

An approach to highly polluted wastewater management for zero liquid discharge: The case of landfill leachate

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ABSTRACT

This work aims to bring the treatment of highly polluted wastewater to the concept of zero liquid discharge, using landfill leachate as a representative example. Achieving this goal involves removing pollution due to organic matter and/or heavy metals and recovering the nutrients contained in the effluent. Thus, the sequential combination of thermally activated persulfate and the Fenton reagent is proposed to eliminate the high concentration of organic matter. This avoids the need of pH adjustment to meet the Fenton process operation criteria and minimizes the amount of persulfate and, consequently, the conductivity in the treated effluent. Furthermore, this solution is particularly attractive in systems with excess energy, such as urban solid waste facilities where biogas is generated. Nutrient recovery (N in the case of landfill leachate) is carried out through precipitation in the form of struvite. Finally, if necessary, a further nanofiltration stage is proposed to minimize the conductivity of the treated effluent, making it suitable for on-site use. Under the optimized operating conditions (Flow rate: 0.5 L h⁻¹, residence time 60 minutes, 0.3 and 0.7 times the stoichiometric amount of persulfate (12 g/g COD₀) and H₂O₂ (2.12/g COD₀), respectively, a H₂O₂/Fe²⁺ ratio of 50/1 and 85°C), a 90% removal of COD is achieved, along with 99% and 95% recovery of the nitrogen content in the effluent and reclaimed water, respectively, confirming the feasibility of this solution as an approach to a more sustainable waste management.

1. Introduction

The implementation of reusing and recycling strategies, among others, within the last decades has significantly reduced the use of landfill as ultimate destination of urban solid waste. According to Eurostat (2021), it has dropped from 61% in 1995 to less than 23% in 2021 (around 530 kg per capita), indicating a shift towards more sustainable and eco-friendly waste management methods. Despite this positive trend, it is crucial to address the issue of landfill leachate formation, as in the absence of adequate collection and management systems it may contaminate surface and underground water (Eurostat, 2021).

Landfill leachate is a liquid effluent characterized by high concentrations of organic compounds, heavy metals, ammoniacal nitrogen, pathogenic microorganisms, and emerging micropollutants. It is usually

treated through the conventional techniques applied in wastewater treatment, such as aerobic and anaerobic oxidation, adsorption or reverse osmosis. Nonetheless, the effectiveness of such processes is limited or highly expensive, and rarely the treated effluent does meet the quality requirements established for discharge into receiving water bodies (Abbas et al., 2009; Silveira et al., 2015). Moreover, this wastewater management approach corresponds to a linear economy logic (extract, produce and discard) and it is not a sustainable alternative as it does not prioritize resource use efficiency or resource recovery (Oliveira and Oliveira, 2023).

In this work we propose an alternative to the traditional technologies, focused on the zero liquid discharge (ZLD) postulates to bring the treatment of waste streams to a more sustainable management. This approach requires the prior removal of pollutants such as organic matter content, heavy metals, pathogenic microorganisms and emerging

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micropollutants. This can be achieved by the application of advanced oxidations processes (AOPs), as these technologies show a high capacity to partially oxidize or mineralize numerous organic compounds by forming highly reactive radicals (Ateş, Argun, 2021). Recently, Gautam et al. (2019) and Usman et al. (2020) published a thorough review on the use of AOP in landfill leachate treatment, and the Fenton process stood out. This treatment is based on the catalytic decomposition of hydrogen peroxide by Fe^{2+} in an acidic medium to produce hydroxyl radicals (HO^\bullet). To lower the pH to the values required to trigger the Fenton reaction without the excessive usage of acidic correctors, the activation of persulfate (PS) with consequent formation of sulfate radicals ($\text{SO}_4^{\bullet-}$) could be a viable option. In a previous work (Silveira et al., 2019) we studied the feasibility of heat-activated persulfate to treat landfill leachate. When the temperature of the leachate was raised above 70°C , the organic matter was almost completely removed, resulting in high percentages of chemical oxygen demand (COD) reduction. Regarding the heavy metals' withdrawal, it occurred along with the sludge produced during the oxidation processes. However, the high concentration of sulfates in the treated effluent was the main drawback of this process since the high stoichiometric doses of PS (12 g / g COD) required to mineralize the organic matter.

It must be noted that the previous techniques did not remove the ammoniacal nitrogen that, therefore, could be recovered as high-quality (free of organic matter and heavy metals) struvite. This represents an alternative to problems related to the overuse of synthetic nitrogen fertilizers (i.e., eutrophication, soil acidification, and loss of biodiversity), and a step in the direction towards a more circular economy (Zhang et al., 2015). In this context, nutrient recovery through struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$) precipitation has received considerable attention worldwide as it is one method for nutrient recovery from wastewater that also meet the principles of circularity (Sena and Hicks, 2018). A rigorous review by Ersahin et al. (2023) highlighted the main challenges of recovering nutrients from landfill leachate. The potential for using waste such as sewage sludge, urban sewage, and animal manure as an alternative source of phosphorus is particularly promising. Huang et al. (2014), Siciliano (2016), and Huang et al. (2017) proposed the use of waste phosphoric acid, seawater bittern, and phosphating wastewater, respectively, as sources of phosphorus for the struvite precipitation.

