

# Phosphorus recovery from organic waste for its agronomic valorization: technical and economic evaluation

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## Abstract

**BACKGROUND:** The present work investigates the use of municipal mixed waste compost (MMWC) residue for phosphorus (P) recycling from a technical, economic, and environmental perspective. The study aims to obtain liquid extracts rich in P from MMWC with a low heavy metals content, suitable for their subsequent precipitation in the struvite form. The effect of inorganic (sulfuric/nitric) and organic (oxalic/citric) acids at different molarities and temperatures was studied using technical analysis. The preliminary economic analysis allows the costs of the extraction section for the optimal extraction strategies to be estimated and compared.

**RESULTS:** Based on the multilevel factorial design, the P extraction optimization shows that sulfuric acid 0.5 M and 30 °C provided the highest P extraction yield, 94.2%. However, oxalic acid 0.1 M and 30 °C is the best choice to maximize the P extraction yield, while also minimizing the heavy metals concentration, reaching a P recovery of 2.5 g P/kg. The extraction kinetics for all tested acids were satisfactorily modelled using a second-order model ( $r^2 > 0.99$ ). The preliminary economic analysis, estimated for a P extraction pilot plant of 100 kg h<sup>-1</sup> of MMWC, noted that sulfuric acid 0.5 M provided the lowest total investment cost (130 000 €) and a minimum sale price of theoretical struvite at 4.96 €/kg.

**CONCLUSION:** MMWC is a promising raw material for P recycling as fertilizer due to an appreciable P concentration (7 g P/kg), which can be used together with other residues rich in P to obtain an economical and sustainable extraction process.

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**Keywords:** municipal mixed waste compost; phosphorus recovery; kinetic study; organic waste recycling; circular economy

## INTRODUCTION

Phosphorus (P) is one of the critical nutrients in the growth of organisms on Earth. It is mainly obtained from phosphate minerals to produce inorganic fertilizers, feed, and detergents.<sup>1–3</sup> Nowadays, demand is growing due to the continuous increase in both population and industry.<sup>4</sup> So, resources could be exhausted in 50 to 100 years<sup>5</sup> and could be critical by 2050.<sup>6,7</sup> Under such circumstances, new phosphorous resources must be found from organic materials.

The use of acid solvents and the subsequent precipitation in the form of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is one of the most common ways to recover P from organic waste.<sup>3</sup> The struvite can be used as a solid fertilizer in agriculture as it is easily spread and has a high P content and low concentrations of heavy metals.<sup>8</sup> In addition, struvite releases P slowly as crop growth occurs, so P is released more efficiently, depending on the needs of the plants, which demand P during growth. So, using chemical phosphoric fertilizers can be decreased, thus diminishing the environmental impact, as the slower dissolution of struvite avoids high P concentrations in soil particles or being released through land runoff.<sup>9–11</sup>

The European Union (EU) produces around 250 Mt of municipal waste per year.<sup>12</sup> Mechanical-biological treatment (MBT) plants

commonly manage this waste. In 2017 alone, there were about 570 MBT plants in the EU, whose treatment capacity was 55 Mt.<sup>13</sup> The organic fraction of municipal waste obtained by MBT is habitually composted and stabilized. The result of this treatment is municipal mixed waste compost (MMWC), which is low-quality compost. MMWC is restricted in agriculture by European regulations,<sup>14</sup> so MMWC is disposed of in landfills. However, landfill restrictions are increasingly stringent to comply with the principle of the circular economy. In this sense, according to European regulations, only 10% of the waste generated may be disposed of in landfills in 2035.<sup>15</sup> Therefore, it is necessary to develop alternatives that take advantage of the MMWC as a raw material.

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The P composition of MMWC ranges from 6 to 19 g kg<sup>-1</sup>.<sup>16</sup> Similarly, other studies of P extraction from various wastes reported similar values of initial P concentration in the raw material. For example, the municipal solid waste digestates used by Oliveira *et al.*<sup>17</sup> had a P content of 8.11 g kg<sup>-1</sup> and more than 90% was extracted using nitric acid (HNO<sub>3</sub>) extraction. Kalmykova & Karlfeldt Fedje<sup>18</sup> studied P recovery from municipal solid waste incineration (MSWI) fly ash. They achieved a recovery rate of 70% using acidic leaching-precipitation from MSWI residue with an initial P concentration of 5.9 g kg<sup>-1</sup>.

To the best of our knowledge, no previous papers reported using MMWC as a raw material for P recovery. Moreover, there are no references related to the economic evaluation of P recovery from organic wastes. P extraction is mainly based on extraction with acid solvents because of its high efficiency and low cost, although metal/metalloids can also be extracted.<sup>19</sup> It is also necessary to find a suitable acid to extract P. Inorganic acids can extract all types of P and different alkali metals from the raw material. In contrast, organic acids have chelating effects, increasing the concentration of metals and metalloids in the liquid extracts.<sup>20</sup> There are previous studies that efficiently extract P using such organic wastes as sewage sludge and pig manure. For instance, Barca *et al.*<sup>21</sup> studied P extraction from sewage sludge by conventional extraction, comparing the efficiency of 1 M citric acid and 1 M hydrochloric acid; the maximum efficiencies of P extraction were around 65% using citric acid. Liang *et al.*<sup>4</sup> analyzed P extraction from sewage sludge ash, comparing the efficiency of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and oxalic acid at different molarities. The results were that 95% of the P contained in the raw material could be extracted. Ekpo *et al.*<sup>22</sup> recovered phosphorous from pig manure by hydrothermal treatment using water, 0.1 M sodium hydroxide, 0.1 M sulfuric acid, 0.1 M formic acid, and 0.1 M acetic acid as solvents. In this study, the use of sulfuric acid reached the highest extraction efficiencies, recovering 94% of the P in the raw material.

The present work investigates the potential of P recycling from MMWC residue from a technical, economic, and environmental point of view. The aim is to obtain liquid extracts rich in P from MMWC with a low content of heavy metals, suitable for their subsequent precipitation in the form of struvite. The technical study aimed to optimize the acid extraction of P by analyzing the effect of temperature, the type of acid (inorganic and organic) and acid molarity, as well as the heavy metal concentration in the extracts. Sulfuric and nitric acid were used as inorganic acids and citric and oxalic acid as organic acids. Moreover, the extraction kinetics were determined and modelled to obtain a suitable mass transfer correlation for the subsequent scale-up of the extraction process. The environmental study analyzed the environmental impact of mineral and organic acids, considering eutrophication of aquatic areas and aquatic acidification IChemE indicators. From the economic point of view, a preliminary economic study was carried out to compare the optimal strategies of P extraction with inorganic and organic acids. For this purpose, the total costs of the extraction section of a pilot plant for P recovery from MMWC, along with the market value of struvite that could be theoretically produced, were estimated.

## MATERIALS AND METHODS

### Raw material

The MMWC was kindly donated by Resíduos do Nordeste (Mirandela, Portugal), stored at -18 °C until use and dried in an oven at 70 °C before performing the experimental runs.

