



Research Paper

Application of high-intensity static magnetic field as a strategy to enhance the fertilizing potential of sewage sludge digestate

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ABSTRACT

Anaerobic digestion (AD) is a sustainable and well-established option to handle sewage sludge (SS), as it generates a methane-rich biogas and a digestate with potential fertilizing properties. In the past, different strategies have been proposed to enhance the valorization of SS. Among these, the application of a static magnetic field (SMF) has been poorly evaluated. This study aims to determine the effects of a high-intensity SMF (1.5 and 2 T) on the chemical composition of SS anaerobic digestate. Several strategies (i.e., number of magnetization cycles, addition of different sources and quantities of magnesium, and digestate aeration) have been applied to evaluate the possible formation of compounds with valuable fertilizing properties in the digestate. Experimental results showed that by combining different strategies promoting digestate exposure to the magnetic field it is possible to favour the reduction in the liquid phase of NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} and Mg^{2+} concentrations up to 28%, 38%, 34%, 39% and 31%, respectively. The XRD analyses conducted on the solid phase of the same magnetized digestate samples showed an increase in crystalline and amorphous phases of nitrogen and phosphorus compounds with fertilizing value, such as struvite. These results highlight that SMF application can increase the fertilizing potential of sewage sludge digestate and promote its valorization in a sustainable and circular perspective.

1. Introduction

Sewage sludge (SS) management has recently become a key task for wastewater treatment plant operation due to a considerable increase in sludge production, high disposal costs (160–210 €/t dry matter), and other many legal, social, and environmental constraints (Shaddel et al., 2019). Different sludge management choices are practiced globally including landfills, biological stabilization, incineration, pyrolysis, and gasification. In this framework, anaerobic digestion (AD) is certainly one of the most sustainable technologies to transform SS into renewable energy and a fertilizer. AD generates a gaseous (biogas) and a semi-solid product (digestate), the first being an energy vector which can be upgraded to biomethane, the second being a material that can be valorised in agriculture as a valuable source of nutrients (Di Costanzo et al., 2021; Siebielec et al., 2018). During AD, the biological degradation of the organic matter contained in the sludge increases the concentration of soluble nutrients species, i.e., total ammonia nitrogen and

ortho-phosphate (PO_4^{3-}), which are nutrient compounds that can be rapidly assimilated by plants for their growth.

Among the strategies reported for nutrient recovery (Stávková and Maroušek, 2021) reusing SS digestate as a fertilizer fits the circular economy approach and has several advantages, which include the return of the organic materials and nutrients into the bio-cycle (Kelessidis and Stasinakis, 2012; Zilio et al., 2022). Indeed, the agronomic use of sludge-derived digestate has demonstrated to increase the portion of organic carbon in the soil, contributing to the improvement of its agronomic quality (Dubis et al., 2022). Moreover, the application of sludge digestate in agriculture allows reducing the demand for chemical fertilizers and, in turn, the related costs for farmers. In the context of SS valorization, the high-solid anaerobic digestion (HSAD) represents an opportunity to improve the economical balance compared to conventional AD as it reduces treatment volumes, transportation costs, and energy consumption for heating, and generates a digestate with very good agronomic properties and hygienic properties (Di Capua et al., 2020b; Pigoli

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et al., 2021). From this point of view, HSAD can be considered the most sustainable pathway for the reuse of nutrients contained in SS.

A possible strategy to further enhance the agricultural properties of SS digestate is to promote the precipitation of valuable compounds, such as struvite and hydroxyapatite, that can effectively and slowly release the nutrients contained in the digestate to the soil (Di Costanzo et al., 2021). In this way, plants can uptake the released nutrients more efficiently and the risk of nutrient overload and groundwater contamination can be reduced as well. Among the agronomic compounds of greatest interest, there is the struvite, a crystalline mineral composed of equimolar concentrations of magnesium (Mg^{2+}), ammonium (NH_4^+) and PO_4^{3-} with chemical formula $MgNH_4PO_4 \cdot 6H_2O$. Specifically, struvite is considered a valid fertilizing product because it contains essential nutrients for plant growth, which are slowly released into the soil due to its low solubility, thus limiting potentially harmful overdose phenomena (Hertzberger et al., 2020). Struvite precipitation depends on several parameters, i.e. most notably pH, Mg^{2+} source, and the molar ratio of Mg^{2+} , NH_4^+ and PO_4^{3-} in the liquid phase (Lorick et al., 2020). During AD of SS, struvite may precipitate spontaneously from the interaction of the mineralized Mg^{2+} , NH_4^+ and PO_4^{3-} originating from the degradation of organic material (Parsons and Doyle, 2002). However, in practice, struvite precipitation needs a chemical input in the form of additional Mg^{2+} , being typically the limiting compound, and alkali for pH adjustment (Huang et al., 2014), both translating into high operational costs (Drosg et al., 2015). Previous studies have shown that other mineral phases containing macro- and micro-nutrients (such as newberyite, gwihaite, brushite and potassium calcium magnesium sulphate) can improve of agronomic characteristics of soils (Hao et al., 2013; Sniatala et al., 2023). Besides supplying essential nutrients for plant growth, these mineral phases possess a low/moderate solubility that leads to a slow release of nutrients to the soil and mitigates the negative impact of fertilizers on the environment (e.g., leaching to groundwater) (Lubkowski, 2016; Vogel et al., 2010).

In this context, there is a legitimate need to seek alternative, prospective, and competitive methods enhancing the formation of struvite and other valuable precipitates in SS. Recent research has demonstrated that the application of high-intensity static magnetic field (SMF) can represent a novel option. The SMF has often been applied to reduce water hardness (Mascolo, 2021) by promoting the precipitation of ionic species and, more recently, Di Costanzo et al. (2023) reported that it can be used as SS pretreatment to promote the precipitation of compounds with fertilizing properties, including struvite. On the other hand, applying strong SMF as SS pretreatment was shown to reduce methane production during the subsequent AD process (Di Costanzo et al., 2023). In this perspective, applying the high-intensity SMF directly to the digestate can circumvent the negative impacts on methane generation during AD. Moreover, the precipitation effect induced by the SMF might be further improved under certain operating conditions, including those exploiting the paramagnetism of the oxygen molecule. Paramagnetism is the property observed when certain substances, whose molecules possess their own magnetic dipole moment, are immersed in a magnetic field. In the case of air, the paramagnetic effect is at the expense of the oxygen molecule, which possesses split electron doublets in its outer orbitals and makes it affine to the magnetic field. Unpaired electrons, when exposed to magnetic fields, align themselves with the field lines and amplify the effect of the magnetic field. Another strategy to improve the SMF effects may rely on the disturbance of the magnetic field flux lines, which in turn converts the magnetic fields from uniform to non-uniform. Both these strategies (i.e., the exploitation of the oxygen paramagnetism and the magnetic field disturbance) can be obtained by adding oxygen during the magnetization of SS digestate, thus enhancing the SMF effect and likely promoting the precipitation of valuable compounds.