The precipitation of struvite particularly from landfill leachate and its reuse in the production of fertilizers has been studied by different authors. Both Liu et al. (2021), and Yee et al. (2019) highlighted the benefits of the procedure, but also pointed out the direct or indirect health risks to humans and the environment related to the agricultural application of these fertilizers, due to the presence of heavy metals (i.e. Cu, Zn, Cr, Ni, and Pb) in the leachate that can be co-precipitated.

In light of the results obtained in previous studies, this work proposes a viable approach to the treatment of landfill leachate, which can be extended to other agricultural wastewaters, enabling nearly complete recovery of water and nutrients. Heat-activated persulfate and Fenton reagent were sequentially combined to effectively mineralize organic matter whereas nutrients were recovered by precipitation as struvite. Experiments were performed using a pilot system consisted of three reactors in a row, operating under a continuous flow, and optimized through experimental design and response surface analysis. As a final polishing step, a nanofiltration system was employed. To assess the potential hazards of the produced struvite constituents, an in-silico evaluation (USEtox®) was performed along with an assay to evaluate the effects of the produced struvite on a hydroponic lettuce growth cultivation system.

This treatment [Patent: P-09012] is particularly appealing for urban solid waste facilities with thermal energy available from biogas or solar power, rendering it a more sustainable option. Besides, it could also be adapted to a range of agro and industrial wastewater treatment scales, particularly in cases where traditional treatment processes, such as biological treatment, are not feasible.

2. Materials and methods

2.1. Reagents

Except for persulfate (Panreac, Spain), all reagents utilized in this study were obtained from Sigma-Aldrich, USA.

2.2. Sampling and analytical procedure

The leachate sample was collected from a municipal landfill located in Madrid (Spain). The landfill receives about 3340 t/d and the leachate facility is designed to treat up to 200 m³/d. The analytical procedure applied to quantify total organic carbon (TOC), total nitrogen (TN), and chemical oxygen demand (COD) was the same as that described by (APHA, 2012). Table 1 presents the main parameters of the effluent.

The identification of the aromatic by-products of the raw and treated sample was performed using gas chromatography-mass spectrometry (CG-MS) (CP-3800/Saturn 2200, Varian), in an electron impact ionization system equipped with an automatic injector CP-8200/SPME. The detailed procedure is described by Silveira et al., (2018). The presence of metals (Pb, Cd, Cu, Zn, Ni, Hg, and Cr) in struvite was identified through total reflection X-ray fluorescence (TXRF), using a TXRF 8030c spectrometer. The X-ray diffraction (XRD) method adopted to identify struvite made use of a Siemens D-5000 diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$).

2.3. Experimental design

To assess the effectiveness of the proposed system and to get the maximum mineralization and acid pH, an experimental design was implemented using Design Expert v13 software. This involved utilizing a BBD design and examining three independent variables: reaction temperature (ranging from 50 to 90°C), a stoichiometric dose of PS (from 10% to 50%), and residence time (20–60 minutes). A second-order polynomial Eq. (1) was also applied to the analysis.

$$R = \beta_0 + \sum_{i=1}^k \beta_{ii}x_i^2 + \sum_{i=1}^k \sum_{j=1+i}^k \beta_{ij}x_i x_j + \varepsilon \quad (1)$$

Response surface plots were utilized to evaluate the effects of each variable and their interactions. Model fit was determined by ANOVA analysis, which assessed whether the model accurately predicted experimental data, and F-tests were conducted to determine if significant variations were present in the data. The Probability p-value was used to assess whether the F-value was statistically significant.

2.4. Experimental procedure

Fig. S1 shows the experimental setup used in this study. It includes three magnetically stirred borosilicate batch reactors (1500 mL each) placed each in a heating block. Landfill leachate was continuously pumped ($Q: 0.5 \text{ L h}^{-1}$) through the system. The doses of PS and H_2O_2 were calculated based on the stoichiometric amounts required to mineralize the initial COD, specifically 12 g PS/g COD and 2.12 g H_2O_2 /g COD, respectively. PS was continuously supplied to the first

Table 1
Landfill leachate characterization.