### Acid extraction

#### Experimental procedure

The general procedure for P extraction was as follows: solid:liquid (S:L) extraction was conducted using 250 mL sealed flasks in which 10 g MMWC and acid solvent were blended to achieve the set S:L ratio (10% w/v). The extraction was carried out in an orbital shaker (Incubator Shaker ES-60, Miulab, China) under the experimental conditions established. The extraction was carried out with different organic acids (oxalic and citric) and inorganic acids (sulfuric and nitric) at different molarities (0.1–0.5 M) in a range of temperatures between 30 and 60 °C at 200 rpm for 8 h. After that, the mixture was carefully recovered through filtration (Filter-lab 1300/80 0.45 μm, Filters AOIA S.A., Spain) and stored at 4 °C until analysis. Experiments were performed in duplicate.

#### Determination of the kinetics of the P extraction

P extraction kinetics were performed to determine the maximum concentration reached under equilibrium conditions ( $C_e$ ) and the mass transfer coefficient of P recovery from MMWC ( $k$ ).

Experimental runs were carried out with the same conditions as those set out in the previous section under isothermal conditions (30 °C) to determine the kinetic parameters. The integrated pseudo-second-order equation proposed by Ho and McKay<sup>23</sup> (Eq. 1) was used to model the P kinetics. In this equation,  $C_t$  is the P concentration in the liquid at time  $t$  (g P/kg MMWC),  $C_e$  is the P concentration at equilibrium conditions (g P/kg MMWC), and  $k_2$  is the mass transfer coefficient of pseudo-second-order (kg MMWC/(g P · min)).

$$\frac{t}{C_t} = \frac{1}{k_2 \cdot C_e^2} + \frac{t}{C_e} \quad (1)$$

#### Determination of the mass transfer coefficient for S:L extraction

Mass transfer has been widely studied in S:L systems, although principally for first-order coefficients.<sup>24–26</sup> As the mass transfer coefficient obtained in this study is of the second-order; the correlation has been adapted as follows (Eq. 2):

$$k_2 = A_2 \cdot Re^{0.5} \cdot Sc^{0.33} \quad (2)$$

$$Re = \frac{\rho_L \cdot d_p \cdot \omega}{\mu_L} \quad (3)$$

$$Sc = \frac{\mu_L}{\rho_L \cdot D_A} \quad (4)$$

where  $Re$  is the Reynolds number (Eq. 3),  $Sc$  is the Schmidt number (Eq. 4), and  $A_2$  is an experimental constant (g P/(kg MS · min)) that must be determined by regression from the experimental data. The parameters needed from each dimensionless number are the following:  $D_A$  is the molar diffusivity (m<sup>2</sup> s<sup>-1</sup>),  $d_p$  is the particle diameter (m),  $\rho_L$  is the liquid density (kg m<sup>-3</sup>),  $\mu_L$  is the liquid viscosity (Pa s), and  $\omega$  the agitation velocity (1/s).

To calculate  $Re$  and  $Sc$ ,  $\rho_L$  and  $\mu_L$  were analyzed experimentally (Table 5),  $d_p$  was approximated from the particle size characterization (3.16 mm),  $\omega$  was an operation variable (200 rpm), and  $D_A$  was determined by the Stokes-Einstein equation (Eq. 5), where  $k_B$  is the Boltzmann constant.

$$D_A = \frac{k_B \cdot T}{6 \cdot \pi \cdot \mu_L \cdot \left(\frac{d_p}{2}\right)} \quad (5)$$

## Analytical methods

The analytical methods used to characterize both solid and liquid samples were previously described.<sup>13</sup>

### Solid samples

The dried samples of MMWC were sieved to determine the particle size distribution. The organic matter content was determined by gravimetric analysis. The elemental composition (carbon and nitrogen contents) was determined by a LECO CHN-2000 analyzer. Macro and micronutrients and heavy metals were analyzed by ICP Optical Emission Spectrometry and ICP Mass Spectrometry.

### Characterization of the P fractions

Total phosphorus (TP) was extracted from the MMWC by wet digestion with sulfuric acid and nitric acid (HNO<sub>3</sub>). The P fractions were quantified by a sequential extraction protocol described by Barca *et al.*<sup>21</sup> and Lee & Kim.<sup>27</sup> As a result, four P fractions were quantified:

- (1) Weakly bound P extracted under mild alkaline conditions (0.5 M NaHCO<sub>3</sub>)
- (2) Al and Fe bound P compounds obtained under strongly alkaline conditions (0.1 M NaOH)
- (3) Ca bound P compounds extracted under diluted acid conditions (1 M HCl)
- (4) Stable P residual compounds extracted under hot concentrated acid conditions (10 M HCl)

Then, the P concentration in each extract was determined by spectrophotometry (HITACHI UV 2000 spectrophotometer, Hitachi Healthcare Americas, United States) at a wavelength of 720 nm according to the molybdenum blue method.<sup>28</sup>

### Liquid samples

TOC and TN were determined by a TOC-V 5000 analyzer. P was characterized by spectrophotometry using the molybdenum blue method.<sup>28</sup> Macro and micronutrients, as well as heavy metals, were analyzed, as previously described in section 2.3.1.

### Physical properties of extracts

The density of the liquid extracts was measured by gravimetry (30 °C). The viscosity was characterized by a CFRC-100 Cannon-Fenske Routine Viscometer, size 100 (Cannon Instrument Company, Barcelona, Spain). All determinations were made in duplicate.

## Economic evaluation

A pilot plant with a production capacity of 100 kg MMWC/h and a humidity of 25% was considered for the economic analysis. To estimate the struvite's minimum sale price, only the extraction section was included in the economic analysis to compare the feasibility of the different acidic solvents tested. The heavy metals removal and struvite precipitation section was not considered because it would contribute similarly to the total investment cost for all scenarios considered. On the one hand, the heavy metal removal section would consist of membrane equipment. On the other hand, the struvite precipitation section would consist of a temperature-controlled stirred tank where Mg compounds and salts are added to adjust the pH of the extract for the optimal precipitation of struvite. On this basis, the theoretical struvite production was calculated. Its market value was estimated to verify whether the sale price is

competitive and if the process could become economically viable.

The Lang Factor method was applied to calculate the economic costs of the pilot plant as this method is commonly used to approximate the costs of process plants. The complete description of this method can be found in the literature.<sup>29</sup> First, the cost of the leading equipment (agitated extraction tank, storage tank, and centrifuge) was considered to compare the setup of each scenario. Next, the agitation power requirements were calculated using the scale-up criterion of the constant extraction mass transfer coefficient. Only these stages were considered because they are within the battery limits of this study. However, it must be considered that, if the heavy metal removal and struvite precipitation stages had been taken into account, the costs obtained, and therefore the sale price of the struvite, would be higher than that obtained in this preliminary economic study.