Currently, literature lacks information regarding the impact of the SMF on the chemical composition of SS digestate. Similarly, no information regarding oxygen contribution to nutrient precipitation during

SMF application is available. In this context, the present study explored for the first time the direct effects of high-intensity SMF on the chemical properties of digestates originating from both AD and HSAD of SS. More specifically, the effects of magnetic exposure, amount and source of Mg^{2+} , and presence of oxygen during magnetization on the precipitation of valuable nutrients in the digestate were investigated at laboratory scale. The outcomes of this study were discussed with the aim to identify practical applications of the proposed methodology to improve nutrient recycling from sludge to agriculture and promote the use of alternatives to chemical fertilizers, thereby limiting the depletion of valuable resources as well as fertilization costs.

2. Materials and methods

2.1. Origin and composition of SS digestate

Two different digestates obtained from HSAD and AD of SS were used in this study. The digestate from HSAD was provided by the “Acqua & Sole” digestion plant located in Lombardy Region (Italy) treating a high-solid feedstock (about 18.5%), mainly composed of municipal sewage sludge. The plant performs a thermophilic (55 °C) HSAD process in three digesters (4,500 m³ each) displaced in series. The digestate from AD was collected at the wastewater treatment plant (WWTP) of Mercato San Severino (Italy) that treats wastewater of predominantly municipal origin and, to a lesser extent, industrial wastewater. In this WWTP, SS is bio-stabilized via a conventional AD process operated under mesophilic conditions (35 °C). Both kinds of digestate were collected during two sampling campaigns (I and II) from the lower withdrawal point of both the HSAD and AD digesters, placed in plastic containers, and transported to the laboratory, where they were stored at 4 °C until use. Prior to magnetic treatment, the HSAD digestate was diluted from a total solids (TS) content of 12% to 7%, to ensure the pumping within the magnetization circuit. Table 1 lists the main characteristics of the digestates used for the experiments.

2.2. Experimental set-up for the magnetic treatment of digestates

Two SMF intensities, i.e., 1.5 T and 2 T, were applied to the sludge digestate samples. The SMF was generated by a patented Purak magnetic polarizer provided by AMS company (Italy) as described by Mascolo (2021). The magnetic polarizer was installed on a circuit made with a plastic tube (diameter = 1.5 cm) and connected to a submersible water pump (Comet, USA) as illustrated by Di Costanzo et al. (2023).

Table 1
Characteristics of the digestates used for the experiments.

Parameter	Unit	Digestate from HSAD		Digestate from AD	
		I	II	I	II
Sampling campaign					
pH	–	8.3 ± 0.3	8.1 ± 0.1	6.8 ± 0.1	6.8 ± 0.2
Total solids (TS)	%	7.0 ± 0.1	7.0 ± 0.1	2.1 ± 0.1	2.5 ± 0.2
Volatiles solids (VS)	%	3.7 ± 0.2	3.7 ± 0.1	1.0 ± 0.1	1.5 ± 0.2
NH_4^+	mg/L	510 ± 2	329 ± 1	283 ± 1	296 ± 1
PO_4^{3-}	mg/L	187 ± 1	203 ± 4	213 ± 2	235 ± 2
Nitrate (NO_3^-)	mg/L	38 ± 1	40 ± 1	9 ± 0	11 ± 0
Sulphate (SO_4^{2-})	mg/L	21 ± 1	23 ± 0	22 ± 1	24 ± 0
Mg^{2+}	mg/L	20 ± 0	19 ± 0	10 ± 0	10 ± 0
$Mg^{2+}:NH_4^+:PO_4^{3-}$	–	0.04:1:0.36	0.06:1:0.62	0.03:1:0.75	0.03:1:0.79

2.3. Experimental design

To assess the impact of the high-intensity SMF, the following operating conditions were investigated: SMF intensity; number of magnetization cycles (NMC), which is the number of digestate passages within the magnetic polarizer; $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio, which was varied by adding Mg^{2+} either as hydroxide ($\text{Mg}(\text{OH})_2$) or as chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), as well as PO_4^{3-} as phosphoric acid (H_3PO_4), to promote the precipitation of struvite; digestate aeration, under two alternative configurations (Fig. 1). In the first one, air was supplied through an aquarium pump equipped with a porous stone directly into the SS digestate feeding tank (Fig. 1a); in the second one, air was supplied directly within the magnetization circuit (*in-line oxygenation*) (Fig. 1b). The first strategy was chosen to take advantage of the paramagnetic effect of the oxygen molecule. Specifically, the digestate saturated in oxygen and circulating in the polarizer is subjected to local increases of SMF intensity. Conversely, the *in-line oxygenation* strategy was considered to evaluate both the effect induced by the paramagnetism of the oxygen molecule and the effect of the airflow turbulence during the SMF application, which was expected to modify the magnetic field from uniform to non-uniform.

Two experimental phases i.e., phase 1 (P1) and phase 2 (P2), were carried out as detailed in Table 2. In P1 tests, the effect of a 1.5 T SMF on the digestates was evaluated at NMCs of 10 and 30 and $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratios of 1:1:1, 1.5:1:1 and 2:1:1. In order to assess the effect of Mg^{2+} source on precipitation, P1 tests on HSAD digestate were conducted twice, using initially $\text{Mg}(\text{OH})_2$ and then $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In all tests, the pH was maintained around 8–9 dosing a 3 M potassium hydroxide (KOH) solution after Mg^{2+} addition. For P1 tests, the flow rate Q of the digestate within the magnetization circuit was maintained constant at 10 L/min and no aeration was performed.

In the second experimental phase (P2), digestate exposure to a higher SMF (2 T) was tested at NMCs of 10 and 30, using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and maintaining the optimal $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 2:1:1 obtained from P1 tests; these experimental settings were tested without aeration as well as by supplying an air flow rate of 5 L/min. Both in P1 and P2 control tests were carried out (test A and B in P1, test I and J in P2), i.e., tests in which the digestate was only magnetized.

After each treatment, the magnetized sludge was analysed in terms of nutrient (N, P) concentrations and the precipitates in the solid phase were identified to evaluate the effects of the applied SMF conditions on the generation of nutrient-based compounds with potential fertilizing properties.