Parameters (g/L)	Raw Sample	Treated by AOPs	Permeate NF
COD	2.7	0.35	0.12
SO_4^{2-}	0.28	8.6	0.28
Cl^-	1.12	0.95	0.90
TN	1.35	1.18	0.64
pH	8.3	5	7.2
Conductivity (mS/cm)	4.6	41	3.3

two reactors at a rate of 25 mL/h, with equal distribution. The third reactor received only H_2O_2 and Fe^{2+} in a continuous manner, with a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 50/1. Nanofiltration (NF) membranes were used in a pilot-scale polishing process after AOP treatment. The NF system operated in cross-flow mode with spiral-wound polyamide membranes (Hydranautics) and had a total membrane surface area of 7.4 m². Treated landfill leachate was recirculated from the feed tank over the membrane cell with an applied inlet pressure of 8 bars and cross-flow rate of 60 L/min. The final NF recovery ratio was > 95%. The main treated landfill leachate quality parameters are shown in Table 1.

2.5. Struvite precipitation

The recovery of nitrogen was carried out at a controlled temperature of 23 °C, in glass batches equipped with a pH meter, magnetically stirring the raw and treated leachate in the optimum conditions. MgCl_2 and MgSO_4 were the magnesium sources used, while $\text{NaH}_2\text{PO}_4 \cdot 0.2 \text{H}_2\text{O}$ served as the phosphate source. Particularly three molar ratios N: P: Mg (1:1:1; 1:1:1.5 and 1:1:2) were investigated. After dosing the reagents, the pH was adjusted to 9 using 1 M NaOH. The mixture was stirred at 200 rpm for 15 min, followed by 60 min of standing to allow precipitation of the struvite. The precipitate was washed with distilled water and dried at ambient temperature.

2.6. Running the USEtox model

USEtox® is an environmental tool developed under the auspices of the Society for Environmental Toxicology and Chemistry and the United Nations Environmental Program (UNEP/SETAC). It has been used in a variety of wastewater and resource recovery system assessments (Harder et al., 2017; Rashid and Liu, 2021; Tarpani et al., 2020; Yoshida et al., 2018; Garbellini et al., 2023). The method provides Characterization Factors (CF) for substances, which are dimensionless value for comparing toxicological potential. CFs are based on a substance's environmental physiochemical fate, biological level of exposure, and its effective toxicological potential, both on humans and ecosystems, in a given environmental compartment and scale. These factors are provided for human and ecological toxicology to freshwater species and they express an estimated cases of disease per mass emitted (cases/kg) and fraction of species potentially affected by the substance's emission in freshwater ($\text{PAF} \cdot \text{m}^3 \cdot \text{day/kg}$). More detailed information on the method is available in the cited literature (Fantke et al., 2017, 2015; Kounina et al., 2014; Rosenbaum et al., 2011).

For this study, we calculated the CF of all the metals detected in the samples, considering their emission into agricultural soils. We utilized the 'European' set of geographic parameters available in the software database. The CFs obtained were then multiplied by the concentrations of the metals found in the raw and in the treated struvite sample, to obtain the Impact Scores (IS) for each substance, which represents a measure of the direct (eco)toxicological potential of each concentration.

2.7. Hydroponic lettuce growth cultivation

To check the effects of the produced struvite on the growth of common crops a hydroponic test was performed. The experiment involved placing six discs of coconut fiber (each of 5 cm diameter) in hydroponic smart kitchen gardens. Five seeds of romaine lettuce (*Lactuca sativa*) were evenly distributed on each coconut fiber, and three replicates were set for each treatment. The kitchen gardens were operated in a recirculating mode, where the nutrient solution was pumped from a reservoir to the lettuce roots, which were immersed in two different media: a control (1000 mL of deionized water + 2.5 g of fertilizer), and a produced struvite from treated landfill leachate (1000 mL of deionized water + 2.5 g of struvite). For control experiments, a commercial fertilizer NPK (16–4–24) was used. The N-P-K-ratio into the dried struvite precipitate was equal to 11/22/2. The kitchen gardens

were placed in the dark for 2 days, after which they were exposed to conditions of a 12/8 h light/dark cycle for 21 days, with top illumination of 3000 lux. Following the incubation period, the number of germinated seeds, above-ground parts growth (length), and fresh weight of the above-ground parts of the seedlings were recorded. The hydroponic test followed the recommendation provided by the kitchen gardens manufacturer.

3. Results and discussion

3.1. Removal of organic load by thermally activated persulfate and Fenton oxidation

To apply the presented method in a realistic scenario, the operating conditions were optimized in a continuous-flow system (formed by three batch in a row) on a pilot scale. The indications of the experimental matrix (Table 2) were followed to obtain a model with higher efficiency in mineralization.

The design matrix in Table 2 consists of 15 runs with different temperatures, persulfate concentration, and residence time to determine the optimal operating conditions for sequential activation of persulfate. The experimental results show the percentage of organic carbon mineralized in each run compared to the theoretical X_{TOC} (%). The ANOVA test provides statistical evidence of the model's significance in predicting TOC removal efficiency. The F-value of 211.7 and p-value of <0.0001 further confirm the model's statistical significance. The individual factors A (temperature), B (persulfate), C (residence time), AB, AC, BC, and A² are also significant in removing TOC. The regression coefficient of $R^2=0.996$ indicates that the model performs well in explaining the variation in the data. The lack of fit is not significant (p-value > 0.05), indicating that the model adequately fits the data. Overall, the ANOVA test results provide strong evidence that the model is effective in predicting the TOC removal efficiency (Table S1).