Then, the Equipment Cost (PCE) was estimated with the CAPCOST software. Finally, the Total Investment Cost (TIC) was calculated using the solid-liquid factors proposed by the Lang Factor method from the PCE. Eqs. 6–8, to estimate these costs, are as follows:

$$\text{Physical Plant Cost (PPC)} = \text{PCE} * 3.15 \quad (6)$$

$$\text{Fixed Capital Cost (FCC)} = \text{PPC} * 1.40 \quad (7)$$

$$\text{TIC} = \text{FCC} * 1.05 \quad (8)$$

The cost of the raw materials used was estimated from the references: MMWC: 12 €/t,<sup>30</sup> process water: 3.16 €/m<sup>3</sup>,<sup>31</sup> sulfuric acid 98% w/v: 77 €/t, nitric acid 50% w/v: 300 €/t, oxalic acid: 1.14 €/kg, and citric acid: 0.75 €/kg.<sup>29</sup>

The following assumptions were necessary to estimate the plant's profits and the minimum sale price of struvite: All scenarios had a plant lifetime of 10 years. The annual production cost and the production cost per kg of struvite were estimated operating at 8000 h/y. Equipment amortization was estimated in 10 years. Finally, the minimum sale price could be calculated, considering an internal rate of return (IRR) of 10%,<sup>13</sup> and a net present value (NPV) of the plant of 0 €.

## Environmental analysis

IChemE metrics<sup>32</sup> can be applied to compare any industrial process from an environmental perspective. In this case, the parameters selected were the eutrophication of aquatic areas (equivalent tonnes of phosphate (PO<sub>4</sub><sup>3-</sup>) per year) and aquatic acidification (equivalent tonnes of released H<sup>+</sup> ions per year).

## Data analysis

An ANOVA test was carried out with the *Statgraphics Centurion XVIII* version. The ANOVA test was used to conclude the statistical differences at a confidence level of 95% ( $P < 0.05$ ).

# RESULTS AND DISCUSSION

## Raw material composition

The MMWC particle size was determined by sieving with the following size distribution: 0.02% greater than 20 mm; 0.37% between 10 and 20 mm; 2.02% between 5 and 10 mm; 47.61% between 1 and 5 mm; and the rest being under 1 mm. The MMWC was not milled before the experimental runs.

Table 1 shows the complete characterization of the MMWC used in this study. On average, the MMWC had the following composition ( $\text{g kg}^{-1}$  dry weight basis):  $488.5 \pm 5.0$  organic matter (OM),  $309.0 \pm 4.9$  total organic carbon (TOC),  $22.6 \pm 0.5$  total nitrogen (TN),  $7.0 \pm 0.3$  TP.

### Influence of the extraction conditions on P recovery

P fractionation indicates that 65% of TP in the raw material is formed mainly by compounds with Ca bound P, while 17% of the P belongs to compounds with weak bonds, 13% is P relative to stable compounds, and 5% corresponded to P bound Fe and Al. The Ca and Fe concentrations verify that the majority fraction in the MMWC is Ca bound P. Thus, P extraction has to be performed under acidic conditions.<sup>18,27</sup> Barca *et al.*<sup>21</sup> recovered P from sewage sludge under these conditions, which showed 86.3% of Ca bound P and 3.5% of Fe and Al bound P.

Therefore, due to its composition, the MMWC used in this study is a potential P feedstock, which can be recovered to obtain liquid extracts rich in P suitable to be precipitated in the form of struvite.

Three critical factors were identified to extract P efficiently. First, the effects of temperature (30, 45, and 60 °C), type of extraction solvent (sulfuric, nitric as inorganic acids and oxalic, and citric as organic acids) and solvent concentration (0.1, 0.25, and 0.5 M) on the P recovery were analyzed. According to previous results (data not shown), these operating ranges and the literature data on P extraction from solid organic waste were selected.<sup>17,21,33–36</sup>

In this study, the constant operating parameters were: S:L ratio 10% w/v, agitation speed of 200 rpm, and operation time of 8 h. These values were selected from previous studies and have not been optimized.<sup>21,37,38</sup>

### Temperature effect on the P extraction

First, the temperature effect on the S:L extraction was analyzed. Table 2 summarizes the TP, TOC, and TN concentrations in the extracts using organic and inorganic acids as solvents. It should be noted that blanks with acids were also performed to consider the nitrogen and organic carbon concentration in the extraction solvents.

An increase in temperature involves higher carbon and nitrogen concentrations in the extract due to the solubilization of the organic matter.<sup>22,39</sup> Regarding the TOC concentration, the temperature effect was more significant when oxalic acid was used. A seven-fold increase in the TOC concentration, from 0.6 g TOC/kg MS to 44.0 g TOC/kg MS, was observed when the temperature increased from 30 to 60 °C. However, the effect of temperature was less pronounced for inorganic acids and citric acid. In general, the TOC concentration increased significantly with temperature (by 1.05 and 1.60 times). This produced significant differences ( $P < 0.05$ ) in the range of temperatures studied. Similar results were obtained by Ekpo *et al.*,<sup>22</sup> who reported P extraction from swine manure using a hydrothermal treatment. Increasing the temperature from 120 to 170 °C enhanced the TOC concentration by 1.16 times using sulfuric acid and 1.60 times using formic acid. However, a considerable amount of TOC in the liquid extracts can negatively affect P recovery in the subsequent P precipitation as struvite due to an inhibitory effect of the number of carboxyl groups.<sup>40</sup> Therefore, operating at low temperatures is highly recommended so the TOC concentration in the extracts can be kept low.

On the other hand, the total nitrogen concentration in the extracts increased with temperature for all tested acids. In general, the TN concentration ranged from  $4 \text{ g kg}^{-1}$  MS to  $6 \text{ g kg}^{-1}$

**Table 1.** Composition of the MMWC

Parameters	Units	MMWC
pH		7.5
Moisture <sup>a</sup>	%	20.9
Ash content <sup>a</sup>	%	40.5
Organic compounds <sup>b</sup>		
OM	$\text{g kg}^{-1}$	488.5
TOC	$\text{g kg}^{-1}$	309.0
Principal and secondary nutrients <sup>b</sup>		
TN	$\text{g kg}^{-1}$	22.5
P	$\text{g kg}^{-1}$	7.0
K	$\text{g kg}^{-1}$	14.5
Calcium (Ca)	$\text{g kg}^{-1}$	55.3
Magnesium (Mg)	$\text{g kg}^{-1}$	7.2
Sodium (Na)	$\text{g kg}^{-1}$	7.2
Micronutrients and heavy metals <sup>b</sup>		
Iron (Fe)	$\text{g kg}^{-1}$	12.3
Arsenic (As)	$\text{mg kg}^{-1}$	10.9
Copper (Cu)	$\text{mg kg}^{-1}$	218
Manganese (Mn)	$\text{mg kg}^{-1}$	354
Zinc (Zn)	$\text{mg kg}^{-1}$	516
Lead (Pb)	$\text{mg kg}^{-1}$	119
Total Chromium (Cr)	$\text{mg kg}^{-1}$	161
Nickel (Ni)	$\text{mg kg}^{-1}$	52.7
Mercury (Hg)	$\text{mg kg}^{-1}$	0.5
Cadmium (Cd)	$\text{mg kg}^{-1}$	2.4

Data were shown as the mean value with less than 5% of relative error.

<sup>a</sup> Total weight basis.

<sup>b</sup> Dry weight basis.