2.4. Analytical methods

The concentrations of COD, TS and VS were analysed according to the Standard Methods (A.P.H.A., 1999). NH_4^+ concentration was

determined spectrophotometrically using the indophenol blue method (APAT, 2003). Anionic concentrations were measured by ion chromatography (IC) as described by Di Capua et al. (2020a). Mg^{2+} concentration was measured by ICP-MS (Perkin Elmer Nexion 300, USA) operating in dual detector mode. The mineralogical characterization of the digestates was performed by X-ray diffraction (XRD) analysis as reported by Di Costanzo et al. (2023).

2.5. Statistical analysis

Statistical comparison of the reported data from the control and each samples under the different treatment conditions were compared by one-way analysis of variance (ANOVA) followed by the Tukey post hoc test (Lee and Lee, 2018; Oliva et al., 2021). All analyses were performed with Minitab 17 Statistical Software (Minitab LCC, USA), where a difference marked with a p-value lower than 0.05 was considered statistically significant.

3. Results and discussions

3.1. Impact of magnetization conditions on ionic precipitation in HSAD and AD digestates

3.1.1. SMF intensity and NMC

The exposure of the HSAD digestate to a high-intensity SMF led to a reduction of the monitored ionic concentrations in the liquid phase. At a SMF of 1.5 T, all monitored ionic concentrations decreased by 5–16% at NMC = 10 and by 8–23% at NMC = 30, indicating that increasing the NMC from 10 to 30 enhanced precipitation (Fig. 2a). These results are in line with those outlined in a previous work (Di Costanzo et al., 2023), showing that increasing the NMC from 1 to 10 at a SMF of 1.5 T enhanced the reduction of ionic species in the liquid phase of pre-thickened sludge up to 20%. These results further confirm that an NMC increase amplifies the SMF effect in terms of precipitation efficiency. A higher reduction in the concentration of ionic species was observed at a SMF intensity of 2 T both at an NMC of 10 (6–18%) and 30 (9–25%). This indicates that increasing the SMF intensity from 1.5 to 2 T had a significant impact on enhancing nutrient precipitation from HSAD digestate.

Fig. 2b shows the results obtained from the same tests on the AD digestate. Likewise, it can be observed that at a SMF of 1.5 T all the monitored ionic concentrations in the liquid phase decreased by 4–22% at NMC = 10 and by 7–25% at NMC = 30, indicating that increasing the NMC from 10 to 30 improved ion precipitation. At the same time, at a SMF of 2 T, higher ionic species reduction was observed both at NMC of 10 (6–23%) and 30 (9–26%).

The reduction percentages of the ionic species observed for the AD digestate were slightly higher (+0.1–1%) compared to those obtained

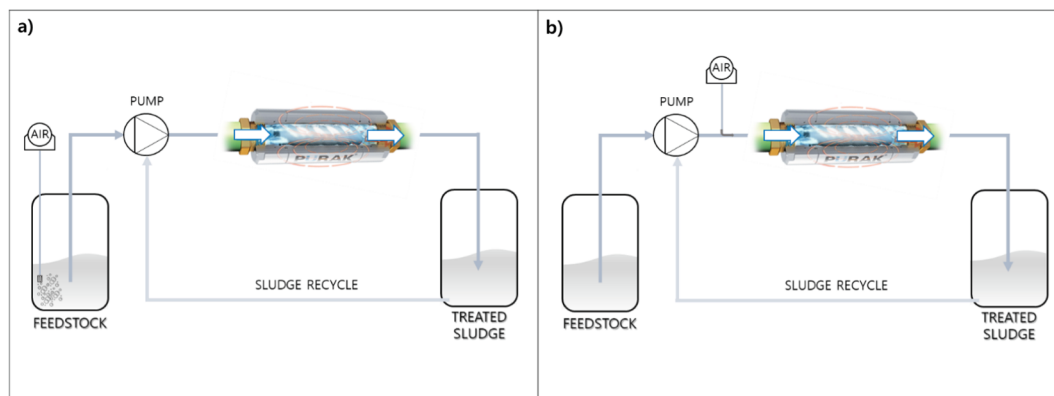


Fig. 1. Scheme of the experimental set-up for the magnetic treatment of digestates using direct air injection into the supply tank (a) or in-line aeration (b).

Table 2

Design of P1 and P2 tests.

Experimental phase	Test	NMC	Mg ²⁺ :NH ₄ ⁺ :PO ₄ ³⁻	Mg ²⁺ source	SMF intensity (T)	Qair (L/min)
P1	A	10	–	–	1.5	–
P1	B	30	–	–	1.5	–
P1	C	10	1:1:1	Mg(OH) ₂	1.5	–
P1	D	30	1:1:1	or MgCl ₂ ·6H ₂ O	1.5	–
P1	E	10	1.5:1:1	Mg(OH) ₂	1.5	–
P1	F	30	1.5:1:1	or MgCl ₂ ·6H ₂ O	1.5	–
P1	G	10	2:1:1	Mg(OH) ₂	1.5	–
P1	H	30	2:1:1	or MgCl ₂ ·6H ₂ O	1.5	–
P2	I	10	–	–	2	–
P2	J	30	–	–	2	–
P2	K	10	2:1:1	MgCl ₂ ·6H ₂ O	2	–
P2	L	30	2:1:1	MgCl ₂ ·6H ₂ O	2	–
P2	M	10	2:1:1	MgCl ₂ ·6H ₂ O	2	5
P2	N	30	2:1:1	MgCl ₂ ·6H ₂ O	2	5

for the HSAD digestate. This effect is due to the fact that AD digestate is a less complex matrix than HSAD digestate, as it is characterised by a lower TS content and reduced interaction within the solid phase that can disturb the formation of precipitates, as previously found by Di Costanzo et al. (2023). As a consequence, the effect induced by the magnetic field on the aggregation and precipitation of ionic species is stronger.

3.1.2. Dose and source of magnesium

Fig. 3a plots the concentrations of NH₄⁺, NO₃⁻, PO₄³⁻, SO₄²⁻, Mg²⁺ in the HSAD digestate at the end of P1 tests with Mg(OH)₂ as Mg²⁺ source. It can be observed that increasing the amount of added Mg²⁺ led to lower ionic concentrations at the end of the magnetization treatment: at NMC of 10, shifting from an equimolar Mg²⁺:NH₄⁺:PO₄³⁻ ratio of 1:1:1 to 2:1:1 increased the precipitation of NH₄⁺, NO₃⁻, PO₄³⁻, SO₄²⁻ and Mg²⁺ by 2%, 3%, 4%, 3% and 10%, respectively; at NMC of 30, the increase of the Mg²⁺:NH₄⁺:PO₄³⁻ ratio from 1:1:1 to 2:1:1 resulted in greater precipitation efficiency of 5%, 7%, 5%, 11%, and 10% for NH₄⁺, NO₃⁻, PO₄³⁻, SO₄²⁻ and Mg²⁺, respectively.

