




Article

Extraction and Purification of Phosphorus from the Ashes of Incinerated Biological Sewage Sludge

Marco Baldi ¹, Andrea Martinotti ¹, Sabrina Sorlini ^{2,*}, Ioannis A. Katsoyiannis ³, Alessandro Abbà ² , Marco Carnevale Miino ⁴  and Maria Cristina Collivignarelli ^{4,5} 

¹ Department of Chemistry, University of Pavia, Viale Taramelli 10, 27100 Pavia, Italy; marco.baldi@unipv.it (M.B.); andrea.martinotti03@universitadipavia.it (A.M.)

² Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, Via Branze 43, 25123 Brescia, Italy; alessandro.abbà@unibs.it

³ Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; katsogia@chem.auth.gr

⁴ Department of Civil Engineering and Architecture, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy; marco.carnevalemiino01@universitadipavia.it (M.C.M.); mcristina.collivignarelli@unipv.it (M.C.C.)

⁵ Interdepartmental Centre for Water Research, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy

* Correspondence: sabrina.sorlini@unibs.it; Tel.: +39-030-371-1299

Abstract: Phosphorus depletion represents a significant problem. Ash of incinerated biological sewage sludge (BSS) contains P, but the presence of heavy metals (e.g., Fe and Al) is the main issue. Based on chemical characterization by SEM-EDS, ED-XRF and ICP-OES techniques, the characteristics and P content of bottom ash (BA) and fly ash (FA) of incinerated BSS were very similar. On BA, P extraction carried out in counter-current with an S:L ratio of 1:10 and H₂SO₄ 0.5 M led to better extraction yields than those of a similar test with H₂SO₄ 1 M and an S:L ratio of 1:5 (93% vs. 86%). Comparing yields with H₂SO₄ 0.5 M (S:L ratio of 1:10), the counter-current method gave better results than those of the crossflow method (93% vs. 83.9%), also improving the performance obtained with HCl in crossflow (93% vs. 89.3%). The results suggest that the purification of the acid extract from heavy metals with pH variation was impractical due to metal precipitation as phosphates. Extraction with H₂SO₄ and subsequent treatment with isoamyl alcohol represented the best option to extract and purify P, leading to 81% extraction yields of P with low amounts of metals.

Keywords: phosphorus recovery; sewage sludge; circular economy; acid extraction



Citation: Baldi, M.; Martinotti, A.; Sorlini, S.; Katsoyiannis, I.A.; Abbà, A.; Carnevale Miino, M.; Collivignarelli, M.C. Extraction and Purification of Phosphorus from the Ashes of Incinerated Biological Sewage Sludge. *Water* **2021**, *13*, 1102. <https://doi.org/10.3390/w13081102>

Academic Editor: Christos S. Akrotos

Received: 29 March 2021

Accepted: 13 April 2021

Published: 16 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

On average, in 2020, more than 13 million tons of biological sewage sludge (BSS) were produced in EU27 [1]. This quantity is destined to increase in the coming years due to the expected increase in the number of wastewater treatment plants (WWTPs) due to the stricter limits for the discharge of treated effluents into the water body [2,3]. As for all waste, hierarchical criteria must also be followed for the management of BSS: (i) minimization of production, (ii) material recovery, (iii) energy recovery, and (iv) residual disposal [4].

To date, there are several techniques for minimizing BSS that make it possible to significantly reduce production within the WWTPs [5,6]. In any case, a residual share of BSS will still be produced by biological treatments. These must be valorized first through the recovery of matter and then through energy recovery. To date, one of the most applied techniques for material recovery is spreading in agriculture, which aims to supply the soil with nutrients (mainly C, N, and P) [7,8]. This is essential for the development of crops [9] and is extremely important, especially in territories such as the Mediterranean area (e.g., Spain, Portugal, and Italy), where soil organic matter and nutrient depletion has reached worrying levels [10,11]. Other forms of material recovery, currently a minority in Europe, concern reuse in the construction sector (e.g., bricks and cement production and road construction) [12–14] and as adsorbent materials [15].

After material recovery, the hierarchy criteria of the EU requires energy recovery to be adopted before final disposal of the residue [4]. To date, there are several techniques that can be used to recover energy from BSS, namely (i) combustion [16], (ii) pyrolysis [17], and (iii) gasification [18]. The main drawbacks of these technologies are represented by (i) the need for pre-dewatering treatment; (ii) the need for disposal of final residues in combustion, such as bottom ash (BA) and fly ash (FA); and (iii) limited experience of real scale plant management for pyrolysis and gasification [5,19–21]. Recent studies [22,23] evaluated the presence of P within these residues, which could therefore be a potentially exploitable source.

P depletion represents a significant problem [24–26]. Even if a complete depletion of P deposits is not expected in the short to medium term [27], the significant increase in its use has led to greater attention being paid to the possibility of its recovery and reuse. While BSS-based fertilizers proved to be more suitable alternatives of P sources than chemical fertilizers [28], P is also contained in ashes of incinerated sludge [29], but in this form, it is not available for crops [30]. Moreover, the presence of heavy metals (e.g., Fe and Al) represents a barrier [30]. The evaluation of which techniques can be adopted to separate and valorize P in the ashes resulting from the BSS incineration is fundamental.

Wet extraction of P from incinerated BSS is a widely studied technique [31–34]. It is based on the application of acids or other leaching agents to extract P from BSS ash and on the subsequent purification of the extract by different techniques, such as ion exchange, filtration, precipitation, and solvent extraction [32]. Xu et al. [35] extracted more than 95% of the total P content from BSS ash as struvite by applying 0.5 mol L^{-1} of HCl at a liquid/solid ratio of 50 mL g^{-1} . Moreover, they also found that extracted material had low heavy metal content and high P bioavailability [35]. Fang et al. [33] studied the minimization of P co-precipitation with heavy metals present in incinerated BSS ashes. They found that by using $\text{Ca}(\text{OH})_2$ (at $\text{pH} = 4$) and adopting a two-step extraction method, the presence of heavy metals in the extract significantly decreased (50%) compared to a single-step method of extraction [33].