MS, except when nitric acid was used, which reached  $11 \text{ g kg}^{-1}$  MS when the extraction was performed at the maximum temperature and acid concentration (60 °C and 0.5 M). The temperature increase in the analyzed range did not significantly improve ( $P > 0.05$ ) the TN concentration in the extracts. Ekpo *et al.*<sup>41</sup> also concluded that temperature did not significantly affect the nitrogen solubilization from chicken manure and digestate. The nitrogen solubilization could be due to the breakdown of proteins, which is mainly influenced by the extraction temperature and operation time, as pointed out by other authors, such as Sun *et al.*<sup>39</sup>

Regarding P extraction, an opposite trend was observed for temperature: lower P concentrations were achieved at higher temperatures (Table 2). In our study, in the temperature range studied (30–60 °C) for all acids and molarities, P concentration could decrease by up to 50%. However, the results did not change significantly ( $P > 0.05$ ). These results agree with Ekpo *et al.*,<sup>22</sup> who studied the P extraction from swine manure with such solvents as water, sulfuric acid, and organic acids. The possible reason for the decrease in P concentration could be that, at high temperatures, dissolved P can precipitate with cations of Ca, Mg, and Fe.<sup>22,41</sup> Oliver-Tomas *et al.*<sup>34</sup> studied P extraction from the organic fraction of municipal solid waste. This study analyzed the temperature effect on P extraction using such inorganic acids as sulfuric, nitric, and hydrochloric acid. The study concluded that high temperatures did not improve the P extraction and that the process can be operated at temperatures of 40 °C.

Moreover, working with acids at high temperatures is not recommended in safety terms due to material corrosion and

**Table 2.** P, TOC, and TN concentrations in the extracts using inorganic and organic acids as solvents

Type of acid	Molarity (M)	P (g kg <sup>-1</sup> MS)			TOC (g kg <sup>-1</sup> MS)			TN (g kg <sup>-1</sup> MS)		
		Temperature (°C)			Temperature (°C)			Temperature (°C)		
		30	45	60	30	45	60	30	45	60
Sulfuric acid	0.1	2.1	1.9	1.8	27.2	33.0	34.4	4.1	4.8	5.4
	0.25	5.5	5.2	5.1	31.7	42.4	43.8	4.7	5.1	5.7
	0.5	6.6	6.3	6.1	32.8	44.4	47.4	4.9	5.5	6.4
Nitric acid	0.1	0.4	0.3	0.2	25.1	31.2	30.4	3.9	6.3	6.8
	0.25	1.9	1.6	1.2	27.5	29.6	30.4	5.8	7.1	8.5
	0.5	5.1	5.0	4.9	40.6	40.8	41.3	9.7	10.5	11.2
Oxalic acid	0.1	2.5	1.7	1.6	0.6	18.7	44.0	4.3	4.3	4.6
	0.25	4.3	4.3	3.7	3.5	26.3	45.0	4.5	4.6	5.4
	0.5	5.3	5.0	4.8	5.1	35.1	51.2	4.9	5.0	5.8
Citric acid	0.1	3.1	3.2	2.9	7.5	19.7	31.5	4.0	4.3	4.6
	0.25	5.0	4.8	4.8	20.6	25.1	32.0	4.1	4.5	4.9
	0.5	5.9	5.3	5.2	26.7	27.8	32.1	4.4	4.6	5.0

Data were shown as the mean value with less than 5% of relative error. In the TOC and TN concentrations, only the concentration of these compounds extracted from MMWC have been taken into account. Operation conditions were: 10% w/v, 200 rpm and 8 h.

maintenance. From a technical and economic point of view, working at low temperatures, such as 30 °C, could be the most suitable option.

#### Influence of acid type and concentration

The effects of the concentration and type of acid were analyzed. As can be seen, the increase in acid concentration enhanced TOC, TN, and P extraction (Table 2). This increment means that when the pH decreased, more chemical bonds were broken, and the concentration of solubilized compounds in the extracts increased.<sup>42</sup>

Concerning the TOC concentration, the ANOVA test shows that the results obtained with inorganic and organic acids are statistically different ( $P < 0.05$ ). However, no significant differences were observed between sulfuric and nitric acids or between oxalic and citric acids, respectively. Regarding the molarity, the statistical analysis showed that the results were significantly different ( $P < 0.05$ ) when the acid concentration increased from 0.1 to 0.5 M, but not when the acid concentration increased from 0.1 to 0.25 M.

As explained in the previous section, a high concentration of TOC in the liquid extracts can inhibit the subsequent P precipitation as struvite.<sup>40</sup> Therefore, using organic acids at higher molarities could be a disadvantage compared to inorganic acids.

Analyzing the TN concentration, the ANOVA test showed that only nitric acid presented significant differences ( $P < 0.05$ ) in comparison to the other acids, whose results were similar. Regarding the acid molarity, the statistical results showed significant differences ( $P < 0.05$ ) when the acid concentration increased from 0.1 to 0.5 M, but not when the acid concentration increased from 0.1 to 0.25 M. The TOC and TN extraction trends were similar. These results can be explained because most TN extracted was organic nitrogen (organic nitrogen in samples ranged from 50% to 85% of the total nitrogen, data not shown). Similar results were achieved by Szögi *et al.*,<sup>36</sup> who extracted P from pig manure solids using acids, obtaining extracts in which most TN was in the organic form.

No significant differences were observed regarding P extraction when sulfuric acid and citric acid were used at concentrations of

0.25 and 0.5 M ( $P > 0.05$ ). However, P concentrations were significantly lower ( $P < 0.05$ ) when oxalic acid and nitric acid were used. If the amount of P extracted is compared, sulfuric acid and citric acid could extract 20–50% more P than oxalic and nitric acid when concentrations of 0.25–0.5 M were used. The extraction with sulfuric acid and citric acid is favored because the H<sup>+</sup> concentration was two times higher than when the extraction with nitric acid and oxalic acid was performed.<sup>20,35</sup> The P content increases with the concentration of acid in all cases. The ANOVA test also showed that an increase in acid concentration led to a significant increase in P concentration ( $P < 0.05$ ). It should be noted that, at low molarities (0.1 M), the use of organic acids favored the extraction of P. Concentrations of P were 2.5 and 3.1 g kg<sup>-1</sup> MS when oxalic and citric acid were used at 30°C, higher than when sulfuric or nitric acids were employed (2.1 and 0.4 g kg<sup>-1</sup> MS).

This fact occurs because organic acids behave like strong acids at low molarities, since they can completely dissolve in an aqueous solution. At low molarities, organic acids can solubilize P more effectively than inorganic acids. However, with increasing molarity, organic acids cannot fully dissociate, and therefore P extraction is favored by inorganic acids. Under these conditions, inorganic acids can extract all the P in the raw material, obtaining better yields.<sup>2,20,43,44</sup> On the other hand, Kpombekou-A & Tabatabai<sup>44</sup> suggested that the presence of Ca and Mg ions can contribute to the decrease in the P solubility because these ions increase the pH during extraction. Kostra *et al.*<sup>43</sup> studied the effect of the pH of sulfuric acid and oxalic acid in P extraction from pig manure. This study found that at pH 4, oxalic acid obtained a P extraction yield of 70% compared to the 50% obtained by sulfuric acid. However, at pH 2, the sulfuric acid could extract practically all the P (~99%) from the raw material, exceeding the P yield obtained by oxalic acid.