Therefore, increasing the Mg²⁺ dose over the equimolar Mg²⁺:NH₄⁺:PO₄³⁻ ratio led to a higher precipitation of the monitored ionic species at both the NMC tested. This is attributable to the formation of new aggregates in the solid phase, as better discussed in section 3.2.1.

Not only the concentration, but also the source of Mg²⁺ can play an important role in terms of ion precipitation. Comparing the reduction percentages obtained with HSAD digestates treated under the same SMF conditions but supplied with a different Mg²⁺ source, i.e., Mg(OH)₂ (Fig. 3a) and MgCl₂·6H₂O (Fig. 3b), it can be seen that, in the latter case, the obtained values turned out to be 1–5% higher. This result can be due to the much greater availability in the liquid phase of Mg²⁺ when added as chloride (468.7 g/L at 20 °C) than as hydroxide (9.12 mg/L at 25 °C), facilitating the formation of Mg²⁺ precipitates in the solution.

The same tests were also carried out on AD digestate (Fig. 4) but only with MgCl₂·6H₂O as Mg²⁺ source, which was found to perform better in terms of ionic precipitation with HSAD digestate. At NMC = 30, switching from a Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio of 1:1:1 to 2:1:1 improved the precipitation of NH₄⁺, NO₃⁻, PO₄³⁻, SO₄²⁻ and Mg²⁺ concentrations by 3%, 4%, 4%, 6% and 8%, respectively. Again, the effect of SMF application on a digestate with a lower TS content was more evident, which can be attributed to a reduced interaction between inorganic and organic phases and, therefore, to a higher availability of the ionic species to form new precipitates.

Once the best condition in terms of ions reduction (i.e., use of MgCl₂·6H₂O as Mg²⁺ source and of a Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio of 2:1:1) were established at a SMF intensity of 1.5 T, the same experiments

were also performed by applying a SMF with a higher intensity (2 T). Fig. 5 shows that the use of a higher SMF induced a reduction of ionic concentrations up to 21% for NH₄⁺, 24% for NO₃⁻, 18% for PO₄³⁻, 39% for SO₄²⁻, and 23% for Mg²⁺ on HSAD digestate, and up to 27% for NH₄⁺, 35% for NO₃⁻, 20% for PO₄³⁻, 38% for SO₄²⁻ and 27% for Mg²⁺ on AD digestate. These precipitation efficiencies were higher than those obtained at a SMF of 1.5 T using the same Mg²⁺ dose and source, confirming that increasing the SMF intensity promotes precipitation.

3.1.3. Aeration strategy

The effect of oxygen supply to the digestate on ionic precipitation was evaluated in the second experimental phase (P2) either by blowing air directly into the influent tank prior to SMF application or by injecting oxygen in the magnetization circuit (in-line aeration). A slight increase in the reduction of the ionic species in the liquid phase, ranging from 0.2 to 3% for HSAD digestate (Fig. 6a) and from 0.4 to 3% for AD digestate (Fig. 6b), were obtained with in-line aeration. This strategy has led to a reduction in the liquid phase of 23% for NH₄⁺, 28% for NO₃⁻, 32% for PO₄³⁻, 36% for SO₄²⁻, and 25% for Mg²⁺ on HSAD digestate (Fig. 6a) and 28% for NH₄⁺, 38% for NO₃⁻, 34% for PO₄³⁻, 39% for SO₄²⁻, and 31% for Mg²⁺ on AD digestate (Fig. 6b).

3.2. Impact of magnetization conditions on precipitate formation in HSAD and AD digestates

3.2.1. NMCs and magnesium dose

From Figure S1, it is possible to observe that SMF application on HSAD digestate both at NMC = 10 and NMC = 30, as well as the addition of increasing concentrations of MgCl₂·6H₂O, enhanced the precipitation of the monitored ionic species compared to the control test, in agreement with the observed reductions in the liquid phase (Figs. 2a–3b).

PO₄³⁻ reduction in the HSAD digestate treated at a SMF intensity of 1.5 T and NMC of 10 (Figure S1 A, C, E and G) is due to the precipitation of different phases including newberyite (MgHPO₄(H₂O)₃), sodium phosphate hydrate ((NaPO₃)₄·H₂O), and ammonium calcium phosphate hydrate ((NH₄)₂Ca₃(P₂O₇)₂·6H₂O), whose XRD peaks are characterised for all samples by a higher intensity, and consequently a greater amount, than that of the control sample peaks. For samples treated with a SMF intensity of 1.5 T and NMC = 30 (Figure S1 B, D, F and H), the reduction of PO₄³⁻ ions in the liquid phase is additionally linked to the precipitation of struvite and other solid phases such as calcium iron magnesium hydroxide phosphate hydrate (CaMgFe(OH)(PO₄)₂·(H₂O)₄) and iron phosphate (Fe₇(PO₄)₆). Doubling the Mg²⁺ dose promoted the precipitation of these phases, as indicated by the intensity increase of the XRD