However, to determine the large-scale application feasibility of P recovery from incinerated BSS ashes, evaluation of how effectively this element can be extracted from the ashes and separated from the other metals contained therein is necessary to optimize the process. This work, therefore, aims to provide a basis on which to develop a future technical–economic analysis of the feasibility of recovering P from ashes of incinerated sludge. BA and FA samples of incinerated BSS were chemically characterized by non-destructive (SEM-EDS and ED-XRF) and destructive (ICP-OES) techniques to quantify the presence of P for potential recovery. On the BA sample, acid extractions with H_2SO_4 and HCl were performed in crossflow and counter current modes to evaluate the best option. The acid extract was then subjected to two different purification processes (pH variation and addition of isoamyl alcohol) to evaluate which is more effective in separating the P from the metals present within the liquid matrix. The purification of phosphorus from phosphate rocks by organic solvents (specifically isoamyl alcohol) is a known and applied procedure [36,37]; however, the innovative aspect of this work is that the same approach has been applied to purify the phosphorus contained in the acid extract of BA.

2. Materials and Methods

2.1. Sample Preparation

Combustion residues were obtained from a fluidized bed incineration plant of BSS. BA (1 kg) was sampled from the bottom of the combustion chamber, while FA (1 kg) was sampled from cyclones placed on the fume's treatment line. Before the subsequent analyses, both samples were ground to reduce the particle size ($\leq 200 \mu\text{m}$) using a PM100 planetary ball mill (Retsch GmbH, Germany) in 500 mL zirconia jars with zirconia spheres with a diameter of 40 mm and a 20:1 (spheres mass:powder mass) ratio. The plate rotation speed was set to 400 rpm.

2.2. Sample Characterization

2.2.1. SEM-EDS

These analyses were performed coupling an energy dispersion spectroscopy (EDS) X-max 50 mm² probe (Oxford Instruments, UK) with an EVO MA10 (Zeiss, Germany) scanning electron microscope (SEM). For the EDS analyses, 2 mm² of area was analyzed. In SEM, the samples were analyzed at 8.5 mm and with a voltage of 20 kV.

2.2.2. ICP-OES

Before the analysis, the samples were mineralized with four different methods:

- m1: 2 mL HNO₃ + 7.5 mL HCl + microwave (P = 800 W; T = 175° C; t = 10 min);
- m2: 6 mL HNO₃ + 2.5 mL HCl + microwave (P = 800 W; T = 175° C; t = 10 min);
- m3: 7.5 mL HNO₃ + 1 mL H₂O₂ + microwave (P = 800 W; T = 175° C; t = 10 min);
- m4: 2 mL HNO₃ + 7.5 mL HCl (boiling temperature; t = 150 min) according to [32];

The microwave oven used was a Mars 5 (CEM, Charlotte, NC, USA) with temperature control via an infrared sensor. In m1, m2 and m3, 0.25 g of BA was used, while in m4, 0.5 g BA was tested. Before mineralization, samples were micronized in agate mortar. HNO₃ (65%) and H₂O₂ (30%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). HCl (30%) was purchased from Merck. After m2, m3 and m4, the suspension was filtered through a 1.2 µm glass microfiber filter (GF/C) (Whatman, Maidstone, UK) and analyzed by IPC-OES.

For the analysis of the matrices by inductively coupled plasma-optical emission spectrometry (ICP-OES), an iCAP7000 (Thermo Fisher Scientific, Waltham, MA, USA) was used following the method developed for the analysis of water and waste by the U.S. EPA [38]. The instrument allowed operation in both axial and radial modes. Based on the relative sensitivity of the spectral line, the measure modes of the instrument were chosen as a function of the expected signal (Table S1). The radiofrequency power was 1150 W. The nebulization gas flow, the cooling gas flow, and the auxiliary gas flow were 0.5 L min⁻¹, 12 L min⁻¹, and 0.5 L min⁻¹, respectively. The peristaltic pump speed and the frequency were maintained at 50 rpm and 500 Hz, respectively.

2.2.3. ED-XRF

A total of 1 g of Li₃BO₃ was added to the samples (4 g) as a binder. The mixture was then placed in a homogenizer for 5 min. At the end of this phase, the powders were pressed (150 MPa) for 4 min, and 32 mm diameter tablets with a smooth surface were obtained. A Spectro XEPOS ED-XRF spectrometer (Spectro Analytical Instruments GmbH, Germany) was used.

2.3. Phosphorus Extraction

P was extracted from BA with crossflow and counter-current methods.

2.3.1. Extraction in Crossflow

A total of 80 g of the BA sample was placed in contact with 240 mL of H₂SO₄ 3 M (95–97%), purchased from Sigma-Aldrich (U.S.A), using a Teflon propeller stirrer to keep the resulting suspension homogeneous and dispersed. The suspension was centrifuged after 240 min, and the solid was treated again with 80 mL of H₂SO₄ 3M under stirring for 240 min. This operation was then repeated, thus carrying out three consecutive extractions, maintaining the solid:liquid (S:L) ratios at 1:3, 1:1, and 1:1, respectively. The same tests were also conducted using HCl 3 M (30%) in place of H₂SO₄. These tests were performed in duplicate.

To study the optimal P extraction time defining the extraction curves, during the first step of extraction, small aliquots of suspension during and after 30 min, 60 min, 120 min and 240 min were sampled; filtered in a glass microfiber filter (GF/C); and analyzed by ICP-OES.

2.3.2. Extraction in Counter Current

Each portion of the solid sample that enters the process comes out after undergoing five consecutive extractions by an acid that is gradually enriching in the extracted elements. Two processes were set up in parallel, one using H_2SO_4 1M in an S:L ratio of 1:5 (5 g of sample and 25 mL of H_2SO_4), and one using H_2SO_4 0.5M in an S:L ratio of 1:10 (3 g of sample and 30 mL of H_2SO_4). Extractions were made in Falcon™ tubes (50 mL) purchased from Thermo Fisher Scientific (USA) moved by a rocking shaker. Each extraction step was kept under stirring for 4 h, and the resulting suspension was subsequently separated by centrifugation. After each extraction cycle, the pH and volume of the resulting liquid phases were measured.

