standard deviation (SD) of three independent measurements ($n = 3$).

Increasing the proportion of sunflower ash resulted in a progressive decrease in the liquid-phase P_2O_5 concentration and a simultaneous increase in K_2O concentration. At a phosphorite waste-to-sunflower ash ratio of 100:10 (w/w), the liquid phase contained 13.51 ± 0.18 g L⁻¹ P_2O_5 and 8.61 ± 0.16 g L⁻¹ K_2O . At the 100:40 ratio, the corresponding concentrations were 10.40 ± 0.16 g L⁻¹ P_2O_5 and 14.80 ± 0.21 g L⁻¹ K_2O . Further increasing the sunflower ash proportion to 100:60 decreased the P_2O_5 concentration to 7.11 ± 0.15 g L⁻¹, whereas the K_2O concentration increased to 25.83 ± 0.27 g L⁻¹.

One-way ANOVA confirmed that the feedstock ratio had a statistically significant effect on

both P_2O_5 concentration ($F(8,18) = 577.79$, $p < 0.001$) and K_2O concentration ($F(8,18) = 2686.43$, $p < 0.001$). Tukey's HSD post-hoc test showed significant differences among most of the investigated feedstock ratios ($p < 0.05$). For P_2O_5 , no statistically significant difference was observed between the 100:50 and 100:52 ratios or between the 100:54 and 100:58 ratios. For K_2O , the difference between the 100:20 and 100:30 ratios was not statistically significant, whereas the remaining relevant pairwise differences were statistically significant.

The observed trends reflect the complementary roles of the two feedstocks. Phosphorite beneficiation waste represents the principal phosphorus-containing component, whereas sunflower ash provides the major potassium-containing fraction. Consequently, increasing the proportion of sunflower ash increased the K_2O concentration in the liquid phase while decreasing the relative contribution of phosphorus-bearing material and, consequently, the P_2O_5 concentration [3, 6, 10, 19, 21].

Based on the measured liquid-phase nutrient concentrations, the 100:40 (w/w) ratio was selected as the working feedstock composition for the subsequent experimental series. This composition provided an intermediate P_2O_5 – K_2O balance while avoiding the pronounced decrease in P_2O_5 concentration observed at higher sunflower ash additions. Therefore, the 100:40 ratio should be regarded as a selected working composition within the investigated range rather than as a mathematically determined global optimum.

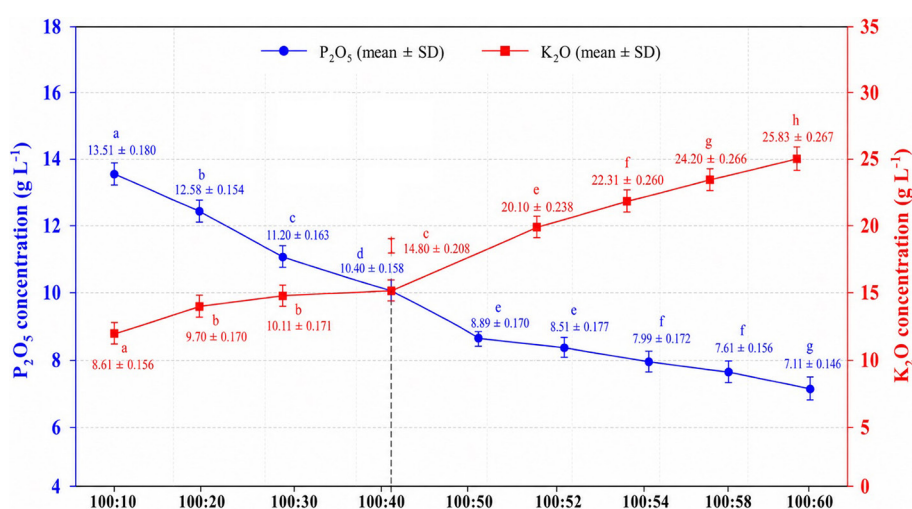


Figure 7. Effect of phosphorite beneficiation waste-to-sunflower ash mass ratio on the liquid-phase concentrations of P_2O_5 and K_2O . Values are presented as mean $\pm$ SD ($n = 3$). Error bars represent standard deviation. Different lowercase letters indicate statistically significant differences among feedstock ratios according to Tukey's HSD test ($p < 0.05$). Experimental conditions: HNO_3 concentration = 57 wt.%, temperature = 70 °C, extraction time = 120 min, solid-to-liquid ratio = 1:3 (w/v), and stirring speed = 200 rpm

Subsequently, the effect of nitric acid concentration was systematically evaluated over the range of 5–57 wt.% HNO_3 using the selected 100:40 (w/w) feedstock composition (Figure 7).

Effect of nitric acid concentration on liquid-phase P_2O_5 and K_2O concentrations

Following the preliminary feedstock-ratio screening, the effect of nitric acid concentration on the transfer of phosphorus- and potassium-containing species into the liquid phase was systematically investigated at HNO_3 concentrations of 5, 10, 15, 20, 30, 40, 50, and 57 wt.% (Figure 8). The selected phosphorite beneficiation waste-to-sunflower ash ratio was maintained at 100:40 (w/w), while the extraction temperature, reaction time, solid-to-liquid ratio, and stirring speed were kept constant at 70 °C, 120 min, 1:3 (w/v), and 200 rpm, respectively. The results are presented as mean $\pm$ standard deviation (SD) of three independent measurements ($n = 3$).