Sulfuric acid led to the best P extraction results (6.6 g P/kg MS at 0.5 M), corresponding to an extraction yield of 94.3%. At low molarities (0.1 M), citric acid showed the best P extraction results (3.1 g P/kg MS, 35.8% extraction yield). These results are in agreement with previous studies. Fang *et al.*<sup>20</sup> compared the effect of the mineral acids and organic acids on P recovery from incinerated sewage sludge ash. At low acid molarity (0.1 M), the amount

of P recovered was two times higher using organic acids (citric and oxalic acid) than mineral acids (sulfuric and nitric acid). However, at the higher acid molarity (0.5 M), the amount of P recovered was similar in all cases, with sulfuric acid obtaining the highest concentrations. Shiba & Ntuli<sup>35</sup> compared the P extraction from sewage sludge using inorganic acids, such as sulfuric and nitric acid. In this study, the percentage of P extracted was 34.3% for nitric acid and 41.6% for sulfuric acid, the latter being selected as a proper solvent. On the other hand, Darch *et al.*<sup>37</sup> compared citric acid, oxalic acid and maleic acid with a molarity of 0.02 mM for P extraction from tropical forest soils. In this study, citric acid led to the highest concentrations (up to 9 mg kg<sup>-1</sup>), followed by oxalic acid (up to 7 mg kg<sup>-1</sup>).

#### Concentration of heavy metals in the extracts

This work aims to obtain a liquid extract rich in P, which can be further precipitated in the form of struvite. Acids usually extract heavy metals from organic wastes. A high concentration of heavy metals in the extract can be a risk, as they can precipitate along with the P, and the final solid product could be contaminated.<sup>45</sup> Therefore, operation parameters have to be selected to maximize phosphorus recovery, while minimizing the concentration of heavy metals in the extracts. Table 3 shows the concentration of secondary nutrients and heavy metals extracted from MMWC under the different experimental conditions tested. Regarding the secondary nutrients, higher concentrations were reached at higher concentrations of acids. This is probably due to solubility changes at low pH, as Quist-Jensen *et al.*<sup>45</sup> and Wang *et al.*<sup>46</sup> verified. Mg, Fe, and Mn concentrations increased considerably when acid concentrations increased from 0.1 and 0.25 M ( $P < 0.05$ ). Otherwise, nutrients such as Ca in the liquid extract rich in P can precipitate in phosphate form and inhibit struvite precipitation.<sup>47</sup> Thus, the concentration of secondary nutrients has to be limited. As can be seen in Table 3, nitric and citric acids extracted significantly ( $P < 0.05$ ) more Ca than sulfuric and oxalic acids. The Ca concentration reached after 0.5 M nitric acid extraction was 3517 mg L<sup>-1</sup>, while when 0.5 M citric acid was used, the Ca concentration reached 4373 mg L<sup>-1</sup>. So, the use of nitric and citric acids for P extraction can show some disadvantages. On the other hand, oxalic acid has an advantage because it extracts fewer Ca<sup>+</sup> ions that could inhibit struvite precipitation. Ca<sup>+</sup> ions can react with the carboxyl group of the oxalic acid, forming calcium oxalate, which precipitates.<sup>4</sup>

Regarding heavy metals, inorganic acids extracted more Cd than organic acids, extracting more than 90% of the Cd in the raw material. Sulfuric acid extracted significantly more Cr (5 mg L<sup>-1</sup>) compared to the other acids (<2 mg L<sup>-1</sup>). Globally, sulfuric acid extracted 66.2 mg L<sup>-1</sup> of heavy metals, followed by citric acid (47.9 mg L<sup>-1</sup>), oxalic acid (45.5 mg L<sup>-1</sup>), and nitric acid (24.9 mg L<sup>-1</sup>). Heavy metals present in the extracts could be removed through such technologies as membranes,<sup>48</sup> biosorbents,<sup>49</sup> or ion exchange resins.<sup>50</sup> This step would provide an extract liquid rich in P that could produce phosphate fertilizer.

#### Optimal extraction conditions

Experimental data previously described were statistically analyzed. A multilevel factorial design was applied to obtain the most suitable conditions for P extraction with the software Statgraphics Centurion.

Two scenarios were considered. Scenario A only considered maximizing the P concentration without considering the content of nutrients and heavy metals in the liquid extracts. On the other

hand, Scenario B considered maximizing the P concentration, while minimizing the content of nutrients and heavy metals so that P could be further precipitated as struvite.

The results obtained from Scenario A were that the most suitable solvent is 0.5 M sulfuric acid (desirability of 99.0%), reaching a P extraction yield of 94.2%. On the other hand, the best conditions obtained from Scenario B were 0.1 M oxalic acid (desirability of 74.5%), reaching a P extraction yield of 35.8%. In any case, the final decision about the type of acid to be used in the extraction will be established based on the economic evaluation, as shown in section 3.4.

#### Kinetics of P extraction

In this section, the kinetics of extraction for all tested acids at 30 °C were determined and modelled with a second-order kinetic model (Eq. 1). This kinetic study, which plays a significant role in the extraction process, is carried out to determine the kinetic extraction parameters for extracting P from MMWC. Moreover, an appropriate correlation for the mass transfer coefficient, required for scaling up the extraction process, is proposed.

Figure 1 shows the experimental points and the predicted kinetic model for sulfuric acid (Fig. 1(A)), nitric acid (Fig. 1(B)), oxalic acid (Fig. 1(C)), and citric acid (Fig. 1(D)).

The experimental P concentration data ( $C_t$ ), shown in Fig. 1, have been adjusted to a second-order kinetic model (Eq. 1), as explained in section 2.2.2. After 8 h, extraction concentrations reached the equilibrium, which allows the parameters  $k_2$  and  $C_e$  to be determined. In Table 4, the parameters  $k_2$ , predicted  $C_e$ , and adjusted coefficient of determination ( $r^2$ ) are shown. As can be seen, the model provided a perfect fit to the experimental data ( $r^2 > 0.996$ ). Also, the estimated equilibrium concentrations are similar to the experimental data obtained at 480 min (Fig. 1), with a maximum margin error of  $\pm 5\%$ , confirming the validity of the proposed fitting model. On the other hand, Table 4 shows that the  $k_2$  coefficient decreased when the acid molarity increased for the four acids studied. The decrease in  $k_2$  varied between 64% and 85%, depending on the acid used. In addition, the parameter  $C_e$  increased along with the molarity (Table 4). This was expected because, at high molarities, acids have a higher capacity for P extraction, as shown in section 3.1.2. The parameter  $C_e$  varied between  $0.40 \pm 0.01$  g P/kg MMWC (nitric acid 0.1 M) and 6.61 g P/kg MMWC (sulfuric acid 0.5 M) (Table 4). Also, a mass transfer correlation was calculated to validate these results.

At high acid molarity (0.5 M), the highest predicted equilibrium concentration was  $6.61 \pm 0.01$  g P/kg for sulfuric acid. Compared to a low acid concentration (0.1 M), citric acid provided the highest value ( $3.10 \pm 0.03$  g P/kg). These results agree with the conclusions shown in section 3.1.2. Thus, the organic acids provided better P extraction results when low concentrations were used.