2.4. Phosphorus Purification

2.4.1. Purification by pH Variation

A total of 15 g of bottom ash was placed in contact with 150 mL of H_2SO_4 1 M for 4 h, and, subsequently, the sample was subjected to centrifugation. To purify the P in the form of H_3PO_4 , the pH of the aqueous phase was varied by adding NaOH 0.25 M (Carlo Erba Reagents, Italy) and causing, at pH 3.7, the precipitation of the metals as hydroxides. The starting aqueous phase (pH < 1) and the aqueous phase with pH 3.7 were then analyzed in ICP-OES.

2.4.2. Purification by Organic Solvent Extraction

As suggested by Israel Mining Industries (IMI) [39,40] and subsequently taken up by others (e.g., [41–43]), the purification of phosphorus from phosphate rocks can be achieved with the extraction by organic solvent. In this work, this approach was tested on phosphorus contained in BA.

The procedure was tested on both the HCl (as reported in [39–43]) and H_2SO_4 extracts. The extract with HCl derived from crossflow extraction kinetics tests (Section 2.3.1). As the H_2SO_4 extract obtained during the kinetics tests was no longer available, it was obtained by treating BA in crossflow (ratio S:L equal to 1:10) for 4 h.

Acid solutions, after centrifugation, were treated for three consecutive extractions with isoamyl alcohol (purchased from Carlo Erba Reagents, Italy) in a 1:1 ratio. In this case, the three organic phases were kept separate and analyzed by ICP-OES.

3. Results and Discussion

3.1. FA and BA Characterization

According to the SEM-EDS analysis of both BA and FA, before grinding, BA exhibited a larger particle size than FA according to the literature [44] (Figure 1). Moreover, the content of P in BA and FA is equal to 6.80% and 6.88% (in weight percentage, wt%), respectively, with no substantial difference (Table 1).

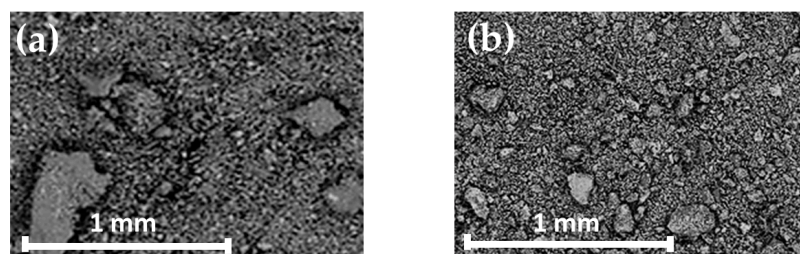


Figure 1. SEM-EDS image of (a) BA and (b) FA (before grinding).

This corresponds to a P titer expressed in P_2O_5 of approximately 16% for both BA and FA. The characterization using the ED-XRF technique highlighted comparable results detecting a content of 6.4–7.4% of P (equal to a P_2O_5 titer of 15–16%). Therefore, concerning P composition, the results obtained with the two techniques were similar. The initial

characterization by mineralization and subsequent analysis in ICP-OES was performed only on the BAs, given the similar FA and BA results obtained with SEM-EDS and ED-XRF.

Table 1. Elements constituting BA and FA. n.a.: not available.

	Bottom ash (BA)					Fly ash (FA)		
	SEM-EDS	IPC-OES				ED-XRF	SEM-EDS	ED-XRF
		m1	m2	m3	m4			
Mg (%)	1.7	1.4	1.5	1.3	1.4	1.8	1.8	2.1
Al (%)	4.1	2.2	2.1	1.9	2.1	4.7	3.9	5.2
Si (%)	14.5	n.a.	n.a.	n.a.	n.a.	18	12.9	15
P (%)	6.8	4.5	5.1	5	5.1	6.4	6.88	7.4
S (%)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.35	n.a.
K (%)	1.53	0.71	0.58	0.57	0.62	1.8	1.36	1.6
Ca (%)	7	5.7	5.8	5.6	5.7	5.8	7.7	7.2
Ti (%)	0.66	n.a.	n.a.	n.a.	n.a.	n.a.	0.66	n.a.
Fe (%)	15.4	9.4	11	7	11	11	17.5	15
Cu (%)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.29	n.a.

The data obtained using ICP-OES after different mineralization were subjected to statistical analysis to verify the absence of outliers (Q test) and the differences between mineralization methods in relation to the recovery of P. From the statistical analysis (ANOVA) of the data related to the P element, the variances in the results cannot be considered the same for 95% of cases ($p < 0.05$). The results obtained with m1 differed significantly from those obtained with m2, m3, and m4, which on the contrary gave similar results ($p > 0.05$). Excluding the results of m1, the average value of P obtained with ICP-OES was equal to $5.1 \pm 0.1\%$ (P_2O_5 titer in BA equals 12%) (Table S2).

The results obtained with IPC-OES were significantly different ($p < 0.05$) from the data obtained by the non-destructive techniques (SEM-EDS and ED-XRF), which provided an average value of $6.6 \pm 0.3\%$ of P content.

P content in incinerated sewage sludge ashes was consistent with previous literature results. For instance, Kleeman et al. [45] found 7.2–7.5%, and Franz [29] stated that P content in sewage sludge ash varied from 4% to 9%. Moreover, Donatello et al. [46] studied seven different samples of incinerated BSS ash (precisely FA) and evaluated a P content of 5.7–7.8%.

This P content was decidedly lower than usual content in the minerals (e.g., phosphorites and apatite) used as source to extract P [47–50]. However, it was considerable and could make this waste a sustainable alternative source to produce phosphate fertilizers. The main barrier to the use of these materials in the conventional cycles of production of P compounds by wet processes is represented by the concentration of Fe (7–15.4% in BA and 15–17.5% in FA) and Al (1.9–4.7% in BA and 3.9–5.2% in FA). This limit was also highlighted by other authors (e.g., [29,34,51]) and, therefore, involves the need for purification post-treatments of the extracted P. These results are therefore particularly interesting for understanding the feasibility of the recovery of P from the ashes of BSS after incineration.