Increasing the HNO_3 concentration resulted in a progressive increase in the liquid-phase concentrations of both P_2O_5 and K_2O . At 5 wt.% HNO_3 , the concentrations were $10.21 \pm 0.16 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $13.01 \pm 0.18 \text{ g L}^{-1} \text{ K}_2\text{O}$. At 20 wt.% HNO_3 , the corresponding concentrations increased to $14.46 \pm 0.22 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $15.96 \pm 0.23 \text{ g L}^{-1} \text{ K}_2\text{O}$. At the highest investigated acid concentration of 57 wt.% HNO_3 , the liquid phase contained $17.81 \pm 0.16 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $21.11 \pm 0.20 \text{ g L}^{-1} \text{ K}_2\text{O}$.

One-way ANOVA confirmed that HNO_3 concentration had a statistically significant effect on both P_2O_5 concentration ($F(7,16) = 710.05$, $p < 0.001$) and K_2O concentration ($F(7,16) = 563.47$, $p < 0.001$). Tukey's HSD post-hoc test showed statistically significant differences among all investigated HNO_3 concentration levels for both P_2O_5 and K_2O ($p < 0.05$), as indicated by different lowercase letters in Figure 8. The increase in P_2O_5 concentration with increasing HNO_3 concentration is consistent with enhanced proton-assisted dissolution of calcium phosphate-bearing phases, particularly apatite-type phases. Increasing acid concentration promotes decomposition of the phosphate-bearing mineral matrix and facilitates the transfer of phosphorus-containing species into the liquid phase. Potassium-containing constituents of sunflower ash are comparatively more readily extractable; therefore, the increase in K_2O concentration is interpreted primarily as enhanced transfer of potassium-containing species into the liquid phase rather than as evidence that highly concentrated nitric acid is intrinsically required for potassium dissolution [6, 13, 16, 17, 19, 21].

The increase in nutrient concentration was more pronounced at lower acid concentrations, particularly up to approximately 20 wt.% HNO_3 , whereas further increases in acid concentration produced a more gradual increase in the measured P_2O_5 and K_2O concentrations. This behavior may reflect progressive dissolution and depletion of the more readily reactive fractions as acid

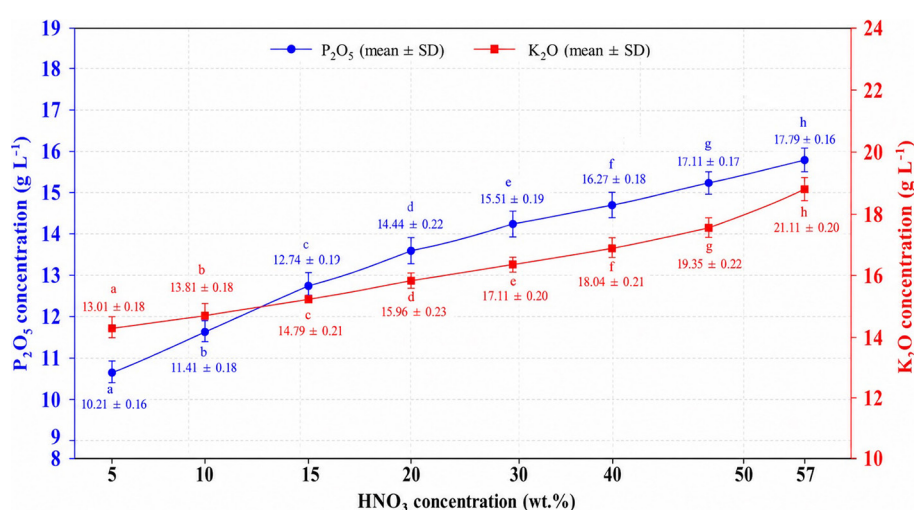


Figure 8. Effect of nitric acid concentration on the liquid-phase concentrations of P_2O_5 and K_2O . Values are presented as mean $\pm$ SD ($n = 3$). Error bars represent standard deviation. Different lowercase letters indicate statistically significant differences among HNO_3 concentration levels according to Tukey's HSD test ($p < 0.05$). Experimental conditions: phosphorite beneficiation waste-to-sunflower ash ratio = 100:40 (w/w), temperature = 70 °C, extraction time = 120 min, solid-to-liquid ratio = 1:3 (w/v), and stirring speed = 200 rpm

concentration increased [13, 16, 21]. Within the investigated range, 57 wt.% HNO_3 produced the highest liquid-phase concentrations of both P_2O_5 and K_2O and was therefore selected as the operating acid concentration for the subsequent experimental series. This concentration represents the most favorable level within the investigated range and should not be interpreted as a mathematically determined global optimum.

Because the total initial phosphorus and potassium inventories and the residual nutrient contents of the post-extraction solids were not independently quantified, the results are interpreted in terms of liquid-phase P_2O_5 and K_2O concentrations rather than absolute phosphorus and potassium recovery efficiencies.