Response surface models were determined to optimize the process efficiency. In this sense, Fig. 1 represents the 3D response surface, showing the relation among temperature (°C), PS dose (%), and residence time (min) in the removal of TOC. Based on the model, the mineralization rate was fitted to quadratic polynomial equations in terms of real coefficients (Eq. (2)).

$$\text{TOC removal} = + 60.043 - 1.21042 \cdot ^\circ\text{C} - 1.26813 \cdot \text{PS} - 0.470417 \cdot \text{RT} + 0.017063 \cdot ^\circ\text{C} \cdot \text{PS} + 0.008500 \cdot ^\circ\text{C} \cdot \text{RT} + 0.010687 \cdot \text{PS} \cdot \text{RT} + 0.005146 \cdot ^\circ\text{C}^2 \quad (2)$$

Optimized conditions refer to those where higher mineralization and acidic pH were achieved. The ideal operating conditions were: temperature: 85 °C, PS stoichiometric dose of 30%, and residence time of

Table 2
The BBD design matrix and experimental results.

Run	Temperature (°C)	Persulfate (%)	Residence time (min)	X_{TOC} (%)	
				Exp.	Theo.
1	50	10	40	9,0	10,7
2	70	10	60	11,5	13,7
3	70	10	20	5,0	4,4
4	90	10	40	10,1	11,5
5	70	30	40	13,8	16,4
6	70	30	40	14,4	16,1
7	70	50	20	7,4	10,0
8	50	30	60	14,0	16,4
9	90	30	60	35,1	37,7
10	90	30	20	11,5	13,1
11	50	30	20	4,1	5,4
12	70	50	60	31,0	36,4
13	50	50	40	8,3	11,2
14	90	50	40	36,7	39,3
15	70	30	40	14,8	16,3

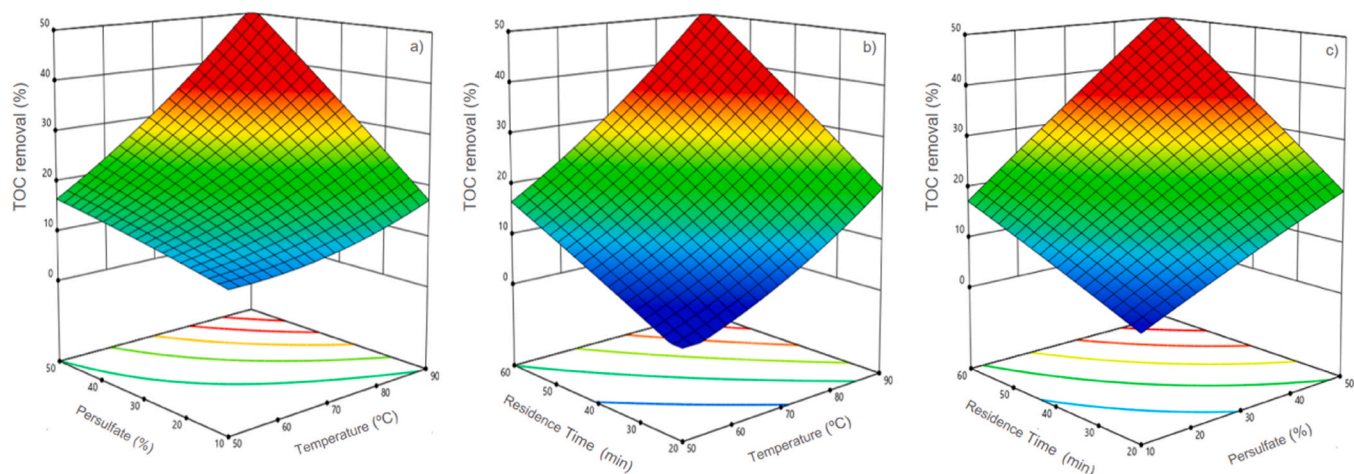


Fig. 1. Response surface plot showing the interaction of persulfate dose and temperature (a), residence time and temperature (b), residence time and persulfate dose (c) on TOC removal.

60 minutes. Under these conditions, the pH is acidic (3.3), and the experimental elimination of TOC is slightly lower than that obtained by the model ($X_{TOCexp} = 40\%$ vs $X_{TOCmodel} = 37.7\%$).