3.2. Phosphorus Extraction

The use of acid attacks to extract P from BA allowed promising results. The results show that the complete equilibrium situation between the solid sample and the extracting acids (H_2SO_4 and HCl) was reached between 2 h and 4 h (Figure 2a). This result agrees with the findings of Biswas et al. [52]. The result is also consistent with the findings of Donatello et al. [46]. Using H_2SO_4 , they extracted about 85% of the P present in the incinerated BSS sample in the first 30 min and over 90% after 2h, while the total extraction was observed after approximately only 12 h [46]. However, it is not necessarily convenient to conduct extraction with extremely long acid attack times. For example, Ottosen et al. [30]

found that the acid attack with H_2SO_4 of incinerated sludge for 1 week led to a concentration of metals (i.e., Cu) in the extract greater than that obtained with an attack time of 2 h.

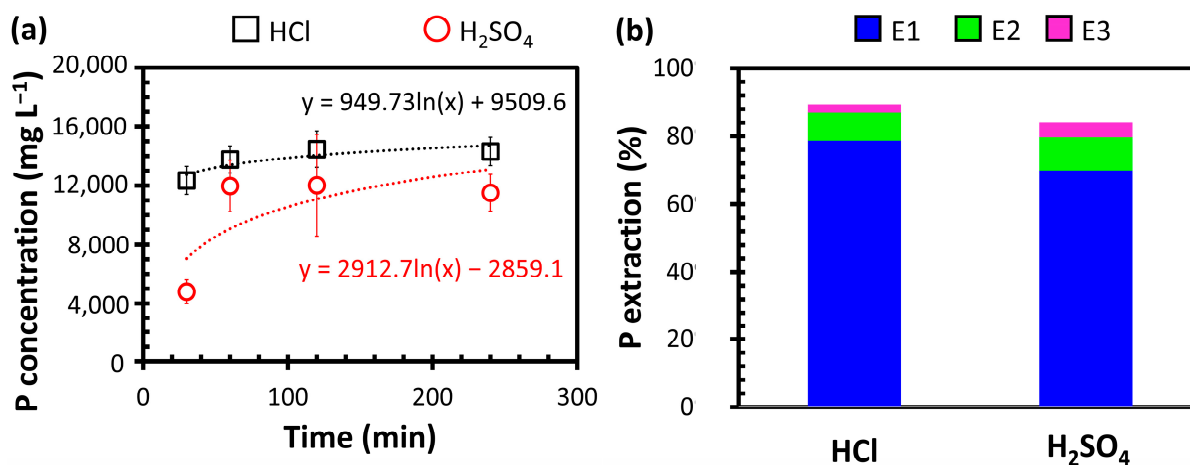


Figure 2. P extraction in crossflow mode. (a) Kinetics of P extraction during the first acid attack with the addition of H_2SO_4 and HCl. (b) P extracted in each of the three sequential acid attacks (E1, E2, and E3). The analysis of P content was performed by ICP-OES. (n = 2).

In the present study, the extraction of P by acid attack in three-stage crossflow mode with S:L 1:3, 1:1 and 1:1 ratios granted recovery yields of 83.9% and 89.3% with H_2SO_4 and HCl, respectively (Figure 2b). Moreover, the results show that the highest share of P was extracted after the first attack with H_2SO_4 (83.5% of total P extracted) and HCl (88.2% of total P extracted).

Taking into consideration a future industrial application, the extraction was conducted also as a five-stage counter current process. This type of extraction was carried out only with H_2SO_4 , with two different S:L ratios (1:5 and 1:10) while maintaining the ratio of ash mass attacked and mole numbers of H_2SO_4 . The results obtained show that the extraction carried out in conditions of a 1:10 S:L ratio and H_2SO_4 0.5 M led to better extraction yields compared to the similar test with H_2SO_4 1 M and an S:L ratio of 1:5 (93% vs. 86%) (Figure 3). Therefore, providing a higher volume of acid with the same moles number of H_2SO_4 allowed us to obtain better results in terms of P extraction. Comparing yields with H_2SO_4 0.5 M, the counter-current method gave better results than those of the crossflow method (93% vs. 83.9%), also improving the performance obtained with HCl in crossflow (93% vs. 89.3%).

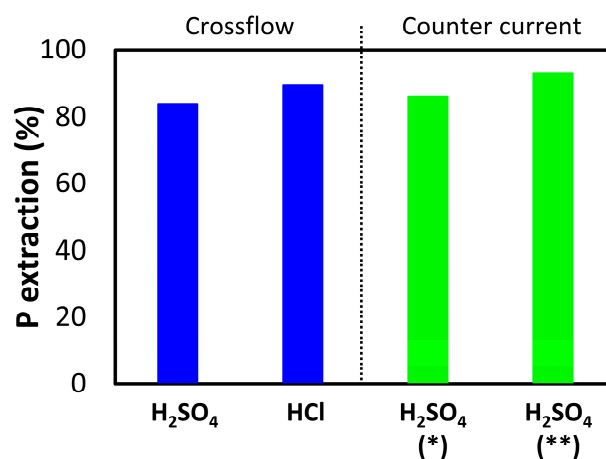


Figure 3. Percentages of P recovery with the different extraction procedures (extraction time: 4 h). (*) H_2SO_4 1 M (S:L ratio 1:5), (**) H_2SO_4 0.5 M (S:L ratio 1:10).

3.3. Phosphorus Purification

The acid extract still contained an important share of Fe and Al, which, overall, exceeded 2 wt% (Table 2). The use of H₂SO₄ and the consequent presence of high-concentration SO₄²⁻ ions led to the precipitation of Ca²⁺ as CaSO₄, thus producing an extract with a much lower concentration of this element than that obtained by extraction with HCl. To obtain a separation between the phosphorus and metals, the acid extracts were subjected to a purification process. The need to proceed with a purification phase due to the co-presence of metals within the extract was also reported by several other studies [46,52–54]. In the present study, two different treatments were tested: (i) separation by pH variation and (ii) separation with organic solvent extraction.

Table 2. Elements constituting the extracts obtained with the different extraction procedures (extraction time: 4 h). The analysis was performed by ICP-OES.