In contrast, comparing the kinetics with 0.5 M for both inorganic acids, non-significant differences ( $P > 0.05$ ) in extracted P concentrations were observed due to the possible complete acid digestion of the raw material.

#### Correlation of the mass transfer coefficient for the S:L extraction process

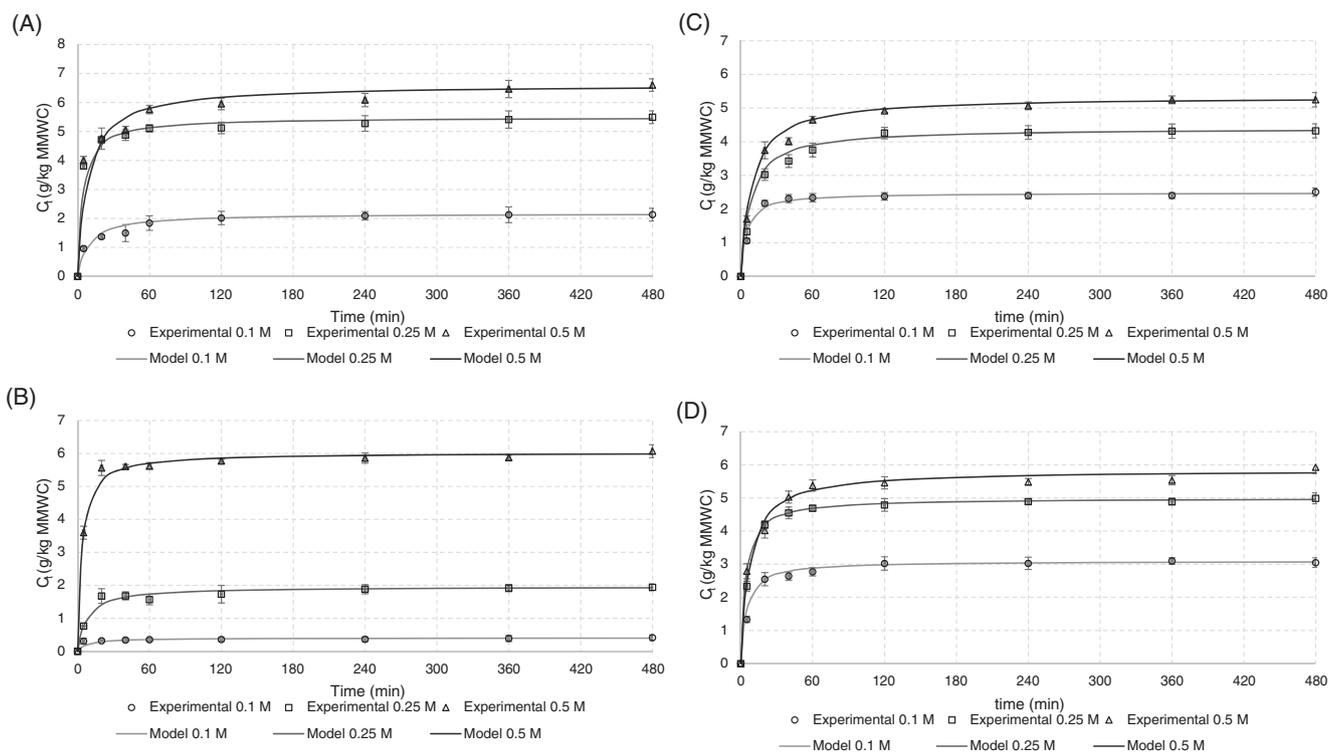
A correlation of the mass transfer coefficient has been proposed, based on dimensionless numbers to justify the effect of molarity on the mass transfer coefficient.

Table 5 shows the parameters needed to calculate the  $A_2$  and the predicted mass transfer coefficient ( $k_2$ ). An increase in molarity from 0.1 to 0.5 M involved increased density and viscosity

**Table 3.** Nutrients and heavy metal concentrations in the extracts using inorganic and organic acids as solvents

Compound	Units	Sulfuric acid Molarity (M)			Nitric acid Molarity (M)			Oxalic acid Molarity (M)			Citric acid Molarity (M)		
		0.1	0.25	0.5	0.1	0.25	0.5	0.1	0.25	0.5	0.1	0.25	0.5
<b>Nutrients</b>													
Mg	mg L <sup>-1</sup>	273	415	420	166	198	287	208	348	372	259	265	319
Na	mg L <sup>-1</sup>	634	663	678	498	546	639	527	545	556	530	539	548
Ca	mg L <sup>-1</sup>	532	589	725	1147	2757	3517	51	64	81	1938	4227	4373
Fe	mg L <sup>-1</sup>	15.4	619	786	7.5	9.5	11.1	132	830	868	261	372	384
Mn	mg L <sup>-1</sup>	16.1	27.9	28.3	4.2	8.4	17.6	8.7	23.3	25.2	19.9	26.7	27.9
Total nutrients	mg L <sup>-1</sup>	1470.5	2313.9	2637.3	1822.7	3518.9	4471.7	926.7	1810.3	1903.1	3007.9	5429.7	5651.9
<b>Heavy metals</b>													
Cd	µg L <sup>-1</sup>	16	201	217	6.4	21.6	224	12.0	14	15.1	28.3	83.5	103
Hg	µg L <sup>-1</sup>	0.6	1.6	3.1	1.4	1.54	1.7	1.3	1.8	2.1	2.1	2.6	2.7
Ni	mg L <sup>-1</sup>	0.5	2.5	2.6	0.3	1.9	2.4	0.6	1.4	2.0	0.6	0.9	0.9
Pb	mg L <sup>-1</sup>	0.3	3.2	3.7	0.1	0.2	7.5	0.6	2.3	2.3	1.1	4.0	5.0
Cu	mg L <sup>-1</sup>	0.2	3.4	6.5	1.2	1.3	4.7	2.4	5.0	8.9	1.6	2.1	2.1
Zn	mg L <sup>-1</sup>	8.9	46.4	47.3	2.4	5.8	8.3	14	28.6	30	23.7	36.2	38.6
As	µg L <sup>-1</sup>	366	730	923	155	667	712	440	602	675	446	516	525
Cr	mg L <sup>-1</sup>	0.1	2.9	5.0	0.1	0.1	1.0	0.4	1.1	1.5	0.4	0.6	0.7
Total heavy metals	mg L <sup>-1</sup>	10.4	59.3	66.2	4.2	10.0	24.9	18.5	39.0	45.5	27.8	44.3	47.9

Extraction conditions: 10% w/v, 200 rpm, 30 °C and 8 h. Data were shown as the mean value with less than 5% of relative error.



**Figure 1.** Experimental and model P kinetic extraction using inorganic and organic acids as solvent: (A) sulfuric acid, (B) nitric acid, (C) oxalic acid, (D) citric acid. Operation conditions were: 10% w/v, 200 rpm, and 30 °C.