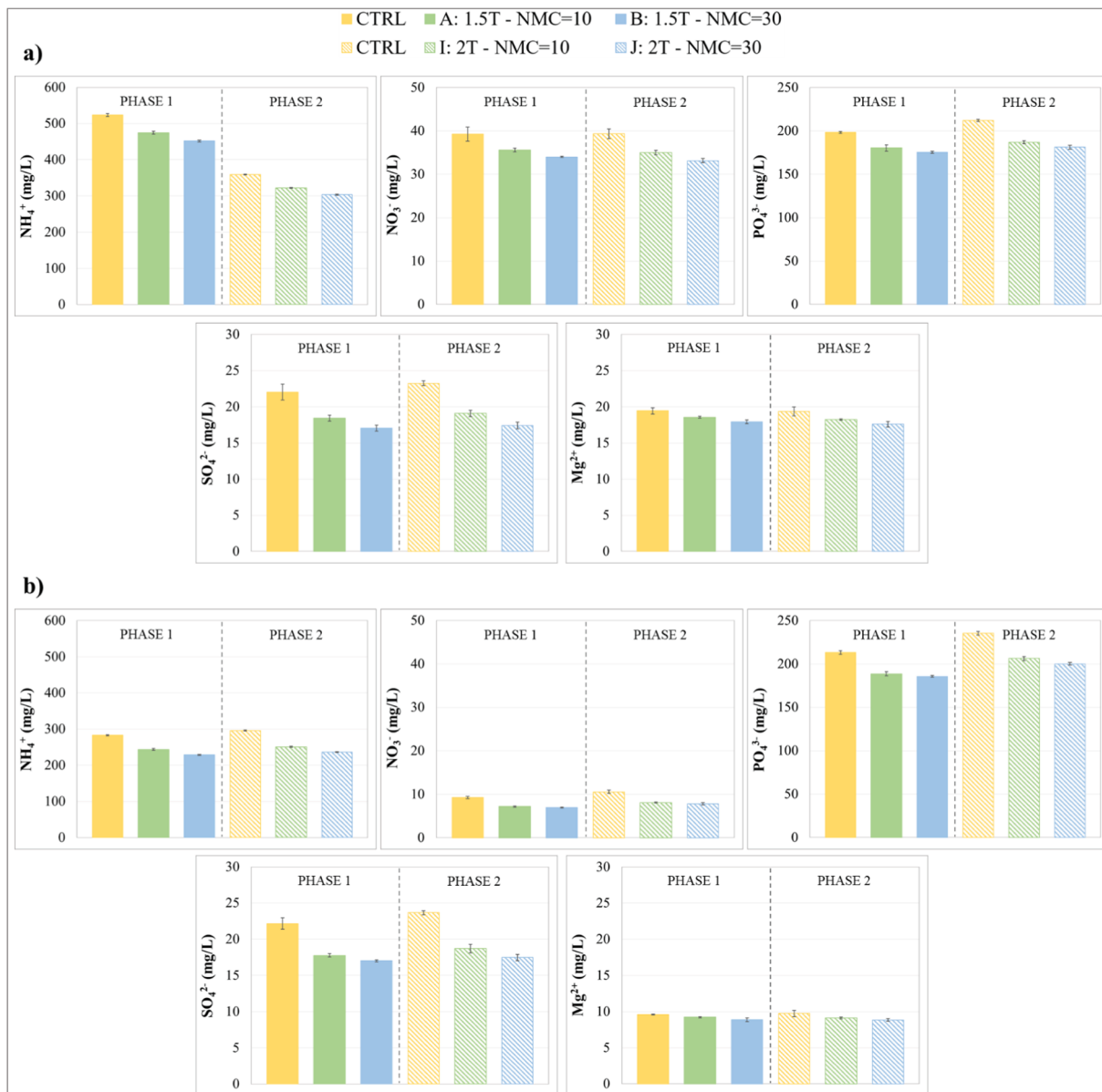


Fig. 2. Concentrations of NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} , Mg^{2+} in the HSAD digestate (a) and AD digestate (b) at the end of P1 and P2 tests with different SMF intensities and NMCs.

peaks at a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ dose of 2:1:1. By comparing the results obtained at similar Mg^{2+} doses but different NMCs (10 and 30), higher XRD peaks of struvite can be observed for samples treated at higher NMC, indicating a slightly higher content of this mineral.

The precipitation of NH_4^+ (Figs. 2a–3b) was linked to the formation of: i) $(\text{NH}_4)_2\text{Ca}_3(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ in samples treated with NMC of 10 and 30, ii) ammonium calcium sulfate $(\text{NH}_4)_2(\text{CaSO}_4)_5 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$ in samples B, D, F and H, iii) struvite in samples F and H, as well as to the presence of amorphous phases containing NH_4^+ (indicated by the amorphous band in the range $2\theta = 15\text{--}35^\circ$).

SO_4^{2-} precipitation could be linked to the formation of several solid phases such as potassium calcium magnesium sulphate $(\text{K}_2\text{CaMg}(\text{SO}_4)_3)$, sodium iron sulphide (NaFeS_2) , and $(\text{NH}_4)_2(\text{CaSO}_4)_5 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$, which were not present in the control sample, and whose amount depends on the exposure to the applied magnetic field and the increasing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations. The higher precipitation of SO_4^{2-} obtained at a NMC of 30 compared to that observed at NMC of 10 can be justified by both the presence of $(\text{NH}_4)_2(\text{CaSO}_4)_5 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$, which was not detected in samples with NMC = 10, and the precipitation of amorphous

SO_4^{2-} due to the presence of an amorphous band in the range $2\theta = 15\text{--}35^\circ$, which is slightly more intense for magnetized samples.

The results of diffractometric analyses on AD digestate are given in Figure S2. All samples were characterized by the presence of quartz, calcite, and microclines. From Figure S2 is also appreciable the presence of sodium magnesium sulphate hydrate $(\text{Na}_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4)$, magnesium phosphate $(\text{Mg}_2\text{P}_4\text{O}_{12})$, sodium phosphate sulphide hydrate $(\text{Na}_3\text{PSO}_3 \cdot 9\text{H}_2\text{O})$, gwihaibaite $(\text{NH}_4\text{K})\text{NO}_3$, potassium iron sulphide (KFeS_2) and aluminum phosphate (AlPO_4) . The intensity increase of the XRD peaks, and consequently the amount of these phases compared to the control sample, follows both the increase in SMF exposure (NMC = 10 and 30) and the dose of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and justifies the reductions of the various ionic species determined in the liquid phase (Fig. 2b–4). Moreover, in the range $2\theta = 5\text{--}35^\circ$ there is an amorphous band whose intensity increases slightly when increasing the SMF exposure (NMC = 10 and 30) and the dose of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, indicating the precipitation of amorphous phases not identifiable by XRD analysis.