	Crossflow Extraction		Counter Current Extraction	
	H ₂ SO ₄	HCl	H ₂ SO ₄ (1:5)	H ₂ SO ₄ (1:10)
Al (%)	0.99	1.20	1.20	1.50
Ca (%)	0.06	5.10	0.32	0.65
Fe (%)	1.30	0.90	0.89	0.89
K (%)	0.16	0.28	0.34	0.27
Mg (%)	0.95	1.10	1.20	1.30
P (%)	4.20	4.40	4.40	4.70

3.3.1. Purification by pH Variation

An onset of precipitation was observed at pH nearly 2. This phenomenon increased with the subsequent additions of NaOH up to a pH of 3.7. The contents of the liquid phase of P, Al, Fe, and Ca decreased drastically with increasing pH (Figure 4). The precipitate was, in fact, constituted by phosphates of Ca, Fe, and Al. It is reasonable to assume that at pH 3.7, the precipitation of Ca₃(PO₄)₂, FePO₄, and AlPO₄ sequestered P from the solution, reducing its extraction yield. This result is consistent with the finding of He et al. [55]. Although at this pH range, P occurred in several forms (including H₂PO₄⁻ and HPO₄²⁻), it precipitated in the form of complex phosphates [56]. Therefore, the extraction yield of P dropped from 90% to 25%, passing from pH lower than 1 to pH of 3.7. The purification of the acid extract from heavy metals with this technique was therefore impractical.

3.3.2. Purification by Organic Solvent Extraction

Since Fe and Al are elements to be removed in the acid extracts obtained, the purification procedure of isoamyl alcohol addition was tested. The purification tests were conducted on both H₂SO₄ and HCl acid extracts.

The solution extracted in H₂SO₄ in contact with isoamyl alcohol did not lead to the separation of two phases unless after adding tridistilled water in the first extraction (10 mL). The extraction of the acid solution from HCl in isoamyl alcohol instead immediately led to the formation of a clear separation surface between the two phases. In terms of P extraction, the addition of isoamyl alcohol on acid extract with H₂SO₄ allowed us to obtain better results: 81% against 64% obtained from the solutions produced by P extraction with HCl (Figure 5).

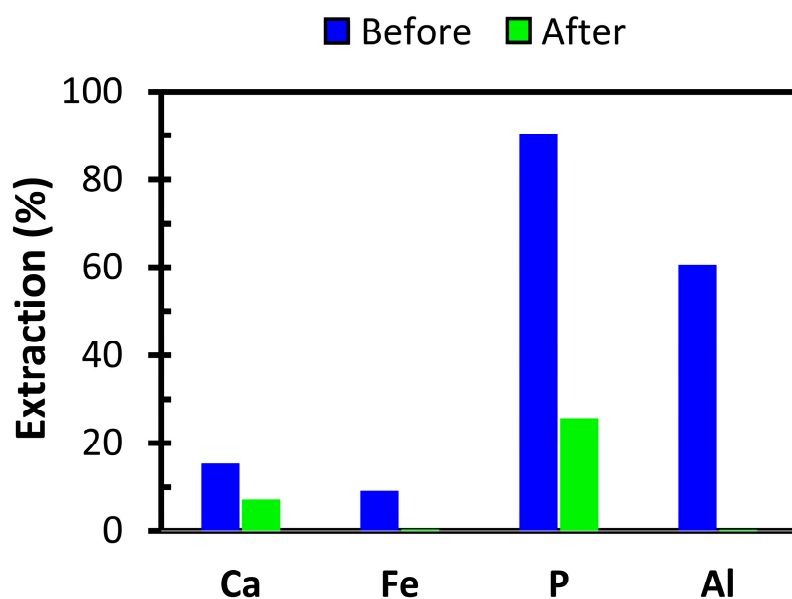


Figure 4. Extraction yields before and after pH variation (initial pH < 1; final pH = 3.7). The analysis on samples was performed by ICP-OES.

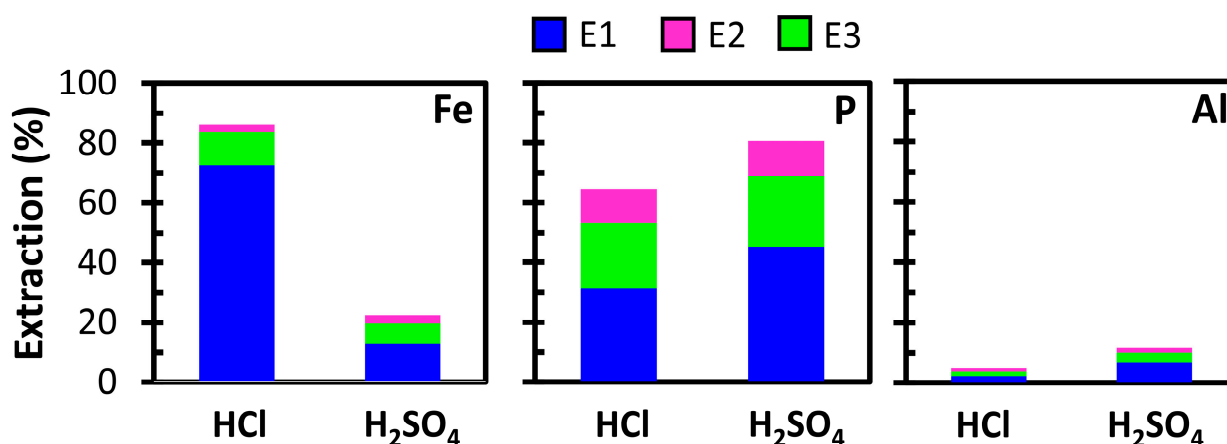


Figure 5. Extraction yields of Fe, P and Al from acid phase obtained with crossflow extractions by HCl and H₂SO₄, after each of the three sequential extractions (E1, E2, and E3) with isoamyl alcohol. In all extractions, the ratio between organic phase and acid phase was 1:1. The analysis on samples was performed by ICP-OES.

The mass of Fe in organic phases after extraction with H₂SO₄ was clearly lower than that in the case of extraction with HCl, and the mass of P was mostly distributed into the organic phases (Figure 5). The situation for the mass of P was also favorable with HCl, even if the recovery was lower than in the previous case. In the case of HCl extraction, the mass of Fe was very high (86%), especially in the first organic phase (84.2% of total Fe extracted). It is reasonable to assume that the high concentrations of chlorides led to the formation of undissociated FeCl₃ species. For these reasons, extraction with H₂SO₄ and subsequent treatment with isoamyl alcohol represented the best option to extract and purify P from BA of incinerated BSS sludge.

