

Process factors affecting the contamination of struvite by selected antibiotics

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Background



Struvite shows a low water but high citrate solubility, is highly plant-available and has a high potential as a recycling fertilizer!

Struvite is a by-product in municipal wastewater treatment plants (WWTPs), which is precipitated and removed to protect pipes and pumps from inadvertent scaling to improve the process. Several studies revealed that struvite is a promising fertilizer and the precipitation process represents a possibility for phosphorus (P)-recovery from wastewater and sludge.

There are different procedures to precipitate struvite in the WWTP taking place at different stages. Struvite can be recovered from the wastewater stream or during digestion of the sludge. Another option is the accelerated acid leaching from sludge followed by solid-liquid separation and struvite precipitation from the liquid phase (Figure 1). The resulting products are of different purity and quality depending on process parameters and purification steps. Digested sludge may contain substantial amounts of organic contaminants such as antibiotics.

The aim of the current study was a screening of struvite raw materials from different processes and WWTPs for their contamination by selected antibiotics out of the classes sulfonamides (SAs), fluoroquinolones (FQs) and tetracyclines (TCs).

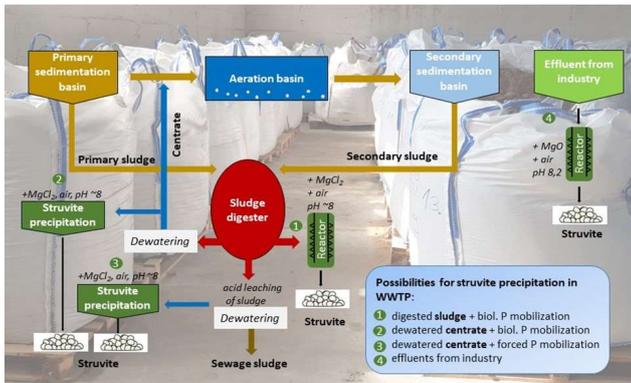


Figure 1. Possibilities for struvite precipitation in waste water treatment plants (WWTP).

Sample collection

25 struvite samples from 6 different WWTP using 4 different technical procedures for the precipitation of struvite were collected at different times to record the variability in struvite quality depending on the process and within the process. 3 of the sampled WWTPs were using process 1 and one WWTP from process 2-4 each were sampled. The samples already showed a high variability in texture and color (Figure 2). Samples were analyzed for total carbon (C) and nitrogen (N) by a C/N analyzer (Vario Max Cube, Elementar) and for antibiotics according to LEHMANN & BLOEM (2021) using LC-MS/MS (4000 Q-Trap, AB Sciex).

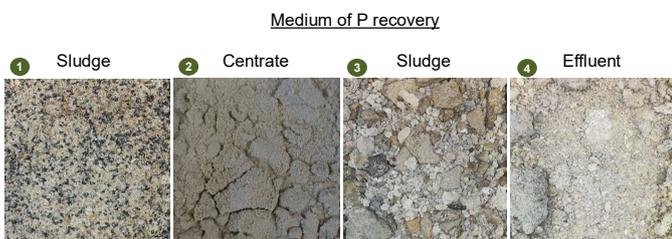


Figure 2. Struvites from different precipitation processes (see Figure 1) showing a different appearance.

Results & Discussion

The struvite samples showed a high variability regarding their total C content. Lowest contents were detected in struvite produced from centrate water and highest when precipitated from sludge. Total N was less variable with an average content of 4.7% N (Table 1).

Table 1. Total carbon (C) and nitrogen (N) content in struvites originating from different processes and WWTPs.

	Processes as indicated in Figure 1			
	1	2	3	4
Medium of P-recovery	Sludge	Centrate	Sludge after forced P-remobilization	Effluent
No of samples	14	3	1	8
Total C [%]				
Range	1.5 – 27.3	0.1 – 1.0	3.6	0.9 – 7.1
Mean ± SD	7.1 ± 7.6	0.6 ± 0.5	3.6	2.3 ± 2.0
Total N [%]				
Range	3.5 – 5.3	5.5	3.5	3.0 – 6.6
Mean ± SD	4.5 ± 0.5	5.5 ± 0.0	3.5	4.7 ± 1.1

The antibiotic determination revealed that while only 3 out of 5 analyzed TCs were found, all 3 analyzed SAs and all 5 analyzed FQs were detected in at least some samples (Table 2). FQs were found with the highest frequency and in highest concentration; for example ciprofloxacin (CP) was detected in 96% of the samples, and could be quantified in 64%.

FQs have a high tendency to bind to the sludge matrix. SAs and TCs were rarely detected in concentrations above the detection limit and only when no further purification steps were conducted.

Antibiotic contamination was highest when struvite was precipitated from sludge but most struvites revealed a very low contamination close to the detection limit. Data indicate that the antibiotic contamination increased with increasing C content but other process factors seem to be more important. In general the antibiotic contamination of sewage sludge is more than 95% higher than in struvite but the precipitates revealed a high variability even in the same WWTP.

It can be concluded that already the precipitation process is very efficient in reducing the antibiotic contamination level. Additional ultrafiltration or washing steps will reveal fertilizer products almost free of antibiotics.

Table 2. Number of struvite samples, where antibiotics were detected (first number) or quantified (second number) in relation to the precipitation process, relative frequency of samples above detection (>LOD) or quantification limit (>LOQ) and maximum contents detected.

Process as indicated in Figure 1	n	Tetracyclines			Fluoroquinolones				Sulfonamides			
		DXC	TC	MTC	CP	DF	EN	OF	NOR	SD	SM	SMX
1	13	2/2	6/1	4/0	13/12	12/5	12/5	12/10	12/4	7/1	2/1	2/0
2	3	0/0	1/0	0/0	3/2	2/1	3/1	2/2	2/0	3/1	1/0	1/0
3	1	0/0	1/0	0/0	1/1	1/0	1/1	1/1	1/1	0/0	0/0	0/0
4	8	0/0	0/0	1/0	7/1	4/0	7/0	8/1	5/0	7/0	1/0	0/0
Relative frequency and maximum contamination of all investigated 25 struvite samples												
Detection [%]	8	32	20	96	76	92	92	80	68	16	12	
Samples >LOQ [%]	8	4	0	64	24	28	56	20	8	4	0	
Max. content [µg/kg DM]	108	31.4	<LOQ	251	16.1	26.2	131	59.9	9.0	3.1	<LOQ	

Antibiotics that were determined: DXC-doxycycline, TC-tetracycline, MTC-metacycline, OTC-oxytetracycline, CTC-chlortetracycline, DMC-demeclocycline, CP-ciprofloxacin, DF-difloxacin, EN-enrofloxacin, OF-ofloxacin, NOR-norfloxacin, SD-sulfadiazine, SM-sulfamethazine, SMX-sulfamethoxazole; CTC, OTC and DMC were not detected in any sample.

Exemplary field application of CP with struvite (worst case scenario):

For a target fertilization of 75 kg/ha P₂O₅, about 260 kg struvite are needed. Calculating with the highest CP content detected in our study (251 µg/kg DM) this implies an input of 65 mg/ha CP to the field. For comparison, this would be equal to 1/6 of a typically sold prescription drug containing 500 mg CP/tablet.

References

LEHMANN L. & BLOEM E. (2021) Antibiotic residues in substrates and output materials from biogas plant – implications for agriculture. Chemosphere 278, 130425