The thermal activation of PS under optimal conditions was followed by adding the stoichiometric amount of H_2O_2 (2.12 g/g COD) in the third reactor to mineralize the residual organic matter. The TOC reduction due to the Fenton reaction achieved nearly 58% of mineralization after 60 min residence time, while the overall efficiency of the combined treatment reached over 85%. Under those conditions, almost complete color reduction (Fig S2), total PS/ H_2O_2 consumption and metals removal were achieved.

Fig. 2 presents the GC-MS analysis of both raw and treated landfill leachate under optimal conditions. The identification of by-products was carried out by matching mass spectra obtained from detected peaks with mass spectra from the NIST Library, with a minimal probability of 70%. Following treatment, the concentration of organic pollutants significantly decreased. A list of identified compounds is provided in supplementary information (Table S2). Raw landfill leachate contains a diverse range of organic compounds, including volatile organics (C_2H_5Cl , CH_2Cl_2 , $CHCl_3$, C_2H_5FO), hydrocarbon (C_6H_{14}), amino acid ($C_2H_5NO_2$), amides (C_2H_2ClN , $C_3H_6ClNO_2$), ketone

($C_7H_3Cl_3O$) and aldehyde ($C_3H_6Cl_2O$). These organic compounds originate from various waste materials, such as solvents, plastics, pharmaceuticals, pesticides, and organic matter, contributing to the leachate's diverse and potentially hazardous nature (Teng et al., 2021).

However, upon applying AOPs, significant changes occur in the leachate composition. Organic compounds such as $C_2H_5NO_2$, $C_7H_3Cl_3O$, C_3HCl_5O , and others were all effectively oxidized and transformed, resulting in only small amounts of low-molecular-weight organics. Notably, short-chain organic acids, primarily acetic and formic acids, constitute the main compounds identified in the residual total organic carbon (TOC).

3.2. Nitrogen recovery by struvite precipitation

The results confirm the feasibility of processes in reducing organic matter in landfill leachate, but nitrogen reduction was found to be limited, at less than 15%, as depicted in Fig. S3. Table 3 presents the nitrogen recovery for various N/P/Mg ratios in raw landfill leachate, treated by combined AOPs, and the permeate obtained from NF. As observed, the percentage of nitrogen removal is generally higher for treated leachate. This outcome can be attributed to the removal of

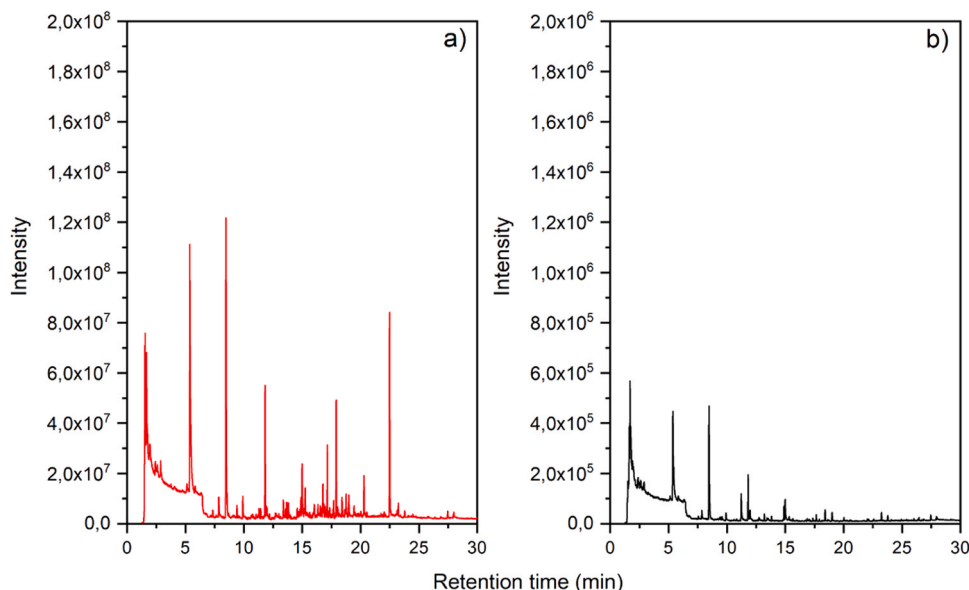


Fig. 2. GC-MS analysis of raw landfill leachate (a) and after coupled treatment (b).

Table 3

Metals concentration in struvite samples, legal thresholds, and (eco)toxicological Impact Scores.