It is established that the efficiency of extraction and purification of P significantly depends on several parameters, such as the initial matrix, the extraction mode (crossflow or counter current), the type of acid used during extraction and the S:L ratio, the type of purification, and the organic solvents used during L:L extraction. Thus, the present results can hardly be compared to results already present in the literature. However, similar results in different conditions were obtained by other authors. For instance, Hong et al. [54]

separated 76% of P present in the acid extract (obtained with HCl extraction) by 1-butanol with an L:L ratio of 1.5:1.

4. Conclusions

In this work, the characteristics of BA and FA generated by the incineration of BSS were analyzed. According to the SEM-EDS analysis, the P content in BA and FA is equal to 6.80% and 6.88%, respectively. Comparable results were obtained with the characterization using the ED-XRF technique (6.4–7.4%). The results obtained with IPC-OES were significantly different ($p < 0.05$) from the data obtained by the non-destructive techniques, which provided an average value of $6.6 \pm 0.3\%$ of P content. The results show that the complete equilibrium situation between the solid sample and the extracting acids (H_2SO_4 and HCl) was reached between 2 h and 4 h. Moreover, the results show that in crossflow, the highest share of P was extracted after the first attack with H_2SO_4 (83.5% of total P extracted) and HCl (88.2% of total P extracted). Extraction carried out in counter current with an S:L ratio of 1:10 and H_2SO_4 0.5 M led to better extraction yields than those of the similar test with H_2SO_4 1 M and an S:L ratio of 1:5 (93% vs. 86%). Comparing yields with H_2SO_4 0.5 M (S:L ratio 1:10), the counter-current method gave better results than those of the crossflow method (93% vs. 83.9%), also improving the performance obtained with HCl in crossflow (93% vs. 89.3%). The results suggest that the purification of the acid extract from heavy metals with pH variation was impractical due to metal precipitation as phosphates. Extraction with H_2SO_4 and subsequent treatment with isoamyl alcohol represented the best option to extract and purify P, leading to 81% extraction yields of P with a low amount of metals. Other aspects that should be further investigated are (i) the optimization of the purification process; (ii) the research for alternative methods of purification, such as the use of diluted H_3PO_4 as an extractant to produce H_3PO_4 enriched in a percentage of P_2O_5 ; (iii) the study of extracted P availability for crops, with leaching tests; and (iv) cost–benefit analysis of this type of P recovery.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13081102/s1>, Table S1: Spectral lines and measure modes used in ICP-OES. Table S2: Average of the experimental results obtained from the characterization in ICP-OES of the bottom ash sample (excluding those obtained with m1 mineralization).

Author Contributions: Conceptualization, M.B.; methodology, M.B. and A.M.; software, A.M.; validation, M.B., S.S. and M.C.C.; formal analysis, M.B., A.M. and I.A.K.; investigation, A.M.; resources, M.B.; data curation, A.M. and M.C.M.; writing—original draft preparation, S.S., I.A.K., A.A., M.C.M. and M.C.C.; writing—review and editing, S.S., I.A.K., A.A., M.C.M. and M.C.C.; visualization, A.A. and M.C.M.; supervision, M.B.; funding acquisition, M.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Acknowledgments: The authors wish to thank Lucia Cucca (Department of Chemistry, University of Pavia) for her technical support during the research activities.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kominko, H.; Gorazda, K.; Wzorek, Z. The Possibility of Organo-Mineral Fertilizer Production from Sewage Sludge. *Waste Biomass Valoriz.* **2017**, *8*, 1781–1791. [[CrossRef](#)]
2. EUR-Lex. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. *Off. J. Eur. Communities* **1991**, *135*, 40–52.
3. EUR-Lex. Commission Directive 98/15/EC of 27 February 1998 amending Council Directive 91/271/EEC with respect to certain requirements established in Annex I thereof. *Off. J. Eur. Communities* **1998**, *67*, 29–30.
4. EUR-Lex. Directive EU/2018/851 of the European Parliament and of the Council of 30 May 2018 Amending Directive 2008/98/EC on Waste. *Off. J. Eur. Union* **2018**, *150*, 109–140.