Effect of extraction temperature on liquid-phase P_2O_5 and K_2O concentrations

Following selection of the operating HNO_3 concentration, the effect of extraction temperature on the transfer of phosphorus- and potassium-containing species into the liquid phase was investigated at 40, 50, 60, 70, 80, and 90 °C (Figure 9). In accordance with the one-factor-at-a-time (OFAT) experimental design, the phosphorite beneficiation waste-to-sunflower ash ratio was maintained at 100:40 (w/w), the HNO_3

concentration at 57 wt.%, the extraction time at 120 min, the solid-to-liquid ratio at 1:3 (w/v), and the stirring speed at 200 rpm. Only the extraction temperature was varied. The results are presented as mean $\pm$ standard deviation (SD) of three independent measurements ($n = 3$).

Increasing the extraction temperature from 40 to 80 °C generally increased the liquid-phase concentrations of P_2O_5 and K_2O . P_2O_5 increased progressively up to 80 °C, whereas K_2O reached its highest measured concentration at 70 °C and remained statistically comparable at 80 °C. The P_2O_5 concentration increased from $10.21 \pm 0.20 \text{ g L}^{-1}$ at 40 °C to $18.72 \pm 0.21 \text{ g L}^{-1}$ at 80 °C, while the K_2O concentration increased from 13.71 ± 0.21 to $20.81 \pm 0.20 \text{ g L}^{-1}$ over the same temperature range. At 90 °C, the concentrations decreased to $16.51 \pm 0.21 \text{ g L}^{-1}$ P_2O_5 and $18.81 \pm 0.20 \text{ g L}^{-1}$ K_2O .

One-way ANOVA confirmed that extraction temperature had a statistically significant effect on both P_2O_5 concentration ($F(5,12) = 821.46$, $p < 0.001$) and K_2O concentration ($F(5,12) = 586.46$, $p < 0.001$). Tukey's HSD post-hoc test showed statistically significant differences among all investigated temperatures for P_2O_5 ($p < 0.05$). For K_2O , no statistically significant difference was observed between 70 and 80 °C or between 60 and 90 °C, whereas the remaining relevant pairwise differences were statistically significant ($p < 0.05$).

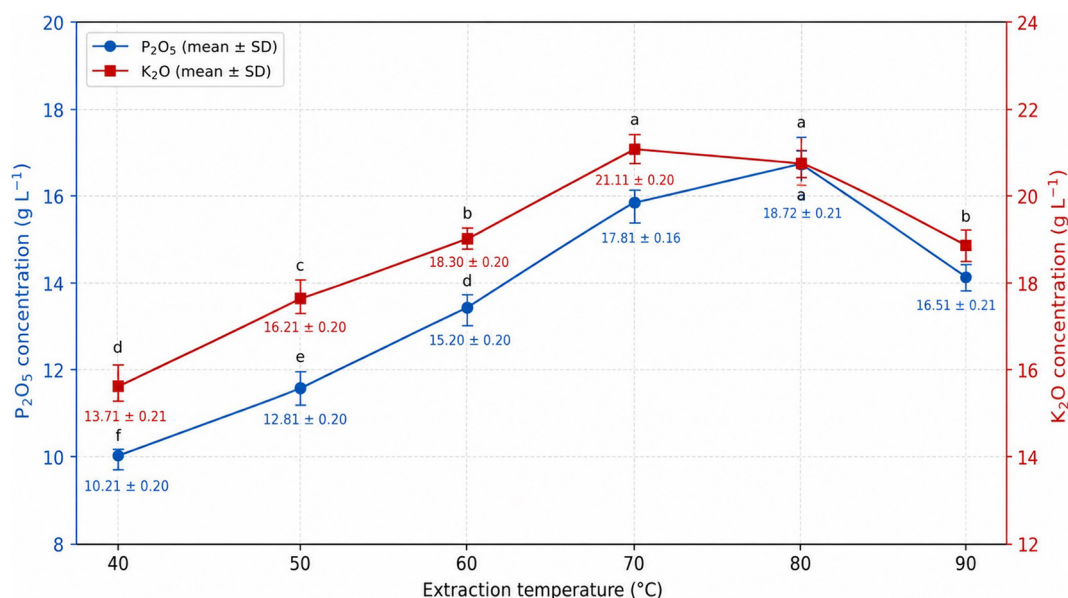


Figure 9. Effect of extraction temperature on the liquid-phase concentrations of P_2O_5 and K_2O . Values are presented as mean $\pm$ SD ($n = 3$). Error bars represent standard deviation. Different lowercase letters indicate statistically significant differences among extraction temperatures within each response variable according to Tukey's HSD test ($p < 0.05$); identical letters indicate no significant difference. Experimental conditions: phosphorite beneficiation waste-to-sunflower ash ratio = 100:40 (w/w), HNO_3 concentration = 57 wt.%, extraction time = 120 min, solid-to-liquid ratio = 1:3 (w/v), and stirring speed = 200 rpm

The increase in nutrient concentration with increasing temperature up to 80 °C is consistent with enhanced acid–solid reaction kinetics, improved mass transfer, and more effective penetration of the extracting solution into the solid matrix. Elevated temperature promotes proton-assisted dissolution of phosphate-bearing phases and facilitates the transfer of phosphorus-containing species into the liquid phase. Potassium-containing constituents of sunflower ash are comparatively more readily extractable, and their transfer into the liquid phase also increased with temperature [6, 13, 16, 19, 21].