**Table 4.** Kinetic model parameters of P extraction from MMWC using pseudo-second-order kinetic equation

Type of acid	Molarity (M)	$k_2$ (kg MMWC/(g P · min))	$C_e$ (g P/kg MMWC)	$r^2$
Sulfuric acid	0.1	0.050 ± 0.001	2.17 ± 0.03	0.9992
	0.25	0.043 ± 0.002	5.49 ± 0.06	0.9996
	0.5	0.018 ± 0.001	6.61 ± 0.01	0.9986
Nitric acid	0.1	0.310 ± 0.039	0.40 ± 0.01	0.9966
	0.25	0.066 ± 0.003	1.96 ± 0.03	0.9991
	0.5	0.048 ± 0.005	6.03 ± 0.07	0.9995
Oxalic acid	0.1	0.093 ± 0.009	2.48 ± 0.04	0.9993
	0.25	0.030 ± 0.001	4.40 ± 0.05	0.9995
	0.5	0.022 ± 0.001	5.34 ± 0.07	0.9995
Citric acid	0.1	0.072 ± 0.003	3.10 ± 0.03	0.9997
	0.25	0.051 ± 0.003	4.99 ± 0.04	0.9998
	0.5	0.025 ± 0.002	5.84 ± 0.01	0.9980

values from 0.4% to 3.2% and from 14% to 26%, respectively. On the other hand, molar diffusivity decreased, as it is inversely proportional to viscosity, according to Eq. 5. The decrease in  $Re$  along with molarity occurred because the physical properties of the liquid extract increased. However, regarding the tendency of  $Sc$ , the major contributing factor was  $D_A$ . So the lower the value, the higher the  $Sc$  because, according to Eq. 4, these numbers are inversely proportional. In this way, using the dimensionless numbers and the experimental  $k_2$ , the constant  $A_2$  could be calculated. For the four acids,  $A_2$  showed the same trend, decreasing as the molarity increased. Once the regression that allows  $A_2$  to be

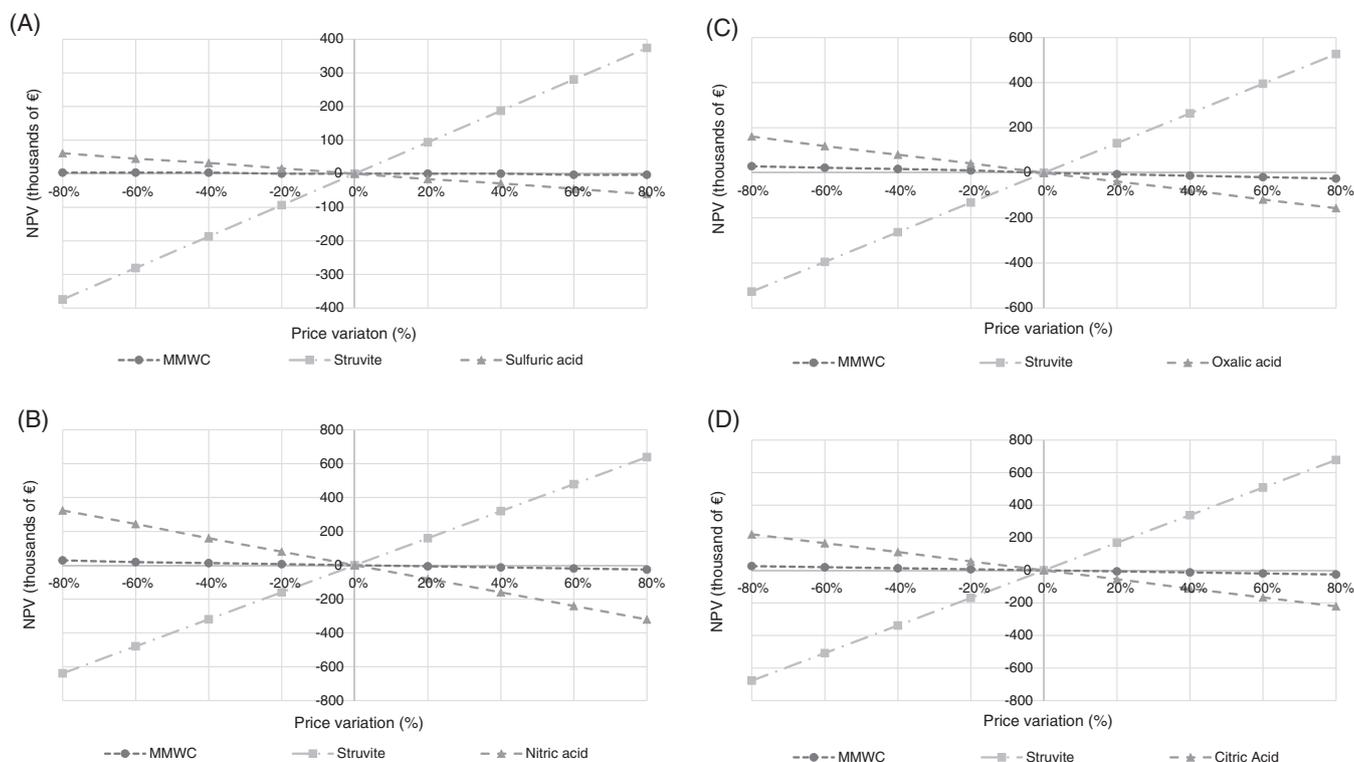
calculated had been obtained,  $k_2$  could be predicted (Table 5). The median absolute deviation of predicted and experimental  $k_2$  values is lower than 15%. From the results, it can be concluded that the most influential factor in the mass transfer coefficient is the  $Re$  number. An increase in the acid molarity (lower pH) causes a decrease in the value of the  $Re$  number, obtaining lower transfer coefficient values (Table 4). Bong *et al.*<sup>43</sup> also reached a similar conclusion. Their study analyzed the effect of solids loading in agitated vessels for the solid–liquid mass transfer to obtain a mass transfer correlation for a range of solid loading (0.08 to 0.4 v/v). The conclusion was that the mass transfer coefficient ( $k_2$ ) and

**Table 5.** Physical properties and dimensionless numbers relative to the extractant liquids used

Type of acid	Molarity (M)	$\rho_L$ (kg m <sup>-3</sup> )	$\mu_L$ (cP)	$D_A \times 10^{13}$ (cm <sup>2</sup> s <sup>-1</sup> )	$Re \times 10^4$	$Sc \times 10^{10}$	$A_2 \times 10^8$ (kg MMWC/(g P·min))	Predicted $k_2 \times 10^2$ (kg MMWC/(g P·min))
Sulfuric acid	0.1	1008	2.50	5.61	2.24	4.38	9.51	5.02
	0.25	1024	2.56	5.39	2.21	4.56	8.12	4.31
	0.5	1041	3.39	4.15	1.69	7.85	3.24	1.81
Nitric acid	0.1	1013	2.24	6.27	2.49	3.53	59.78	30.96
	0.25	1017	2.41	5.83	2.33	4.06	12.58	6.60
	0.5	1022	2.60	5.41	2.17	4.70	9.11	4.84
Oxalic acid	0.1	1013	2.46	5.71	2.27	4.26	17.73	9.33
	0.25	1016	2.59	5.44	2.17	4.68	5.57	2.95
	0.5	1017	2.90	4.85	1.94	5.88	4.01	2.17
Citric acid	0.1	1015	2.48	5.67	2.26	4.31	13.69	7.21
	0.25	1024	2.59	5.43	2.18	4.66	9.58	5.09
	0.5	1044	2.93	4.80	1.96	5.85	4.50	2.45