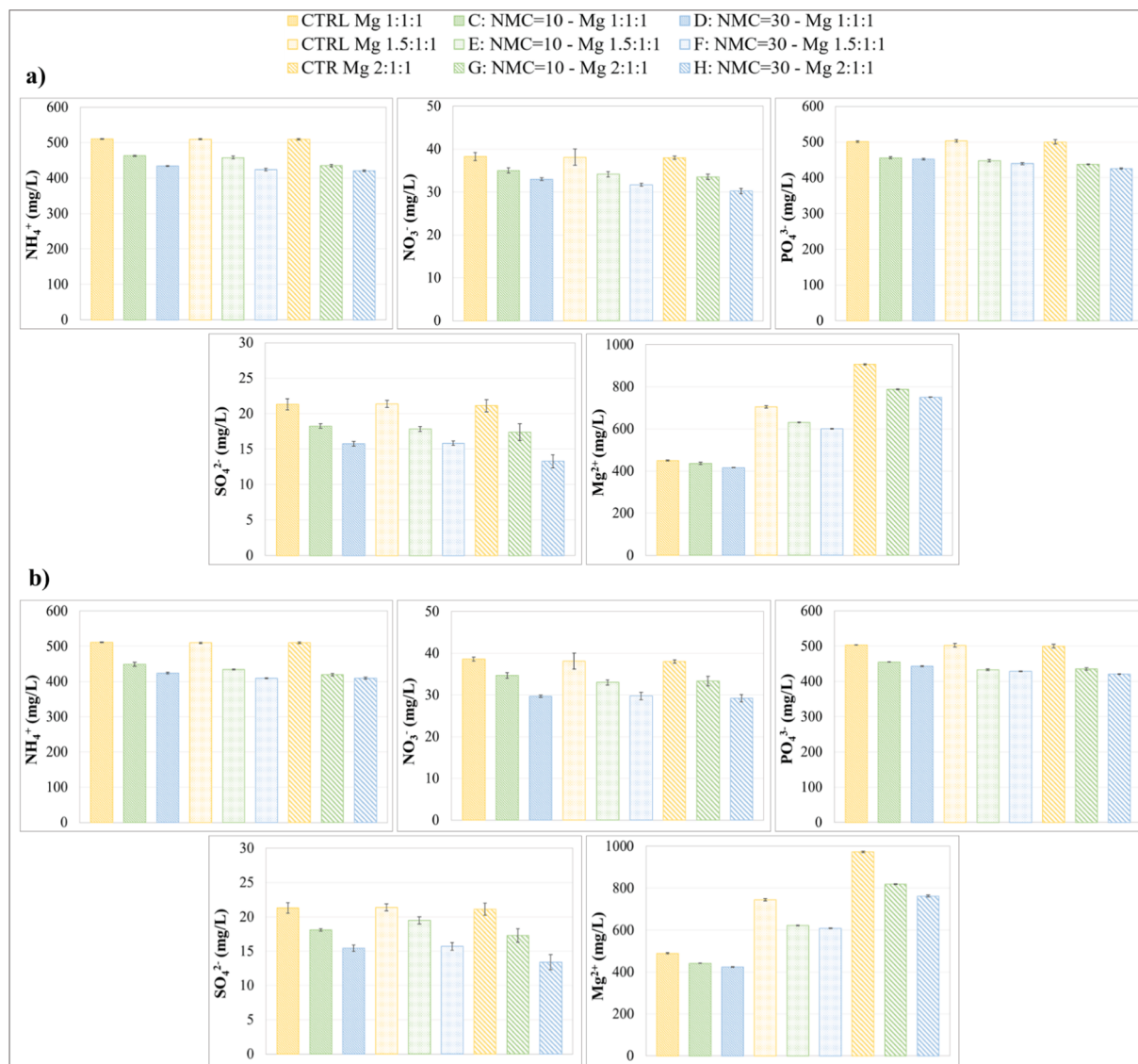


Fig. 3. Concentrations of NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} , Mg^{2+} in the HSAD digestate at the end of P1 tests with $\text{Mg}(\text{OH})_2$ (a) and with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (b) as Mg^{2+} source.

3.2.2. Impact of different aeration strategies on the solid phase of HSAD and AD digestate

Figure S3 and Figure S4 shows the XRD patterns obtained from the magnetization tests at 2 T on HSAD and AD digestate, respectively, with Mg^{2+} addition at the best $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar concentration ratio of 2:1:1 (tests K and L), and include the XRD patterns of the tests with oxygenation (tests M and N) via pre-aeration ($Q_{\text{air,tank}}$) and in-line aeration ($Q_{\text{air,circuit}}$).

The increased reduction of PO_4^{3-} concentration in the liquid phase of HSAD and AD digestate due to oxygenation both at NMC = 10 and NMC = 30 was confirmed by the increase of P-based precipitates. In particular, it can be observed that at NMC = 30, the intensity of the struvite peaks in oxygenated samples increased compared to the non-oxygenated ones. For both digestates, the XRD peaks of other P-based compounds, i.e., $(\text{NaPO}_3)_4 \cdot \text{H}_2\text{O}$ and $\text{MgHPO}_4(\text{H}_2\text{O})_3$, slightly increased in intensity both in the samples at NMC = 10 and NMC = 30 for oxygenated digestate compared to the corresponding samples without oxygenation.

Considering the oxygenated digestate by comparing the results obtained at similar Mg^{2+} doses and NMC = 30, higher XRD peaks of struvite can be observed for digestates magnetized with in-line oxygenation compared to pre-aerated ones, suggesting that in-line oxygenation stimulates struvite precipitation. The higher PO_4^{3-}

reduction observed in the liquid phase for AD digestate compared to HSAD digestate agrees with the additional presence of the XRD peaks of $\text{Na}_3\text{PSO}_3 \cdot 9\text{H}_2\text{O}$ and AlPO_4 in the AD digestate samples, as well as with a greater presence of amorphous PO_4^{3-} precipitates. Regarding NH_4^+ , its precipitation in the solid phase of both HSAD and AD digestates can be linked to the presence of the XRD peaks of $(\text{NH}_4)_2(\text{CaSO}_4)_5 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$, which was slightly higher in the digestates subjected to oxygenation during the magnetization process compared to no oxygenation. The XRD peak intensities in all samples subjected to oxygenation are similar both at NMC = 10 and NMC = 30, indicating that the NMC did not exert a significant impact on NH_4^+ precipitation as crystalline forms at the tested values.

SO_4^{2-} precipitation in the solid phase can be linked to the presence of NaFeS_2 and $\text{K}_2\text{CaMg}(\text{SO}_4)_3$ in all collected samples. However, the XRD peak intensities related to these compounds are similar for both oxygenated and non-oxygenated digestates. Therefore, the effect of oxygenation in the solid phase should not be attributed to the above-mentioned mineralogical phases but to the precipitation of amorphous phases whose entity increased with oxygenation. In fact, the amorphous band included in the 2θ range between 15° and 35° is more intense in diffractograms of oxygenated samples than in those not subjected to air injection. Furthermore, the sample with in-line oxygenation shows a