A decrease in both P_2O_5 and K_2O concentrations was observed when the temperature was increased from 80 to 90 °C. Because no post-extraction solid-phase characterization or solution-speciation analysis was performed, this decrease cannot be conclusively attributed to a specific chemical mechanism. Possible contributions may include secondary precipitation, changes in solution composition, or other temperature-dependent processes; however, these interpretations require further experimental verification.

Within the investigated temperature range, 80 °C was selected as the preferred operating temperature because it produced the highest liquid-phase P_2O_5 concentration, while the K_2O concentration obtained at 80 °C was statistically comparable to that obtained at 70 °C. Accordingly, 80

°C was selected as the working temperature for the subsequent experimental series. This temperature represents a selected operating level within the investigated range rather than a mathematically determined global optimum. Because the total initial phosphorus and potassium inventories and the residual nutrient contents of the post-extraction solids were not independently quantified, the results are interpreted in terms of liquid-phase P_2O_5 and K_2O concentrations rather than absolute nutrient recovery efficiencies.

Effect of extraction time on liquid-phase P_2O_5 and K_2O concentrations

The effect of extraction time on the transfer of phosphorus- and potassium-containing species into the liquid phase was investigated at 30, 60, 90, 120, and 150 min (Figure 10). In accordance with the one-factor-at-a-time (OFAT) experimental design, all other process conditions were maintained constant at a phosphorite beneficiation waste-to-sunflower ash ratio of 100:40 (w/w), an HNO_3 concentration of 57 wt.%, a temperature of 80 °C, a solid-to-liquid ratio of 1:3 (w/v), and a stirring speed of 200 rpm. The results are presented as mean $\pm$ standard deviation (SD) of three independent measurements ($n = 3$). Increasing the extraction time resulted in

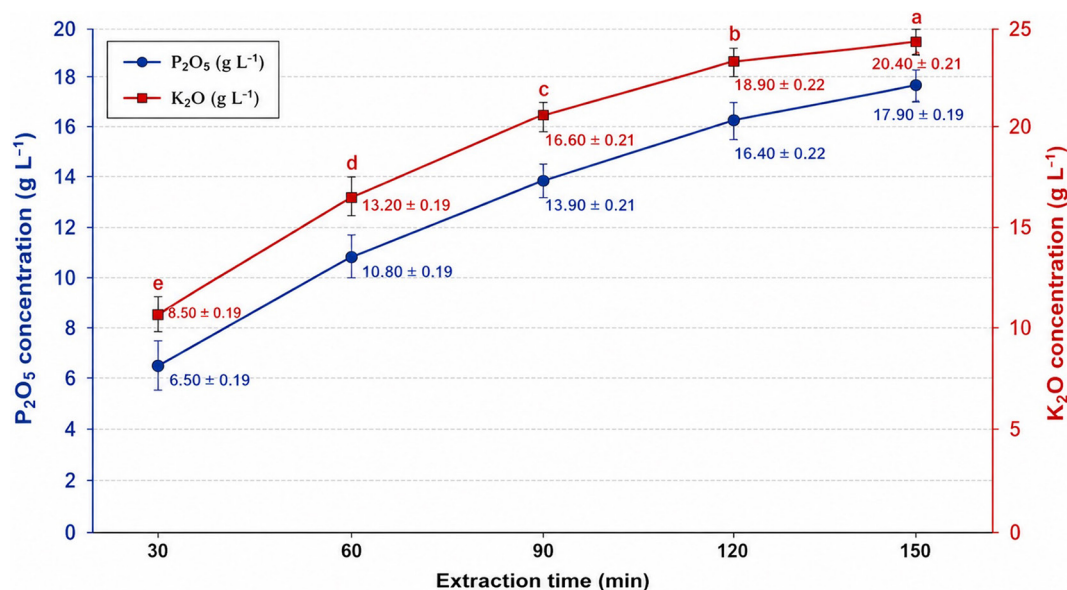


Figure 10. Effect of extraction time on the liquid-phase concentrations of P_2O_5 and K_2O . Values are presented as mean $\pm$ SD ($n = 3$). Error bars represent standard deviation. Different lowercase letters indicate statistically significant differences among extraction times according to Tukey's HSD test ($p < 0.05$). Experimental conditions: phosphorite beneficiation waste-to-sunflower ash ratio = 100:40 (w/w), HNO_3 concentration = 57 wt.%, temperature = 80 °C, solid-to-liquid ratio = 1:3 (w/v), and stirring speed = 200 rpm

a progressive increase in the liquid-phase concentrations of both P_2O_5 and K_2O . At 30 min, the concentrations were $6.50 \pm 0.19 \text{ g L}^{-1} P_2O_5$ and $8.50 \pm 0.19 \text{ g L}^{-1} K_2O$. Increasing the extraction time to 90 min increased the corresponding concentrations to $13.90 \pm 0.21 \text{ g L}^{-1} P_2O_5$ and $16.60 \pm 0.21 \text{ g L}^{-1} K_2O$. At 150 min, the highest values within the investigated time range were obtained, reaching $17.90 \pm 0.19 \text{ g L}^{-1} P_2O_5$ and $20.40 \pm 0.21 \text{ g L}^{-1} K_2O$.

