

How does the source of waste activated sludge influence the release of phosphorus when treated by thermal hydrolysis?

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Keywords: Phosphorus release; P speciation in WAS; Thermal hydrolysis.

Summary of key findings

Two sludge samples were subjected to thermal hydrolysis under the same conditions to evaluate P release to the liquid phase. P species were characterised after and before the treatment. Different P release (%) was obtained for both samples, leading to the formulation of 2 hypotheses which are currently under investigation: the release kinetics of polyphosphates during thermal hydrolysis treatment and the different polyphosphate structures in the two samples.

Background and relevance

Phosphorus recovery from waste activated sludge involves at least two steps: its release from the sludge and its crystallisation into a usable product. Significant effort is being set into studying the sludge composition regarding the different P species present to establish a basis for choosing the appropriate technology to increase P release. There are still few studies on the impact of sludge sources when a particular technology is used. Thermal hydrolysis (TH) is an established technology used as a pre-treatment for anaerobic digestion of waste activated sludge and is also being evaluated for its capacity to release nutrients. This work aims to evaluate P release by thermal hydrolysis using two different sludge samples. The interest in both samples comes from their different total phosphorus contents (gTP/gTS), where S1 has less total phosphorus content than S2.

Materials and Method

Sludge samples

S1: Biomass from a full-scale continuous system with anaerobic/anoxic/aerobic zones for the treatment of the wastewater from a malting industry.

S2: Biomass generated in a lab-scale sequencing batch reactor (SBR) inoculated with S1 and fed with synthetic wastewater. The reactor was operated with 3 cycles/day with an anaerobic and an aerobic step.

Thermal hydrolysis reactor

Sludges were thermally pretreated in a 2 L sealed batch reactor at a steam pressure corresponding to 165 °C. This temperature was maintained for 30 min for all the tests. After the set TH time, the reactor was cooled to room temperature without a steam explosion. These conditions are commonly used in commercial technologies for sewage biosludge, such as Exelys (Gahlot et al., 2022). TH were performed in triplicate for both substrates (S1 and S2).

Analysis

Liquid samples were centrifuged at 6500 rpm for 15 minutes after TH to analyse COD, ammoniacal nitrogen, and P fractions (soluble total phosphorus sTP, soluble reactive phosphorus sRP, soluble nonreactive phosphorus sNRP and soluble acid-hydrolysable phosphorus sAHP) according to the Standard Methods protocols.

Calcination at 450 °C for 3 hours followed by an extraction protocol with 3.5 M of HCl was used to determine total phosphorus in sludge samples (pTP) before TH, following the Standards in Measurements and Testing (SMT) Programme extraction protocol (Gonzalez et al., 2005). The extracted P was measured using the standard ascorbic acid method. All analysis were performed in triplicate.

³¹P solution NMR spectroscopy Quantitative

The P fractionation of sludges S1 and S2 before TH was determined by solution ³¹P NMR following a sequential extraction protocol according to Staal et al. (2019). An initial pre-extraction using 0.05 M EDTA for 1 hour was followed by a main extraction with 0.25 M NaOH for 16 hours. The extract was then neutralized with 1 M HCl. After neutralization, the solution was lyophilized to concentrate the P content. Finally, the prepared sample (0.63 mL of supernatant the centrifuged mixture: lyophilized + 1 mL of solution (0.25 M NaOH + 0.05 M EDTA) + 0.2 mL of 10 M NaOH + 0.07 mL of D2O) was analysed employing solution ³¹P NMR spectroscopy.

Solution ³¹P NMR spectra were obtained using a Bruker Avance Neo 400 Spectrometer (Bruker, Germany) operating at 161.98 MHz with a PABBO 5-mm probe. A 30° pulse of 5 µs was used, with a spectral width of 9615.385 Hz (59.36 ppm) centred around 0 Hz, an acquisition time of 1.0 s (19230 complex points), and a recycling delay of 5 s. Typically, 2000 scans were acquired for a total acquisition time of 1 h and 42 min. The temperature was maintained constant at 25 °C. The FID was processed using Bruker Topspin 4.3.0 with an exponential weighting function between 1 and 3 Hz and 131072 points. The chemical shift referencing was set using the orthophosphate signal at 6.0 ppm, employing spiking to identify the signals of polyphosphates and pyrophosphates. Compound identification was performed using IIm-NMR-P31 database (Hack et al., 2023) and published sources (Turner et al., 2003).