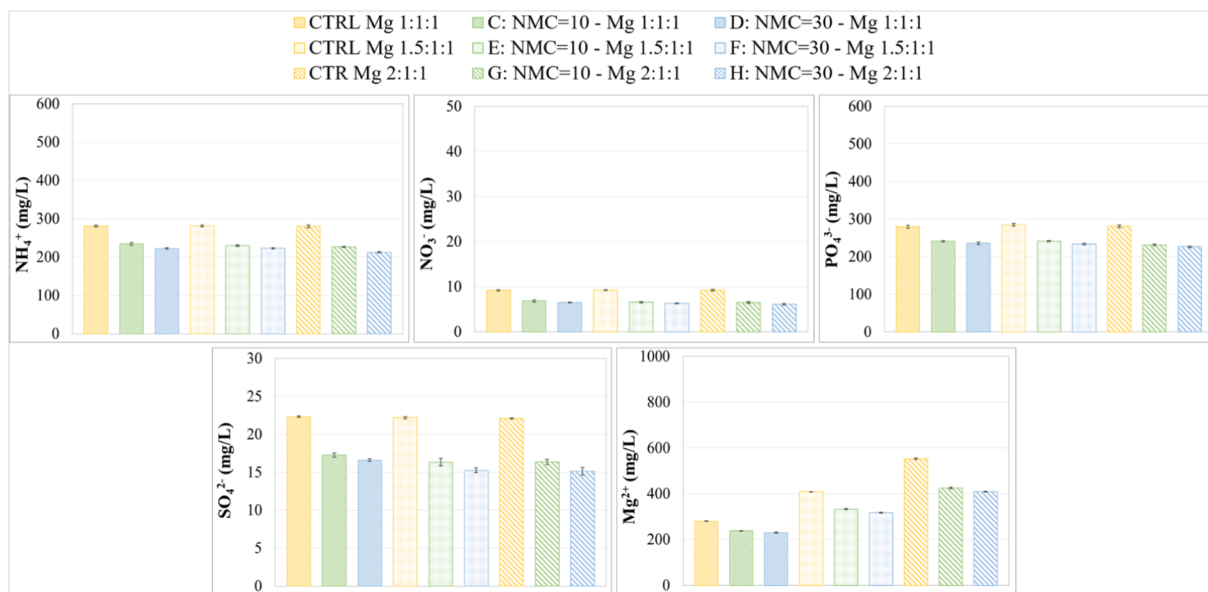


Fig. 4. Concentrations of NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} , Mg^{2+} in the AD digestate at the end of P1 tests with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as Mg^{2+} source.

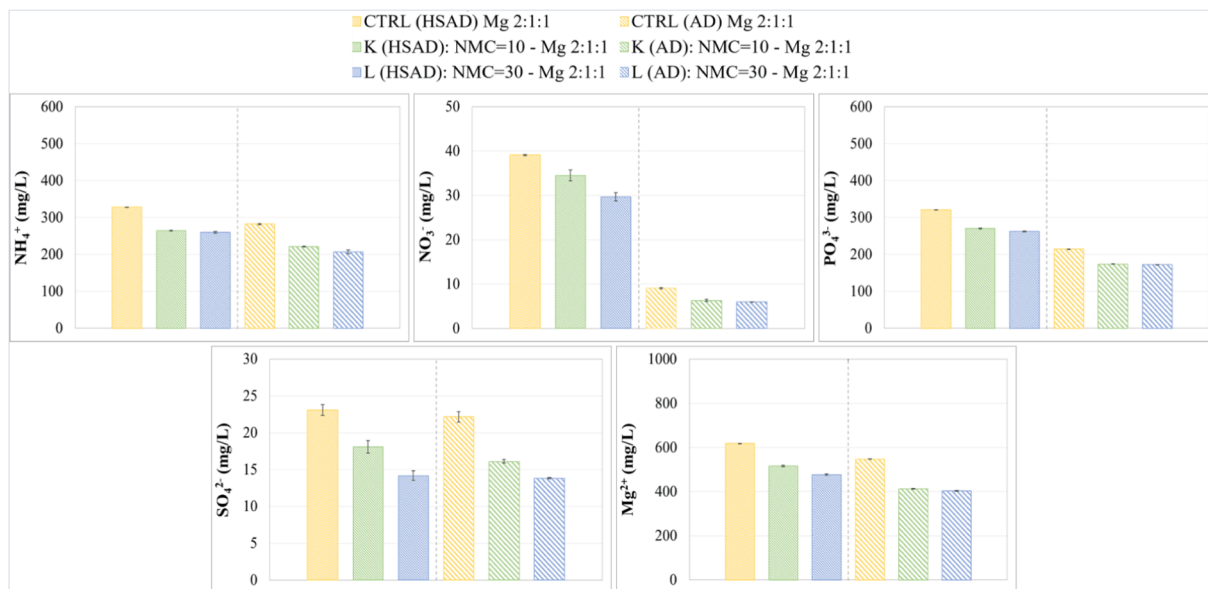


Fig. 5. Comparison in ionic concentration reduction of ionic species between HSAD and AD digestate after treatment with 2 T SMF using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as Mg^{2+} source at a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 2:1:1 at different NMCs.

slightly more intense band than the other samples, indicating a greater presence of amorphous phases. Conversely, oxygenation seems to have played a role in the precipitation of crystalline SO_4^{2-} precipitates in AD digestate. The intensity of the XRD peaks of $\text{Na}_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, KFeS_2 , and $\text{Na}_3\text{PSO}_3 \cdot 9\text{H}_2\text{O}$ phases are higher than those of the corresponding peaks in samples without oxygenation (Figure S4 K and L) in agreement with the higher SO_4^{2-} reductions observed in the liquid phase. For AD digestate also the NMC seems to have played a role on precipitation. While the intensities of the XRD peaks of $\text{Na}_2\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Na}_3\text{PSO}_3 \cdot 9\text{H}_2\text{O}$ in sample N (NMC = 30) are similar to those of the corresponding peaks of sample M (NMC = 10), the intensity of the KFeS_2 peaks in sample N is greater than those in sample M, justifying the greater reduction of SO_4^{2-} observed in the liquid phase at higher NMC. Figure S4 also highlights both XRD peaks of greater intensity and an amorphous band in the range $2\theta = 15\text{--}25^\circ$ more pronounced in the case of in-line oxygenation (M and N: $Q_{\text{air,circuit}}$) compared to pre-

oxygenation (M and N: $Q_{\text{air,tank}}$).

3.3. Practical implications and future research perspectives

This study shows that the application of a high-intensity SMF to SS digestate significantly reduces ionic concentrations in the liquid phase, leading to the formation of nutrient-based compounds with potential fertilizing properties, such as struvite. Specifically, struvite precipitation was promoted by maximizing the exposure of HSAD and AD digestate to the SMF. The highest precipitation yield was observed at the highest intensity tested of 2 T, NMC = 30, Mg^{2+} addition at a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 2:1:1, and with in-line oxygenation of the digestate.