One-way ANOVA confirmed that extraction time had a statistically significant effect on both P_2O_5 concentration ($F(4,10) = 1557.89$, $p < 0.001$) and K_2O concentration ($F(4,10) = 1635.56$, $p < 0.001$). Tukey's HSD post-hoc test showed statistically significant differences among all investigated extraction times for both P_2O_5 and K_2O concentrations ($p < 0.05$). Accordingly, the groups are represented by different lowercase letters in Figure 10, progressing from e at 30 min to a at 150 min.

The relatively rapid increase observed during the earlier stages of extraction can be attributed to dissolution of more readily accessible nutrient-bearing phases and to the initially high concentration gradient between the solid particles and the liquid phase. As extraction proceeded, the increase in nutrient concentration became less pronounced, which is consistent with progressive depletion of the more reactive fractions and

increasing mass-transfer limitations within the solid matrix [13, 16, 21].

Although the concentration profiles became less steep toward the end of the investigated period, a true equilibrium state cannot be conclusively established because no measurements were performed beyond 150 min. Therefore, the 150 min extraction time was selected as the operating extraction time for the subsequent experimental series on the basis of the highest nutrient concentrations measured within the investigated range, rather than as a confirmed equilibrium time.

Because the total initial phosphorus and potassium inventories and the residual nutrient contents of the post-extraction solids were not independently quantified, the results are interpreted in terms of liquid-phase P_2O_5 and K_2O concentrations rather than absolute phosphorus and potassium recovery efficiencies.

Effect of solid-to-liquid ratio on liquid-phase P_2O_5 and K_2O concentrations

The effect of the solid-to-liquid ratio on the liquid-phase concentrations of P_2O_5 and K_2O was investigated at solid-to-liquid ratios of 1:2, 1:3, 1:4, 1:5, and 1:6 (w/v) (Figure 11). In accordance with the one-factor-at-a-time (OFAT) experimental design, all other process conditions

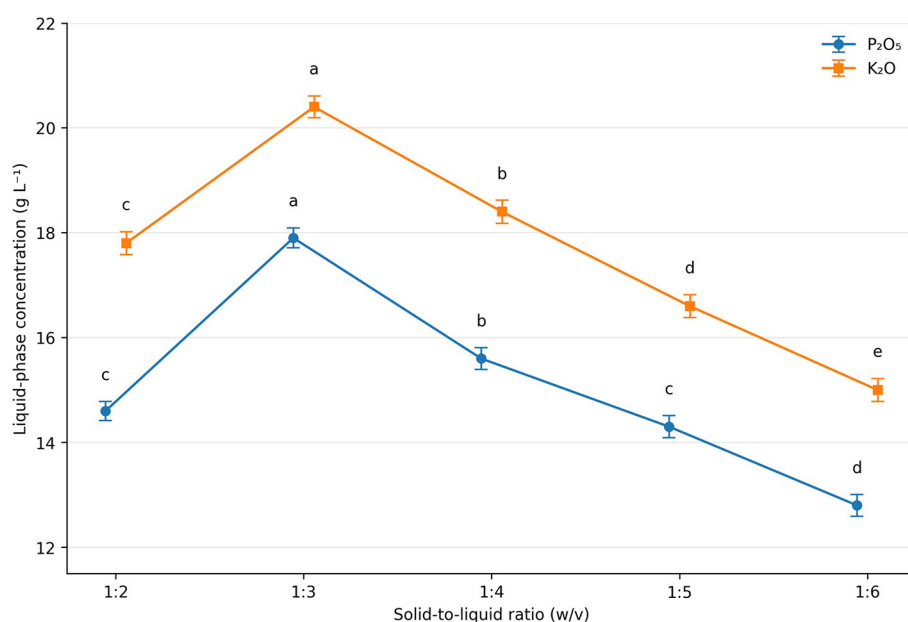


Figure 11. Effect of solid-to-liquid ratio on the liquid-phase concentrations of P_2O_5 and K_2O . Values are presented as mean $\pm$ SD ($n = 3$). Error bars represent standard deviation. Different lowercase letters indicate statistically significant differences among solid-to-liquid ratios according to Tukey's HSD test ($p < 0.05$). Experimental conditions: phosphorite beneficiation waste-to-sunflower ash ratio = 100:40 (w/w), HNO_3 concentration = 57 wt.%, temperature = 80 °C, extraction time = 150 min, and stirring speed = 200 rpm

were maintained constant at a phosphorite beneficiation waste-to-sunflower ash ratio of 100:40 (w/w), an HNO_3 concentration of 57 wt.%, a temperature of 80 °C, an extraction time of 150 min, and a stirring speed of 200 rpm. The results are presented as mean $\pm$ standard deviation (SD) of three independent measurements ($n = 3$).