Substance	Concentration (mg/kg)		Real Decreto 506/(2013) (class A)	Impact Scores			
				Human toxicological (cases/kg _{emitted})		Ecotoxicological (PAF.m ³ .day/kg _{emitted})	
	Raw	Treated	mg Kg	Raw	Treated	Raw	Treated
As 3	4,14	1,25	—	1,09E-06	3,29E-07	1,17E-01	3,52E-02
As 5	4,14	1,25	—	1,09E-06	3,29E-07	3,10E-01	9,35E-02
Cd	n.d	—	0.7	0	0	0	0
Cr3	9,2	4,2	70	4,04E-14	1,85E-14	9,34E-02	4,26E-02
Cr6	n.d	n.d	n.d	0	0	0	0
Cu2	12,2	1,61	70	1,03E-08	1,36E-09	9,71E-01	1,28E-01
Fe2	15,4	58	—	n/a	n/a	5,07E-01	1,91E+00
Fe3	15,4	58	—	n/a	n/a	7,94E+00	2,99E+01
Hg	n.d	—	0.4	0	0	0	0
Ni	29,6	2,2	25	5,78E-08	4,30E-09	1,09E+01	8,06E-01
Pb	3,75	0,8	45	1,68E-06	3,58E-07	4,26E-02	9,08E-03
Sr	4,6	2	—	n/a	n/a	1,43E+00	6,23E-01
Ti	20,4	10,8	—	7,36E-09	3,89E-09	1,44E+00	7,63E-01
Zn	39,6	17,7	200	7,00E-06	3,13E-06	1,30E+01	5,79E+00

competing ions through these treatments, which may otherwise interfere with the formation of struvite. According to Siciliano et al. (2020), the formation of struvite crystals is governed by mass transfer mechanisms from the solute to the surface of the crystals, dependent on factors such as pH, temperature, and the presence of competitive ions like Na⁺, Ca²⁺, K⁺, Al³⁺, HCO₃⁻, and CO₃²⁻. The nitrogen recovery for the permeate obtained from the NF system reached 99%, a substantial improvement compared to the 40% removal rate observed in the raw sample (Fig. 3).

For instance, to minimize this adverse factor, the applied dosage of Mg increased from the molar ratio of 1.5–2. For example, when leachate was treated by AOPs with the molar ratio of 1.5 of MgCl₂, nearly all nitrogen was recovered, exceeding the nitrogen recovery achieved using only the stoichiometrically required dose of Mg (57%). However, when MgSO₄ was employed, the result was lower, likely due to the lower solubility of MgSO₄ compared to MgCl₂.

The XRD pattern obtained from the raw sample (Fig. 4a) reveals

distinct peaks at angles corresponding to 14.9°, 15.8°, 20.8°, 21.4°, 27.1°, 28.3°, 30.6°, 31.9°, 33.27°, and 44.05°, which are associated with struvite. Additionally, other identified peaks may be attributed to the precipitation of calcium carbonate and calcium oxalate. Furthermore, the treated effluent XRD pattern (Fig. 4b) displays sharp and well-defined peaks at 14.9°, 20.82°, 23.2°, 26.9°, 33.22° and 34.3°, confirming the presence of struvite. These findings are consistent with the JCPDS card no. 00–015–0762, supporting the conclusion that the precipitate formed in the experiment is indeed struvite. Additionally, these results align with the findings reported in the literature (Polat and Sayan, 2020).

The FTIR spectra of struvite precipitates (shown in Fig. 4c-d) reveal distinctive bands that confirm the presence of these compounds. Notably, the peak at 546 cm⁻¹ corresponds to the stretching vibration of Mg–O or Mg–N bonds. Moreover, bands observed between 990 and 1080 cm⁻¹ are indicative of the stretching vibration of phosphate ions,