**Table 6.** Lang factor method for estimating the main costs for the pilot plant for struvite production with the following extraction conditions: 30 °C, 10% w/v, 200 rpm, 100 kg h<sup>-1</sup> of MMWC, and 25% of humidity

	Yield g P/kg DM	Struvite Kg h <sup>-1</sup>	Equipment cost €	TIC €	Production cost		Minimum sale price €/kg struvite
					€/year	€/kg	
H <sub>2</sub> SO <sub>4</sub> 0.5 M	6.60	3.92	30 000	130 000	98 000	3.13	4.96
HNO <sub>3</sub> 0.5 M	5.07	3.57	20 000	110 000	200 000	7.00	8.68
Oxalic acid 0.1 M	2.51	1.47	30 000	130 000	150 000	12.76	16.80
Citric acid 0.1 M	3.05	1.84	40 000	170 000	100 000	6.79	11.93

**Figure 2.** Sensitivity analysis for the proposed scenarios. (A) Extraction with sulfuric acid 0.5 M; (B) Extraction with nitric acid 0.5 M; (C) Extraction with oxalic acid 0.1 M; (D) Extraction with citric acid 0.1 M.

constant coefficient of correlation ( $A_2$ ) were significantly affected by the  $Re$  number.

### Preliminary economic evaluation

#### Investment and production costs

A preliminary economic study was carried out to compare the optimal P extraction strategies from MMWC obtained with inorganic and organic acids as solvents. With this aim, four possible extraction scenarios were established based on the previous technical study. Scenarios A and B, for inorganic acids with high acid concentrations (sulfuric acid 0.5 M, nitric acid 0.5 M) and scenarios C and D, for organic acids with low acid concentrations (oxalic acid 0.1 M and citric acid 0.1 M). Table 6 summarizes the results obtained from the Lang Factor method for the four scenarios proposed.

The total cost of the equipment ranged from 20 000 to 40 000 €, corresponding to nitric acid 0.5 M and citric acid 0.1 M, respectively. The principal budget item of the equipment cost relates to the S:L agitated extractor, with around 42–64% of the total budget. The TIC, which is directly proportional to the equipment cost, was 110 000 to 170 000 €. On the other hand, the determining factor in estimating production costs was the cost of the raw material used. The lower the cost of the raw material, the lower the annual production cost required, and therefore, the production cost of the struvite may be reduced. So, the sulfuric acid 0.5 M had a lower production cost (98 000 €/y), while nitric acid 0.5 M reached the highest cost (200 000 €/y). Otherwise, the production cost per kg of struvite was associated with the amount of P that each acid can extract. So, the inorganic acids, whose yields were higher than the organic acids, had lower production costs per kg of struvite (3.13–7.00 €/kg *versus* 6.79–12.76 €/kg). Finally, the minimum sale price of struvite, shown in Table 6, is the selling price from which the plant would begin to be profitable. As can be seen, the lowest selling price of struvite obtained corresponds to the scenario with sulfuric acid 0.5 M as a solvent with 4.96 €/kg. In comparison, the highest price was reached operating with oxalic acid 0.1 M with a price of 16.80 €/kg. If the precipitation section were considered, the minimum sale price of struvite would be even higher than that calculated in this study. In any case, these prices are above the estimated prices for the sale of struvite found in the literature, indicating that obtaining struvite from MMWC only is not profitable. For example, Dockhorn<sup>51</sup> estimated a sale price of 0.76 €/kg, and in the review of Yetilmezsoy *et al.*,<sup>52</sup> the struvite sale price varied from 0.2 to 3.8 €/kg. The raw material should have a minimum P content of 12–30 g P/kg DM to obtain a competitive price in the most favorable scenario ( $H_2SO_4$  0.5 M). In this case, the sale price of struvite would be in the range of 1–2.5 €/kg.

#### Sensitivity analysis

Based on the economic evaluation, a sensitivity analysis was performed to analyze the influence of the most critical parameters which could affect the NPV (Fig. 2). For the scenarios evaluated, the key parameters that significantly affect the NPV are the struvite sale price and the acid cost.

Among the raw materials costs, the variations in the cost of the acid used is more important than the variations in the MMWC cost (Fig. 2). For the four scenarios, the variation in the cost of the acids could determine the factor of the plant's profitability. An increment of up to 80% in the acid cost equals a decrease in the NPV of between 60 000 € (Fig. 2(A)) and 320 000 € (Fig. 2(B)). In contrast, a decrease of 80% could imply an increase in the NPV of

up to 250 000 € (Fig. 2(B)), depending on the acid. On the other hand, the variation in the MMWC cost does not involve significant changes in the NPV in any of the scenarios evaluated.

Concerning the plant profits, the only income is generated from selling the struvite, and the sensitivity analysis demonstrates that the NPV value is susceptible to changes in this price. For example, a 40% increase in the struvite sale price can increase the NPV by 280 000 € to 320 000 € for inorganic acids (Fig. 2(A),(B)) and by 260 000 € to 340 000 € for organic acids (Fig. 2(C),(D)). However, this increment in the struvite price involves selling struvite at prices above 7 €/kg, which is unfeasible from an economic point of view. The sensitivity analysis shows that if the struvite has to be sold at a competitive price (2 €/kg), the plant losses would be above 350 000 €.

Therefore, an alternative to obtain a viable and competitive extraction process could be to mix the MMWC with other P rich organic compounds, such as agricultural waste (dairy and beef, poultry, swine) or municipal waste (sewage sludge). In this way, the production costs could decrease significantly, and the sale price of struvite could be competitive in the fertilizer market.

### Environmental evaluation

Environmental indicators from the IChemE sustainability metrics<sup>32</sup> were calculated to compare the environmental impact of organic and mineral acids used in the P extraction process.

Sulfuric and nitric acids exhibit the higher eutrophication indicators with values of around 6400  $te PO_4^{3-}/y$ . However, oxalic acid had the lowest eutrophication value of 2300  $te PO_4^{3-}/y$ .

Regarding aquatic acidification, the differences between organic and mineral acids are not so marked. The aquatic acidification indicator relative to organic acids was between 2.4 and 5  $te PO_4^{3-}/y$  for citric and oxalic acids, respectively. For mineral acids, sulfuric acid was the most unfavorable solvent with an acidification value of 6.7  $te PO_4^{3-}/y$ .

Regarding the environmental assessment, organic acids have a less notable environmental impact than mineral acids, considering the eutrophication of aquatic areas and aquatic acidification indicators.<sup>20,34</sup>

## CONCLUSIONS

This study confirms that MMWC is a promising raw material for P extraction due to an appreciable P concentration (7 g P/kg DM). The best extraction solvent would be oxalic acid at 0.1 M and 30 °C, reaching a phosphorus recovery of 2.5 g P/kg, while also considering the maximization of the P extraction yield, but without compromising the environmental sustainability of the process. However, from an economic point of view, sulfuric acid 0.5 M provides the minimum sale price of struvite. An alternative to obtaining a sustainable and competitive acidic extraction process could be to mix the MMWC with other organic wastes rich in P to increase struvite production.

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