The solid-to-liquid ratio had a pronounced influence on the measured nutrient concentrations in the liquid phase. At a ratio of 1:2, the extract contained $14.60 \pm 0.18 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $17.80 \pm 0.22 \text{ g L}^{-1} \text{ K}_2\text{O}$. Increasing the liquid proportion to a ratio of 1:3 increased the corresponding concentrations to $17.90 \pm 0.19 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $20.40 \pm 0.21 \text{ g L}^{-1} \text{ K}_2\text{O}$, which were the highest values observed within the investigated range. Further increases in the liquid proportion progressively decreased the measured concentrations, reaching $12.80 \pm 0.21 \text{ g L}^{-1} \text{ P}_2\text{O}_5$ and $15.00 \pm 0.22 \text{ g L}^{-1} \text{ K}_2\text{O}$ at a ratio of 1:6.

One-way ANOVA confirmed that the solid-to-liquid ratio had a statistically significant effect on both P_2O_5 concentration ($F(4,10) = 266.16$, $p < 0.001$) and K_2O concentration ($F(4,10) = 256.71$, $p < 0.001$). Tukey's HSD post-hoc test showed that, for P_2O_5 , the difference between the 1:2 and 1:5 ratios was not statistically significant ($p = 0.407$), whereas the remaining pairwise comparisons were statistically significant at $p < 0.05$. For K_2O , statistically significant differences were observed among all investigated solid-to-liquid ratios ($p < 0.05$).

The increase in P_2O_5 and K_2O concentrations from 1:2 to 1:3 indicates that this ratio provided more favorable contact between the solid feedstocks and the extracting solution under the applied conditions. However, the decrease in concentration observed when the liquid proportion was increased from 1:3 to 1:6 should be interpreted cautiously. Because the analytical response is expressed in g L^{-1} , increasing the liquid volume causes dilution of the extracted nutrients and therefore does not necessarily indicate a proportional decrease in the absolute amount of phosphorus or potassium transferred from the solid phase [13, 16, 21].

Accordingly, the 1:3 (w/v) solid-to-liquid ratio was selected as the preferred operating ratio because it produced the highest measured liquid-phase concentrations of both P_2O_5 and K_2O within the investigated range. This ratio should be regarded as the most favorable operating level within the tested range rather than as a mathematically determined global optimum.

Because the total initial phosphorus and potassium inventories and the residual nutrient contents of the post-extraction solids were not independently quantified, the results are discussed in terms of liquid-phase P_2O_5 and K_2O concentrations rather than absolute nutrient recovery efficiencies.

Selection of preferred operating conditions for nitric acid-assisted extraction

Based on the systematic OFAT evaluation of the individual process parameters, preferred operating conditions were identified for the nitric acid-assisted extraction of phosphorus- and potassium-containing species from phosphorite beneficiation waste and sunflower ash. The phosphorite beneficiation waste-to-sunflower ash ratio of 100:40 (w/w) was selected as the working feedstock composition because it provided an intermediate P_2O_5 – K_2O composition while avoiding the pronounced decrease in P_2O_5 concentration observed at higher sunflower ash additions.

Following selection of the feedstock composition, the effects of nitric acid concentration, extraction temperature, extraction time, and solid-to-liquid ratio were evaluated sequentially. Within the investigated ranges, an HNO_3 concentration of 57 wt.% provided the highest liquid-phase concentrations of both P_2O_5 and K_2O and was therefore selected as the operating acid concentration. Subsequent temperature experiments showed that 80 °C produced the highest P_2O_5 concentration, while the K_2O concentration at 80 °C was statistically comparable to that obtained at 70 °C.

Extraction-time experiments demonstrated a progressive increase in nutrient concentrations over the investigated period, with the highest measured values obtained at 150 min. Because no measurements were performed beyond 150 min, this duration is regarded as the preferred operating extraction time within the investigated range rather than as a confirmed equilibrium time. The solid-to-liquid ratio experiments further showed that 1:3 (w/v) produced the highest liquid-phase concentrations of both nutrients under the investigated conditions.

Accordingly, the preferred operating conditions identified within the experimental ranges were a phosphorite beneficiation waste-to-sunflower ash ratio of 100:40 (w/w), an HNO_3 concentration of 57 wt.%, an extraction temperature of 80 °C, an extraction time of 150 min, a solid-to-liquid

ratio of 1:3 (w/v), and a stirring speed of 200 rpm. Under these selected conditions, the liquid phase contained up to approximately 17.9 g L⁻¹ P₂O₅ and 20.4 g L⁻¹ K₂O. These values represent the experimentally measured nutrient concentrations in the liquid phase and should not be interpreted as absolute phosphorus or potassium recovery efficiencies because the total initial nutrient inventories and the residual nutrient contents of the post-extraction solids were not independently quantified.

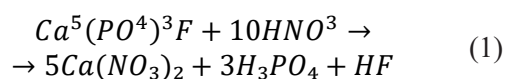
Therefore, the selected conditions represent the most favorable operating levels within the investigated experimental ranges rather than a mathematically determined global optimum. The results demonstrate the feasibility of combining phosphorite beneficiation waste as a phosphorus-containing feedstock with sunflower ash as a potassium-containing feedstock within a single nitric acid-assisted extraction route to obtain a P–K-containing liquid product.