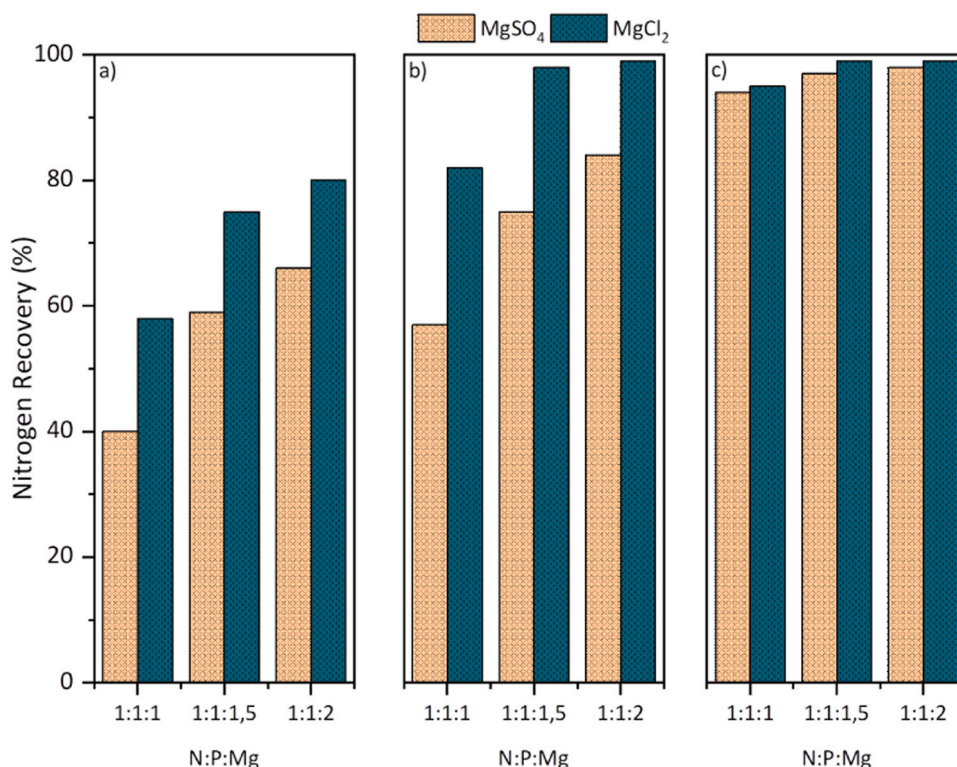


Fig. 3. Nitrogen recovery efficiency during struvite precipitation at different Mg molar ratios. Raw sample (a), treated by AOPs (b) and permeate (c).

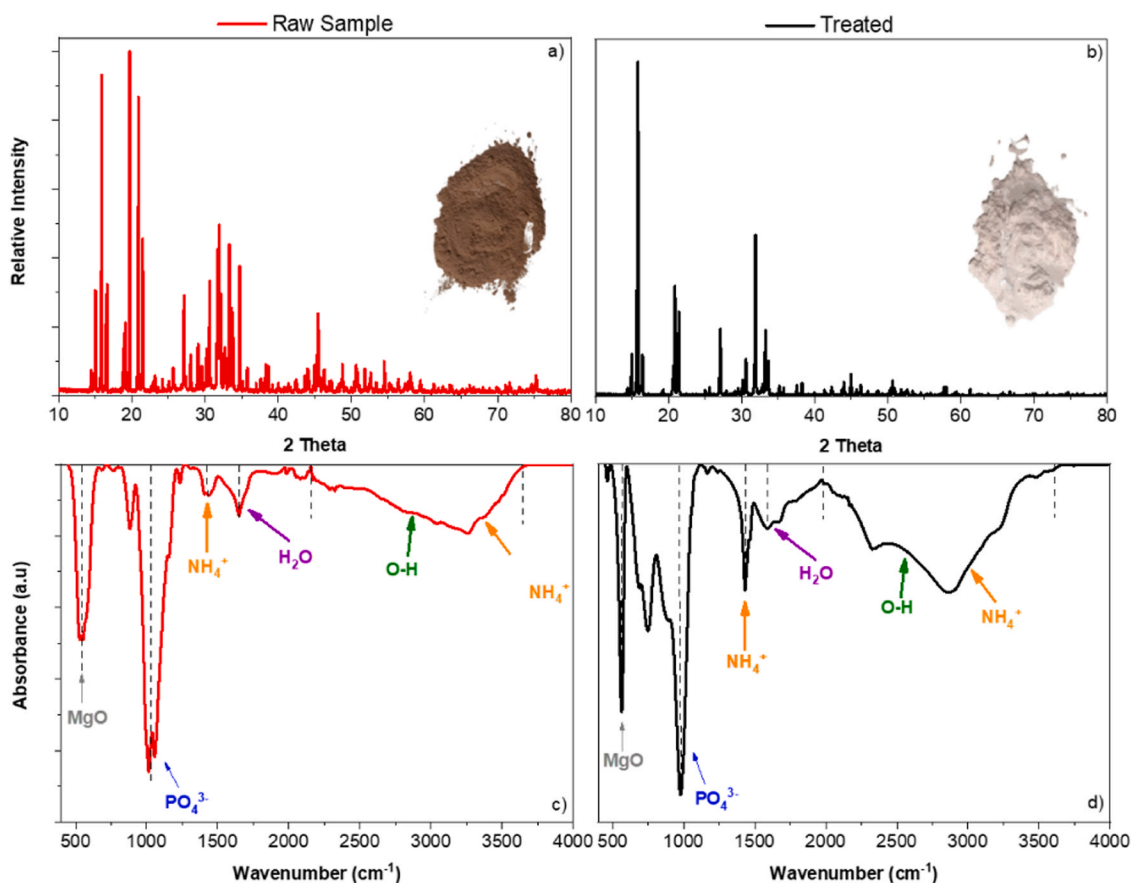


Fig. 4. Normalized XRD patterns of the precipitates obtained from raw and treated landfill leachate (a-b). The inset displays a photograph of the two different struvites (raw sample and treated) with a change of color due to the presence of organic matter. FTIR spectra of struvite precipitates (c-d).

while those found between 1400 and 1480 cm^{-1} are associated with the bending vibration of N-H bonds in the ammonium group. Additionally, the absorption observed between 2900 and 3600 cm^{-1} results from the stretching vibration of O-H and N-H bonds. These findings are consistent with prior studies employing FTIR spectroscopy for the characterization of struvite (Herald et al., 2017; Sidorczuk et al., 2020; Polat and Eral, 2022; Wang et al., 2022).