Results

Sludge samples were analysed before and after the TH treatment and results are shown in the following tables (Tables 1, 2 and 3).

Table 1. Total phosphorus content of sludge samples before the thermal hydrolysis treatment.

Sludge 1*		Sludge 2**	
pTP (mg/L)	TP (%)	pTP (mg/L)	TP (%)
61	1.7	195	
		147	3.6
		152	

* 1 sludge sample was taken from the industrial reactor and fractionated to perform 3 experiences in the TH reactor.

** 3 sludge samples were taken from the lab-reactor while the reactor was operating in steady state and used to feed the TH reactor.

Table 2. Phosphorus fractions in the liquid phase after the thermal hydrolysis treatment.

	sRP (mgP/L)	sAHP (mgP/L)	sTP (mgP/L)	P _{rel} (%) *
Sludge 1 experiences	7.60 ± 0.65	5.40 ± 0.59	10.57 ± 0.54	17%
	7.43 ± 0.22	4.21 ± 0.73	12.51 ± 0.62	21%
	7.11 ± 0.12	3.76 ± 0.57	11.79 ± 0.33	19%
Sludge 2 experiences	146.42 ± 5.23	44.34 ± 18.19	152.43 ± 6.22	78%
	144.92 ± 6.51	10.27 ± 8.22	153.12 ± 4.74	100%**
	123.04 ± 13.70	non determined	142.50 ± 13.70	93%

*P_{rel} = (pTP – sTP)/pTP

**P_{rel} cannot be greater than 100%; we attribute the value obtained to experimental errors in the TSS measurement of the sludge sample before the TH treatment.

Table 3. Functional phosphorus groups concentrations in S1 and S2 sludges prior to thermal hydrolysis as determined by ³¹P solution.

Component	Sludge 1 Percentage	Sludge 2 Percentage
P-orthophosphate	8.04	7.79
P-polyphosphate	80.91	75.21
P-pyrophosphate	3.50	14.79
P-monoester	2.27	11.08
P-diester	not detected	3.44
P-phosphonate	4.41	not detected
P-tripolyphosphate	0.88	0.83

Discussion

Phosphorus release should be maximised before the crystallisation step in the recovery process. Several operations are being evaluated to maximise phosphorus release. Thermal hydrolysis and anaerobic digestion are operations usually present in wastewater treatment plants for sludge management. There are many commercial options for sludge management, one of which is the thermal hydrolysis reactor before the anaerobic digester. We aimed to test this option for phosphorus release (anaerobic digestion results are not shown). The possibility of using the same operations for phosphorus release makes the process more attractive.


The results show that sludge 1 has much lower phosphorus release percentages than sludge 2 when treated under the same conditions. Both samples came from biological treatments with a similar fraction of polyphosphates (poly-P) but different total phosphorus content. This raises the question: Does the TP content influence the quantity of phosphorus released? Yu et al. (2021), suggested that lower total phosphorus concentrations facilitated a high proportion of poly-P being released, whereas higher phosphorus concentration inhibited the release of poly-P, possibly due to a chemical equilibrium during anaerobic release of poly-P. No information was found about the kinetic of phosphorus release during thermal hydrolysis. However, the hypothesis of a chemical equilibrium is not supported in this case; more research is needed to elucidate the release mechanism.

Results obtained from ^{31}P NMR show a high fraction of poly-P in both sludges, which was expected considering that both came from EBPR systems. Even though S1 has a total phosphorus content in the order of what is expected for an activated sludge. As it was mentioned previously, P_{rel} was much higher in S1 than in S2; from the results obtained in S2, most of the poly-P in the sludge was released to the liquid phase, but in S1, poly-P was not completely released. We can affirm that from the quantities of phosphorus released to the liquid phase and the poly-P in the sludge samples for both sludges. In S1, 49 ppm of phosphorus was present as poly-P and 12 ppm as other species and at the liquid phase after the TH, only 10-13 mgP/L were released, so the poly-P was not completely released. In S2, most of the P was released to the liquid phase (the lower P_{rel} was 78%), so most of the poly-P was released in this case. Could poly-P characteristics influence its release capacity? In Wang et al. (2021), the authors present different methods to characterise poly-P structure, an aspect not yet profoundly studied and found distinct poly-P characteristics when different PAOs dominated the community. This aspect is also being investigated.

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