DISCUSSION

Proposed mechanism of nitric acid-assisted extraction

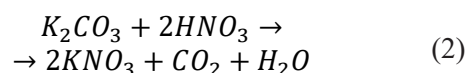
The experimental results indicate that phosphorus- and potassium-containing species were transferred into the liquid phase through different but complementary dissolution processes. The characterization results showed that phosphorite beneficiation waste contains phosphate-bearing mineral phases, whereas sunflower ash provides potassium-containing constituents. Accordingly, the observed extraction behavior can primarily be interpreted as acid-assisted dissolution of poorly soluble phosphorus-bearing phases combined with comparatively easier transfer of potassium-containing species from sunflower ash into the liquid phase.

The increase in liquid-phase P₂O₅ concentration with increasing HNO₃ concentration is consistent with proton-assisted dissolution of calcium phosphate-bearing phases. Under strongly acidic conditions, apatite-type phases may become progressively destabilized as protonation promotes dissolution of calcium- and phosphate-containing components. For fluorapatite, a simplified overall reaction can be represented as [15, 16, 17]:



This equation should be regarded as a simplified representation of a possible dissolution pathway rather than direct evidence of the exact reaction mechanism occurring in the heterogeneous phosphorite waste matrix. The XRD and FTIR results qualitatively support the presence of phosphate-bearing phases; however, quantitative phase analysis and characterization of the post-extraction residues were not performed. Therefore, the contribution of individual mineral phases to phosphorus transfer cannot be quantified conclusively [13, 15, 16, 17, 21].

Potassium exhibited different extraction behavior because potassium-containing constituents of biomass ash are generally more readily transferred into aqueous media than poorly soluble calcium phosphate phases. Nitric acid may additionally promote dissolution and neutralization of alkaline potassium-bearing components. For example, if potassium carbonate is present, its interaction with nitric acid may be represented by the simplified reaction [6, 8, 19]:



This reaction is presented only as a plausible pathway because the individual potassium-bearing phases and their quantitative contributions were not independently determined. Consequently, the measured increase in liquid-phase K₂O concentration should be interpreted as enhanced transfer of potassium-containing species rather than proof of a specific chemical reaction [6, 8, 19].

The effects of temperature and extraction time are also consistent with combined dissolution and mass-transfer processes. Increasing the temperature from 40 to 80 °C increased the concentrations of both P₂O₅ and K₂O, indicating enhanced solid–liquid interaction under the applied conditions. At 90 °C, both concentrations decreased. Because no post-extraction solid-phase characterization or solution-speciation analysis was performed, this decrease cannot be conclusively attributed to precipitation, secondary-phase formation, or another specific mechanism. Thus, the results establish only that 80 °C provided the highest measured nutrient concentrations within the investigated temperature range [13, 16, 21].

Increasing the extraction time from 30 to 150 min progressively increased the liquid-phase nutrient concentrations. The slower increase toward the end of the investigated period may reflect progressive depletion of more readily accessible

fractions and increasing mass-transfer limitations within the solid matrix. However, because measurements were not performed beyond 150 min, establishment of a true equilibrium state cannot be confirmed. Therefore, 150 min is regarded as the preferred operating extraction time within the investigated range rather than as a confirmed equilibrium time [13, 16, 21].

The solid-to-liquid ratio also strongly influenced the measured concentrations. A ratio of 1:3 (w/v) produced the highest liquid-phase P_2O_5 and K_2O concentrations among the investigated ratios. At higher liquid proportions, the observed decrease in concentration should not necessarily be interpreted as lower nutrient transfer because increasing the liquid volume also produces a dilution effect. Accordingly, these results are interpreted primarily in terms of liquid-phase concentrations rather than absolute extracted amounts [13, 16, 21].

The morphological and surface characteristics of the feedstocks may additionally influence their interaction with the extracting solution. SEM observations indicated heterogeneous and irregular particle surfaces, whereas BET analysis confirmed accessible surface and pore characteristics. These properties may facilitate contact between nitric acid and reactive sites in the solid materials. Nevertheless, without kinetic modeling and post-extraction structural characterization, their individual contributions to the extraction process cannot be quantified [3, 8, 10, 21].

Overall, the observed extraction behavior can be described by two complementary pathways: proton-assisted dissolution of phosphorus-bearing phases from phosphorite beneficiation waste and comparatively easier transfer of potassium-bearing species from sunflower ash into the liquid phase [6, 13, 16, 19, 21].

Contextual comparison with previously reported nutrient-processing approaches

Previous studies have demonstrated the potential of mineral-acid-based treatments for dissolving phosphorus-bearing phases from phosphate-containing raw materials and phosphate-processing residues [3, 10, 13, 16, 17, 21]. In parallel, biomass ashes have been investigated as secondary sources of potassium and other mineral nutrients, with potassium-bearing constituents often showing comparatively high aqueous extractability [6, 8, 19]. These studies provide useful

background for interpreting the present results; however, direct quantitative comparison is limited because extraction performance is strongly influenced by the origin and composition of the raw materials as well as by the applied experimental conditions.

In particular, previously reported studies differ with respect to feedstock type and mineralogy, acid type and concentration, temperature, extraction time, solid-to-liquid ratio, particle size, mixing conditions, and analytical methodology [6, 13, 16, 19, 21]. Moreover, most of these approaches consider phosphate-containing materials or biomass-derived ash as separate resource streams, whereas the present study combines phosphorite beneficiation waste and sunflower ash in a single nitric acid-assisted extraction system. Consequently, direct numerical ranking of the present results against studies based on substantially different raw materials and operating conditions would not provide a scientifically meaningful comparison.