Compared to magnetization performed before AD, digestate magnetization avoids the detrimental impacts on methane production and reduces the potential accumulation of struvite within digesters and pumping systems. This novel approach can be exploited in a circular

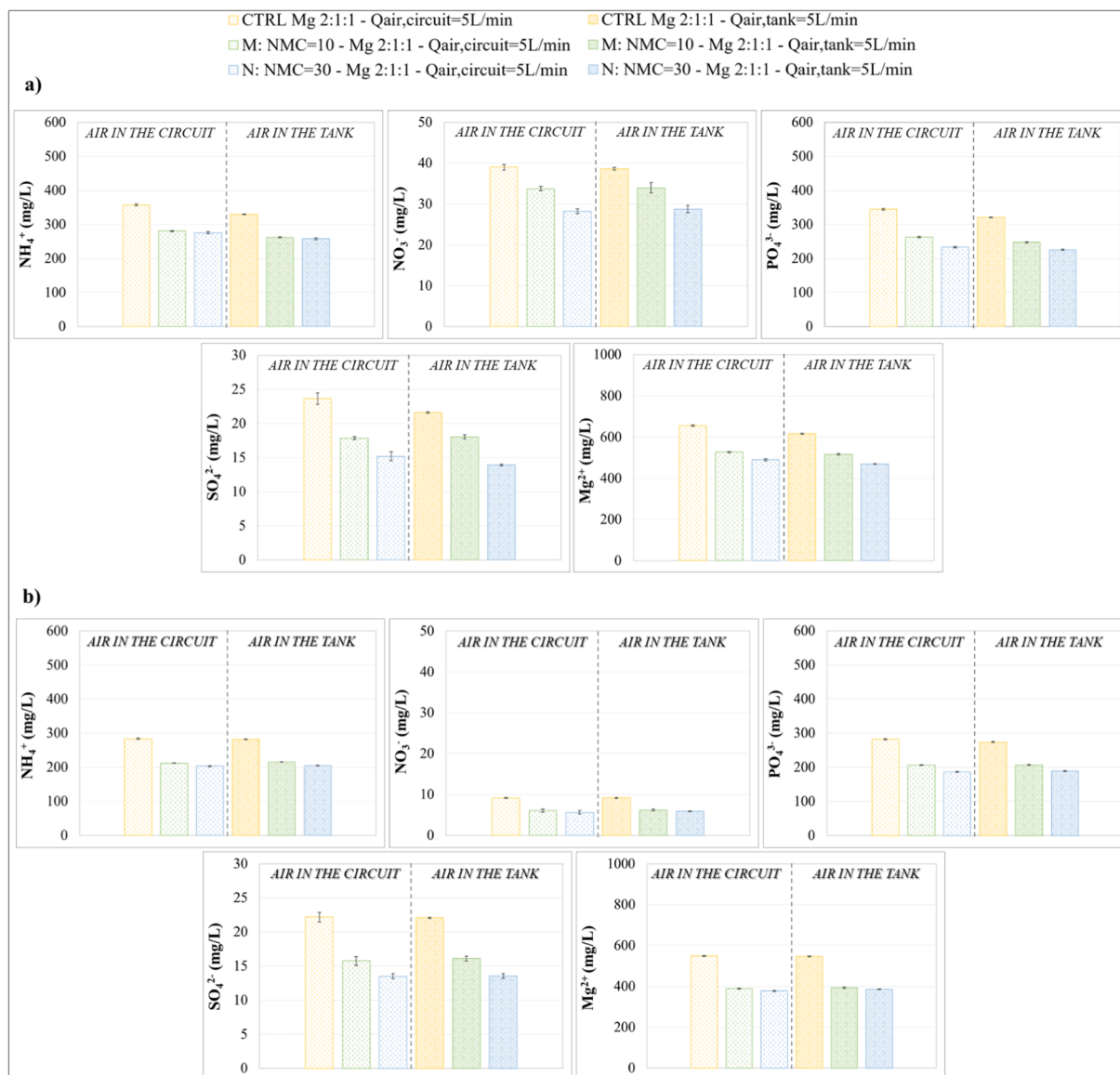


Fig. 6. NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} , Mg^{2+} concentrations in HSAD digestate (a) and in AD digestate (b) obtained at the end of the magnetization treatment with the two different aeration strategies tested.

economy perspective to promote the agricultural application of the digestate, a solution that is considered a good practice as it couples the recycling of nutrients and organics and reduces the landfilling of SS, resulting in reduced disposal costs for wastewater treatment plants (Di Costanzo et al., 2021). In this context, oxygenation of the digestate can help enhancing the precipitation of nutrient-based compounds with fertilizer properties. Future research should investigate additional strategies that can maximise the effect induced by the magnetic field on the formation of valuable precipitates. Moreover, the technical-economic feasibility of SMF application under different operating conditions at larger scale should be assessed to evaluate the potential scale-up of this technology as an integrated system to AD coupled to an oxygenation strategy. In full-scale digesters, pre-oxygenation of digesting sludge can be performed within the recirculation stream to control hydrogen sulfide (H_2S) production and limit its concentration in biogas (Jeníček et al., 2017). To enhance the agronomic quality of the digestate, oxidative H_2S removal within the digesters could be fine-tuned to promote precipitation during the subsequent magnetization step. Furthermore, it is also important to investigate the effect of alternative sources of Mg^{2+} to be added to promote struvite precipitation, perhaps by

favouring recycled materials to make the process more competitive and sustainable.

4. Conclusions

This study demonstrates that combining the exposure of SS digestates from both AD and HSAD processes to a SMF at increasing intensity (from 1.5 to 2 T) and NMC (from 10 to 30), with the addition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as Mg^{2+} source at a $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 2:1:1, promotes the precipitation of nutrient-based compounds that can improve the agronomic quality of SS digestate. At the maximum SMF exposure (SMF intensity of 2 T and NMC = 30), ionic precipitation efficiencies ranged from 18% to 39% for HSAD digestate and from 20% to 39% for AD digestate. Similarly, the formation of solid-phase compounds was stimulated at increasing SMF exposure, in agreement with the results of ionic precipitation. The best conditions for struvite formation were: SMF intensity of 2 T, NMC = 30, Mg^{2+} addition at the maximum dose tested of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 2:1:1$, and in-line oxygenation, which also promoted the formation of other nutrient-based compounds with potential agronomic value such as $\text{MgHPO}_4(\text{H}_2\text{O})_3$,

$(\text{NH}_4\text{K})\text{NO}_3$, $\text{K}_2\text{CaMg}(\text{SO}_4)_3$, $\text{CaMgFe}(\text{OH})(\text{PO}_4)_2 \cdot (\text{H}_2\text{O})_4$, and $(\text{NH}_4)_2\text{Ca}_3(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$, being characterized by the presence in their structure of macro- (N, P, K, S, Ca) and micro- (Fe, Mg, Na) nutrients.

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CRediT authorship contribution statement

Nicola Di Costanzo: Conceptualization, Visualization, Data curation, Investigation, Writing – original draft, Writing – review & editing. **Alessandra Cesaro:** Conceptualization, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Francesco Di Capua:** Conceptualization, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Maria Cristina Mascolo:** Conceptualization, Writing – review & editing, Visualization, Supervision. **Giovanni Esposito:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2023.08.005>.

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