3.3. Toxicological assessment of the components in the struvite sample

To assess the potential risks associated with the application of struvite for soil conditioning, the concentrations of metals in the raw struvite and the treated struvite sample were analyzed (Table 3). None of the metals found in the treated sample exceeds the thresholds for contaminants in the most restrictive class of fertilizing products in the Spanish legislation (Real Decreto 506, 2013). Nevertheless, a toxicological potential assessment was carried out using the USEtox® to evaluate and compare each substance's (eco)toxicological Impact Scores (IS). The results obtained are listed in Table 3.

Human toxicological IS were significantly lower than the ecotoxicological ones, and, for both categories, the treatment reduced the toxicological potential by one order of magnitude. Zinc (Zn) and lead (Pb) hold the highest values for the treated samples ($3.13\text{E-}06$ and $3.58\text{E-}07$ cases/kg_{emitted}, respectively). In terms of ecotoxicological ISs, Nickel (Ni) concentration accounts for the second highest value for the raw struvite sample, but the treatment effectively reduced its impact potential in 2 orders of magnitude (i.e., $8.06\text{E-}01$ PAF.m³.day/kg_{emitted}). Furthermore, the Ecotoxicological IS for Fe and Zn were among the highest, but both substances are essential micronutrients for the development of ecological species, including crops and most of the vegetable

ones. They can be toxic in higher concentrations, but the mass load approach in USEtox® assumes that soil micronutrient concentrations are ideally balanced. Therefore, any additional emission is interpreted as negatively effective, which may not be the case, as discussed in previous studies (Fantke et al., 2018, 2023).

Complementarily, the concentration of the organic compounds in the samples was not quantified, but we assessed the CF of the organic species that seemed most likely to be present in the struvite, according to the chromatographic analysis carried out (Table S2). None of the obtained CFs exceeded those of the metals (Table 3). This assessment confirms that no substances with toxicological potential were overlooked in the treated sample, and it further assures that no toxicological risks were neglected.

To verify the effects of the precipitated struvite on the growth of lettuce a cultivation test was performed (Fig. S4). Based on the statistical analysis, using the Student's t-test, it can be concluded that there is no significant difference in above-ground parts growth between the control and struvite groups. The mean lengths of above-ground parts growth in both groups are similar, with a difference of only 0.23 cm , which is not significant. The p-value of 0.310 indicates that there is a 31% chance that the observed difference in means is due to chance. This level of probability is not low enough to reject the null hypothesis that there is no significant difference in above-ground parts growth between the two groups.

The t-value of 1.033 with a df of 30 suggests that the difference in means may be due to random sampling variation rather than a true treatment effect. The higher the t-value, the more likely it is that the observed difference is due to the treatment and not due to chance. However, a t-value of 1.033 is relatively low, indicating that the observed difference is not very large compared to the variability within

the groups. The statistical analysis suggests that the application of struvite fertilizer did not have a significant effect on above-ground parts growth compared to the control group. However, as this analysis only considers mean lengths of above-ground parts and does not account for other factors such as weather conditions, plant species, etc.

Furthermore, the mean fresh biomass of the control treatment was compared with the mean fresh biomass of the struvite treatment. The results showed that the mean fresh biomass of the struvite treatment (mean=0.95 g, SD=0.36) was inferior to the mean fresh biomass of the control treatment (mean=1.21 g, SD=0.44), with a mean difference of −0.26 g ($t=-5.09$, $df=20$, $p<0.001$).

This indicates that the struvite treatment had a slightly negative effect on the growth of the plant, possibly due to the higher levels of phosphorus and lower potassium content in the struvite fertilizer, which may have negatively impacted the uptake of other nutrients by the plant, or may have caused toxicity due to higher P levels. This analysis suggests that more studies are needed to evaluate the potential benefits and drawbacks of using struvite in different types of soil and with different plant species. It also suggests that studies regarding better dosages and nutrient balancing (i.e., P and K) are necessary for better lettuce yields using the struvite produced in this study.

4. Conclusion

The postulates of zero liquid discharge on the landfill leachate management can be satisfactorily achieved by combining heat-persulfate and Fenton reagent to remove COD, microcontaminants and heavy metals from this effluent, allowing the recovery of nutrients (i.e., nitrogen) as high quality struvite.

The optimized conditions allow COD removal, and nitrogen and water recovery above 90%, 99% and 95%, respectively. The non-toxic nature of struvite has been confirmed through the course of this study. However, to ensure the long-term safety and absence of potential toxicological risks associated with the use of struvite as fertilizer, further research is needed.

Moreover, this treatment method holds promise for treating wastewater with high organic loads and elevated nutrient concentrations, extending its potential application beyond landfill leachate.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.psep.2024.02.028](https://doi.org/10.1016/j.psep.2024.02.028).

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