Nevertheless, the general trends observed in the present study are consistent with the broader literature. Increasing nitric acid concentration enhanced the transfer of phosphorus-containing species into the liquid phase, in agreement with the acid-assisted dissolution behavior reported for phosphate-bearing raw materials [13, 16, 17, 21]. Potassium-containing species from sunflower ash were transferred comparatively readily into the liquid phase, which is consistent with the reported extractability of potassium-bearing constituents from biomass ashes [6, 19]. Temperature, extraction time, and solid-to-liquid ratio also influenced the measured liquid-phase nutrient concentrations, confirming the importance of process conditions in solid–liquid extraction systems.

The main distinction of the present approach is therefore not a claim of superior extraction efficiency relative to previously published processes, but rather the integrated utilization of two chemically complementary waste materials within a single extraction route. Phosphorite beneficiation waste acts predominantly as a phosphorus-containing feedstock, whereas sunflower ash provides potassium-containing species. Their combined treatment enables simultaneous transfer of P- and K-bearing components into a common liquid phase.

Because the total initial phosphorus and potassium inventories and the residual nutrient

contents of the post-extraction solids were not independently quantified, the present results cannot be directly expressed as absolute recovery percentages. Accordingly, comparison with previous studies is restricted to qualitative process behavior and general extraction trends rather than direct comparison of recovery efficiencies.

Environmental and practical significance

The proposed nitric acid-assisted extraction approach has potential environmental significance because it enables the combined utilization of two different secondary raw materials: phosphorite beneficiation waste and sunflower ash. Phosphorite beneficiation waste represents a phosphorus-containing mineral residue, whereas sunflower ash contains substantial amounts of potassium-bearing constituents. Their combined processing therefore offers a potential route for transferring P- and K-containing species from waste materials into a common liquid phase [2, 18, 22].

From a resource-utilization perspective, this approach may contribute to reducing the disposal burden associated with both mineral-processing waste and agricultural biomass ash. At the same time, it provides an opportunity to recover useful nutrient-containing components from secondary resources rather than relying exclusively on primary raw materials. The complementary composition of the two feedstocks is particularly important: phosphorite beneficiation waste primarily supplies phosphorus-containing phases, whereas sunflower ash contributes potassium-containing species [2, 3, 6, 10, 18, 19, 22].

However, the practical feasibility of the process must be evaluated together with its technological limitations. The preferred nitric acid concentration identified within the investigated range was relatively high (57 wt.% HNO_3), which may increase acid consumption, corrosion requirements, process-safety considerations, and operating costs. In addition, maintaining the extraction system at 80 °C for 150 min requires thermal energy. Therefore, further process development should focus on reducing acid and energy demand while maintaining acceptable liquid-phase P_2O_5 and K_2O concentrations [5, 12].

Additional studies are also required before large-scale implementation. These should include evaluation of acid consumption and possible acid recycling, corrosion-resistant construction materials, solid–liquid separation

efficiency, treatment or reuse of residual process streams, and reproducibility under larger-scale operating conditions. The influence of scale-up on mixing and mass transfer should also be investigated [5, 12, 22].

Although the obtained liquid phase contained measurable concentrations of both P_2O_5 and K_2O , its direct suitability for agricultural application cannot be concluded from the present extraction experiments alone. Further assessment should therefore include analysis of potentially undesirable elements, nutrient speciation, storage stability, phytotoxicity, plant-availability, and controlled agronomic testing [2, 5, 12]. Overall, the present results demonstrate the technical feasibility of using phosphorite beneficiation waste and sunflower ash as complementary feedstocks in a single nitric acid-assisted extraction route. Nevertheless, the process should currently be regarded as a laboratory-scale nutrient-transfer approach rather than a fully validated fertilizer-production technology. Further optimization of reagent consumption, energy demand, product quality, environmental performance, and scale-up conditions is required before practical application can be established.

CONCLUSIONS

This study demonstrated the feasibility of nitric acid-assisted extraction for transferring phosphorus- and potassium-containing species from phosphorite beneficiation waste and sunflower ash into a common liquid phase. The OFAT experiments showed that the feedstock ratio, HNO_3 concentration, temperature, extraction time, and solid-to-liquid ratio significantly affected the liquid-phase P_2O_5 and K_2O concentrations.

Within the investigated ranges, the preferred operating conditions were 100:40 (w/w) phosphorite waste-to-sunflower ash, 57 wt.% HNO_3 , 80 °C, 150 min, a solid-to-liquid ratio of 1:3 (w/v), and 200 rpm. These conditions represent the most favorable tested levels rather than a mathematically determined global optimum.

The observed trends are consistent with proton-assisted dissolution of phosphorus-bearing phases and comparatively easier transfer of potassium-containing species from sunflower ash. Because a complete nutrient mass balance and post-extraction solid-phase characterization were not performed, the results should be interpreted as

liquid-phase extraction performance rather than absolute recovery efficiency.

Further work should focus on complete P and K mass balances, residue characterization, reduction of acid and energy consumption, and agroeconomic evaluation of the resulting liquid product.

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