5. Collivignarelli, M.C.; Abbà, A.; Carnevale Miino, M.; Torretta, V. What Advanced Treatments Can Be Used to Minimize the Production of Sewage Sludge in WWTPs? *Appl. Sci.* **2019**, *9*, 2650. [[CrossRef](#)]
6. Bertanza, G.; Papa, M.; Canato, M.; Collivignarelli, M.C.; Pedrazzani, R. How can sludge dewatering devices be assessed? Development of a new DSS and its application to real case studies. *J. Environ. Manag.* **2014**, *137*, 86–92. [[CrossRef](#)]
7. Collivignarelli, M.C.; Abbà, A.; Padovani, S.; Frascarolo, M.; Sciunnach, D.; Turconi, M.; Orlando, M. Recovery of sewage sludge on agricultural land in Lombardy: Current issues and regulatory scenarios. *Environ. Eng. Manag. J.* **2015**, *14*, 1477–1486. [[CrossRef](#)]
8. Ashekuzzaman, S.M.; Forrestal, P.; Richards, K.; Fenton, O. Dairy industry derived wastewater treatment sludge: Generation, type and characterization of nutrients and metals for agricultural reuse. *J. Clean. Prod.* **2019**. [[CrossRef](#)]
9. Collivignarelli, M.C.; Abbà, A.; Bertanza, G.; Baldi, M.; Setti, M.; Frattarola, A.; Carnevale Miino, M. Treatment of high strength wastewater by thermophilic aerobic membrane reactor and possible valorisation of nutrients and organic carbon in its residues. *J. Clean. Prod.* **2021**, *280*. [[CrossRef](#)]
10. Jones, R.J.A.; Hiederer, R.; Rusco, E.; Loveland, P.J.; Montanarella, L. *The Map of Organic Carbon in Topsoils in Europe: Explanation of Special Publication Ispra 2004 No.72 (S.P.I.04.72)*; Joint Research Centre: Luxembourg, 2004.
11. Napoli, M.; Marta, A.D.; Zanchi, C.A.; Orlandini, S. Assessment of soil and nutrient losses by runoff under different soil management practices in an Italian hilly vineyard. *Soil Tillage Res.* **2017**, *168*, 71–80. [[CrossRef](#)]
12. Kanari, N.; Diot, F.; Gauthier, C.; Yvon, J. Use of residual materials for synthesis of lightweight granulates by thermal treatment process. *Appl. Clay Sci.* **2016**, *123*, 259–271. [[CrossRef](#)]
13. Collivignarelli, M.C.; Alessandro, A.; Carnevale Miino, M.; Cillari, G.; Ricciardi, P. A review on alternative binders, admixtures and water for the production of sustainable concrete. *J. Clean. Prod.* **2021**, 126408. [[CrossRef](#)]
14. Ukwatta, A.; Mohajerani, A.; Setunge, S.; Eshtiagh, N. Possible use of biosolids in fired-clay bricks. *Constr. Build. Mater.* **2015**, *91*, 86–93. [[CrossRef](#)]
15. Ricciardi, P.; Cillari, G.; Carnevale Miino, M.; Collivignarelli, M.C. Valorization of agro-industry residues in building and environmental sector: A review. *Waste Manag. Res.* **2020**, 1–26. [[CrossRef](#)]
16. Singh, V.; Phuleria, H.C.; Chandel, M.K. Estimation of energy recovery potential of sewage sludge in India: Waste to watt approach. *J. Clean. Prod.* **2020**, *276*, 122538. [[CrossRef](#)]
17. Das, P.; Khan, S.; AbdulQuadir, M.; Thaher, M.; Waqas, M.; Easa, A.; Attia, E.S.M.; Al-Jabri, H. Energy recovery and nutrients recycling from municipal sewage sludge. *Sci. Total Environ.* **2020**, *715*, 136775. [[CrossRef](#)]
18. Zhang, H.; Gong, M.; Ding, L.; Su, Y. Energy recovery and phosphorus phase behaviour from catalytic gasification of cyanobacterial biomass in supercritical water. *Biomass Bioenergy* **2020**, *134*, 105477. [[CrossRef](#)]
19. Liu, Z.; Mayer, B.K.; Venkiteshwaran, K.; Seyedi, S.; Raju, A.S.K.; Zitomer, D.; McNamara, P.J. The state of technologies and research for energy recovery from municipal wastewater sludge and biosolids. *Curr. Opin. Environ. Sci. Health* **2020**, *14*, 31–36. [[CrossRef](#)]
20. Huber, F. Modelling of material recovery from waste incineration bottom ash. *Waste Manag.* **2020**, *105*, 61–72. [[CrossRef](#)] [[PubMed](#)]
21. Nihalani, S.A.; Mishra, Y.D.; Meeruty, A.R. Handling and Utilisation of Fly Ash from Thermal Power Plants. In *Circular Economy and Fly Ash Management*; Springer: Singapore, 2020; pp. 1–11.
22. Falk, J.; Skoglund, N.; Grimm, A.; Öhman, M. Fate of Phosphorus in Fixed Bed Combustion of Biomass and Sewage Sludge. *Energy Fuels* **2020**, *34*, 4587–4594. [[CrossRef](#)]
23. Nordin, A.; Strandberg, A.; Elbashir, S.; Åmand, L.-E.; Skoglund, N.; Pettersson, A. Co-Combustion of Municipal Sewage Sludge and Biomass in a Grate Fired Boiler for Phosphorus Recovery in Bottom Ash. *Energies* **2020**, *13*, 1708. [[CrossRef](#)]
24. Karamesouti, M.; Gasparatos, D. Sustainable Management of Soil Phosphorus in a Changing World. In *Adaptive Soil Management: From Theory to Practices*; Springer: Singapore, 2017; pp. 189–214.
25. Helin, J.; Weikard, H.-P. A model for estimating phosphorus requirements of world food production. *Agric. Syst.* **2019**, *176*, 102666. [[CrossRef](#)]
26. Alewell, C.; Ringeval, B.; Ballabio, C.; Robinson, D.A.; Panagos, P.; Borrelli, P. Global phosphorus shortage will be aggravated by soil erosion. *Nat. Commun.* **2020**, *11*, 4546. [[CrossRef](#)]
27. Van Vuuren, D.P.; Bouwman, A.F.; Beusen, A.H.W. Phosphorus demand for the 1970–2100 period: A scenario analysis of resource depletion. *Glob. Environ. Chang.* **2010**, *20*, 428–439. [[CrossRef](#)]
28. Wollmann, I.; Gauro, A.; Müller, T.; Möller, K. Phosphorus bioavailability of sewage sludge-based recycled fertilizers. *J. Plant. Nutr. Soil Sci.* **2018**, *181*, 158–166. [[CrossRef](#)]
29. Franz, M. Phosphate fertilizer from sewage sludge ash (SSA). *Waste Manag.* **2008**, *28*, 1809–1818. [[CrossRef](#)]
30. Ottosen, L.M.; Kirkelund, G.M.; Jensen, P.E. Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminum. *Chemosphere* **2013**, *91*, 963–969. [[CrossRef](#)]
31. Ashley, K. International Conference on Nutrient Recovery from Wastewater Streams (Vancouver, 2009). *Water Intell. Online* **2009**, *8*. [[CrossRef](#)]
32. Fang, L.; Wang, Q.; Li, J.; Poon, C.S.; Cheeseman, C.R.; Donatello, S.; Tsang, D.C.W. Feasibility of wet-extraction of phosphorus from incinerated sewage sludge ash (ISSA) for phosphate fertilizer production: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2020**, 1–33. [[CrossRef](#)]

33. Fang, L.; Li, J.; Donatello, S.; Cheeseman, C.R.; Wang, Q.; Poon, C.S.; Tsang, D.C.W. Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation. *Chem. Eng. J.* **2018**, *348*, 74–83. [[CrossRef](#)]
34. Fang, L.; Li, J.; Guo, M.Z.; Cheeseman, C.R.; Tsang, D.C.W.; Donatello, S.; Poon, C.S. Phosphorus recovery and leaching of trace elements from incinerated sewage sludge ash (ISSA). *Chemosphere* **2018**, *193*, 278–287. [[CrossRef](#)] [[PubMed](#)]
35. Xu, H.; He, P.; Gu, W.; Wang, G.; Shao, L. Recovery of phosphorus as struvite from sewage sludge ash. *J. Environ. Sci.* **2012**, *24*, 1533–1538. [[CrossRef](#)]
36. Shlewit, H. Treatment of phosphate rocks with hydrochloric acid. *J. Radioanal. Nucl. Chem.* **2011**, *287*, 49–54. [[CrossRef](#)]
37. Awwad, N.S.; El-Nadi, Y.A.; Hamed, M.M. Successive processes for purification and extraction of phosphoric acid produced by wet process. *Chem. Eng. Process. Process. Intensif.* **2013**, *74*, 69–74. [[CrossRef](#)]
38. U.S. EPA. *Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*; United States Environmental Protection Agency: Cincinnati, OH, USA, 1994.
39. Baniel, A.; Blumberg, R. Process for the Preparation of the Phosphoric Acid. U.S. Patent No. 2880063, 31 March 1959.
40. Baniel, A.; Blumberg, R.; Alon, A.; El Roy, M.; Goniadski, D. The IMI phosphoric acid process. *Chem. Eng. Prog.* **1962**, *58*, 100–104.
41. Giua, M. *Treatise on Industrial Chemistry*; USES Edizioni Scientifiche: Firenze, Italy, 1972. (In Italian)
42. Al-Fariss, T.F.; Özbelge, H.Ö.; El-Shall, H.S.H. Process Technology for Phosphoric Acid Production in Saudi Arabia. *J. King Saud Univ. Eng. Sci.* **1992**, *4*, 239–254. [[CrossRef](#)]
43. Ukeles, S.D.; Raz, I.; Friedman, G.; Kogan, L. Effluent treatment in IMI Phosphoric Acid Process. In *Hydrometallurgy '94*; Springer: Dordrecht, The Netherlands, 1994; pp. 1059–1071.
44. Prabhakar, A.K.; Cadiam Mohan, B.; Tay, T.S.; Lee, S.S.-C.; Teo, S.L.-M.; Wang, C.-H. Incinerated Sewage Sludge Bottom Ash-Chemical processing, Leaching patterns and Toxicity testing. *J. Hazard. Mater.* **2021**, *402*, 123350. [[CrossRef](#)]
45. Kleemann, R.; Chenoweth, J.; Clift, R.; Morse, S.; Pearce, P.; Saroj, D. Comparison of phosphorus recovery from incinerated sewage sludge ash (ISSA) and pyrolysed sewage sludge char (PSSC). *Waste Manag.* **2017**, *60*, 201–210. [[CrossRef](#)]
46. Donatello, S.; Tong, D.; Cheeseman, C.R. Production of technical grade phosphoric acid from incinerator sewage sludge ash (ISSA). *Waste Manag.* **2010**, *30*, 1634–1642. [[CrossRef](#)]
47. Onuigbo, E.N.; Okoro, A.U.; Okolo, C.M.; Chibuzor, S.N. Elemental Composition of the Phosphorites of the Ameki Formation around Bende-Ameke Area, Southeastern Nigeria: Potential for Environmental Pollution. *Int. Res. J. Appl. Sci.* **2020**, *2*, 28–33.
48. Bouabdallah, M.; Elgharbi, S.; Horchani-Naifer, K.; Barca, D.; Fattah, N.; Férid, M. Chemical, mineralogical and rare earth elements distribution study of phosphorites from Sra Ouertane deposit (Tunisia). *J. Afr. Earth Sci.* **2019**, *157*, 103505. [[CrossRef](#)]
49. Pochitalkina, I.A.; Kondakov, D.F.; Artamonova, O.A.; Vinokurova, O.V. Textural and structural characteristics of phosphorites from the Polpinsky deposit. *Russ. J. Inorg. Chem.* **2017**, *62*, 1495–1498. [[CrossRef](#)]
50. Kaljuvee, T.; Tõnsuaadu, K.; Traksmäa, R.; Einard, M.; Jefimova, J.; Petkova, V. Thermal behaviour of Estonian phosphorites from different deposits. *J. Therm. Anal. Calorim.* **2020**, *142*, 437–449. [[CrossRef](#)]
51. Benassi, L.; Zanoletti, A.; Depero, L.E.; Bontempi, E. Sewage sludge ash recovery as valuable raw material for chemical stabilization of leachable heavy metals. *J. Environ. Manag.* **2019**, *245*, 464–470. [[CrossRef](#)] [[PubMed](#)]
52. Biswas, B.K.; Inoue, K.; Harada, H.; Ohto, K.; Kawakita, H. Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. *J. Environ. Sci.* **2009**, *21*, 1753–1760. [[CrossRef](#)]
53. Wang, Q.; Li, J.; Tang, P.; Fang, L.; Poon, C.S. Sustainable reclamation of phosphorus from incinerated sewage sludge ash as value-added struvite by chemical extraction, purification and crystallization. *J. Clean. Prod.* **2018**, *181*, 717–725. [[CrossRef](#)]
54. Hong, K.-J.; Tarutani, N.; Shinya, Y.; Kajiuchi, T. Study on the Recovery of Phosphorus from Waste-Activated Sludge Incinerator Ash. *J. Environ. Sci. Health* **2005**, *40*, 617–631. [[CrossRef](#)]
55. He, P.; Zhang, X.; Lü, F.; Shao, L.; Zhang, H. Leaching behavior of phosphorous compounds from sewage sludge ash based on quantitative X-ray diffraction analysis. *Waste Dispos. Sustain. Energy* **2020**, *2*, 113–125. [[CrossRef](#)]
56. Goldshmid, T.; Rubin, A.J. Determination of Soluble Species and Precipitates of Aluminum Phosphate. *Sep. Sci. Technol.* **1988**, *23*, 2269–2291. [[CrossRef](#)]