

Energy recovery from antibiotic-contaminated waste sludge

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- Anaerobic stabilization – an efficient technology to treat organic waste, especially sewage sludge
- Circular economy: use of waste sludge from wastewater treatment plants pre-treated with anaerobic stabilization

- Antibiotics in the animal sludge inhibit biogas production in anaerobic stabilization
- As non-biodegradable, antibiotics are spreading resistance genes in the environment



Antibiotics are mostly poorly biodegradable and pass into the environment unchanged

WWTP

- without decomposition - adsorption on sludge
- metabolites are converted back to the parent molecule
- rivers in the EU, $<10 \text{ ng L}^{-1}$, without acute toxicity effects

Animal sludge

- Antibiotics represent 80% of all active ingredients found in animal feces
- animal sludge emissions 25% higher than sewage sludge emissions

Anaerobic stabilization

- inhibitory effect
- Anaerobically stabilized animal sludge: risk of developing antibiotic-resistant bacteria and resistance genes

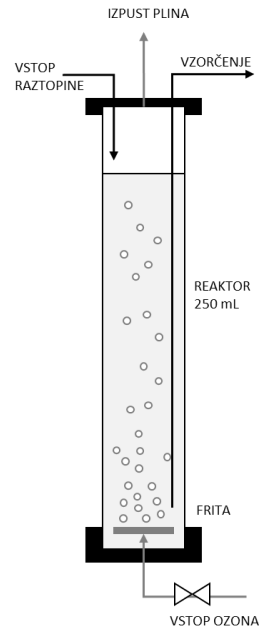
Sludge disposal

- long decomposition time; tetracycline 422 days (-90%)
- fertilization: also present in soil ($\approx \text{mg kg}^{-1}$)

development of resistance genes, disturbances of the wider ecosystem



Ozonation system



Semi-batch ozonation

Experiments done

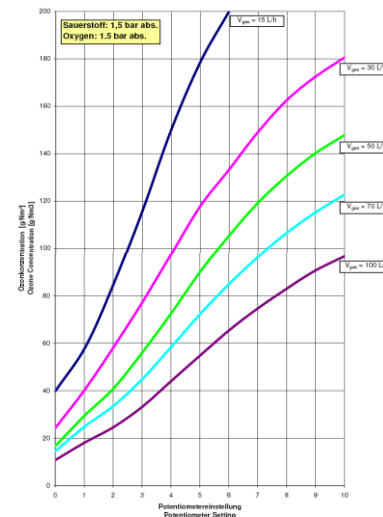
1. Ozonation of sludge
2. Ozonation of contaminated sludge
3. Subsequent measurement of biogas production of non-treated sludge, ozonated, contaminated and contaminated –ozonated sludge

Analytical methods

1. COD, TOC, pH, O_3 presence in the solution
2. Molecular structure analysis after ozonation
3. Anaerobic biogas production
4. Toxicity to aerobic sludge

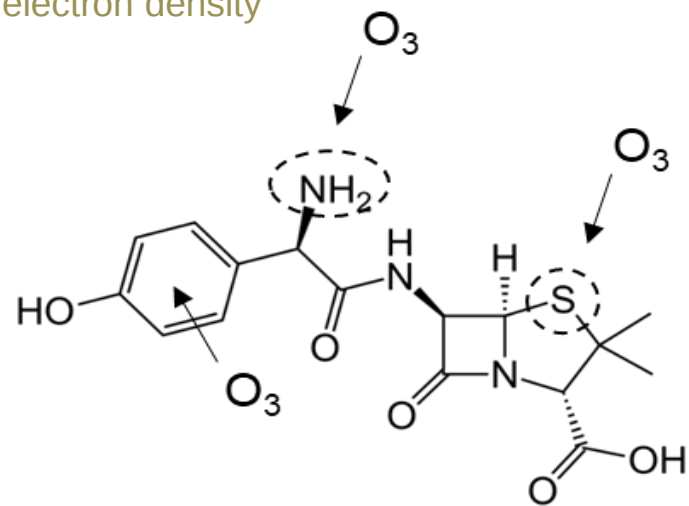
Ozone generation

Concentration of ozone in gaseous phase in dependence of generator settings; Xylem Water Solutions GmbH Herford, type OCS Modular 8 HC



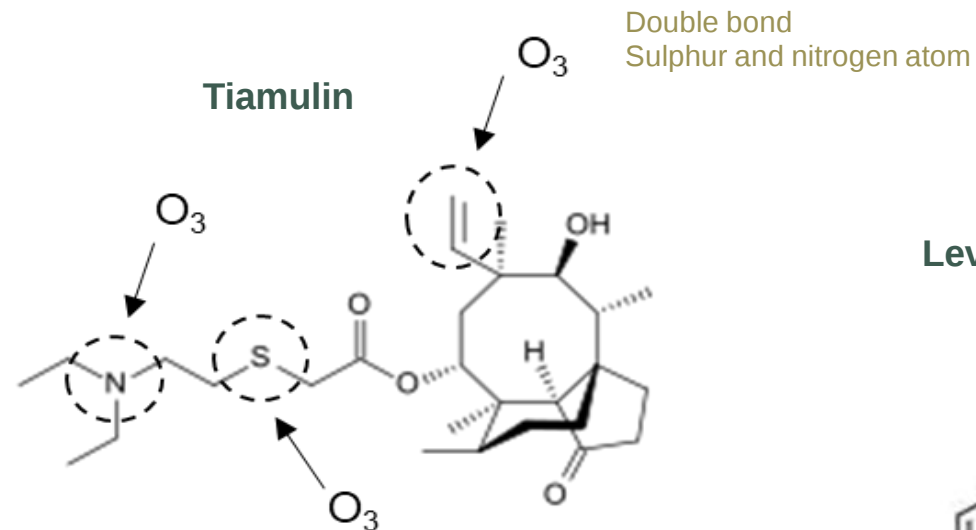
Model antibiotics

Functional groups, susceptible for ozone attack due to electron density



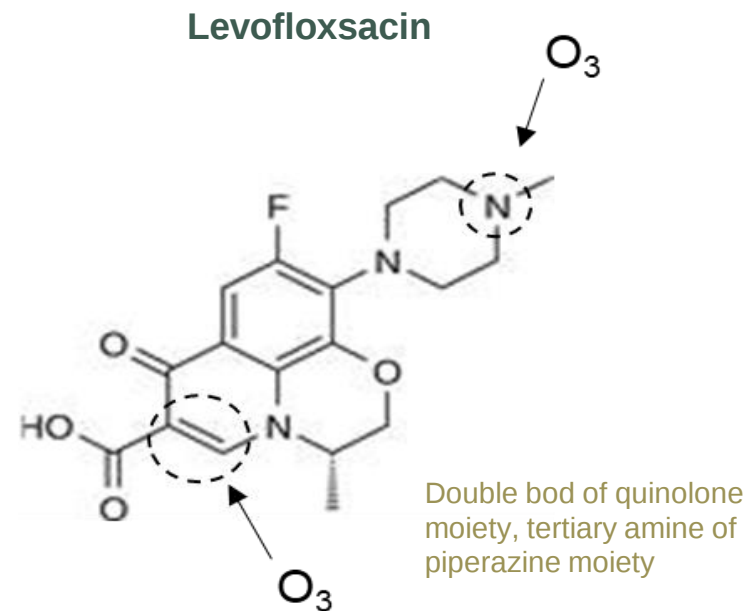
Phenol ring,
 $-NH_2$ group
Sulphur atom

Amoxicillin



Tiamulin

Double bond
Sulphur and nitrogen atom



Levofloxacin

Double bond of quinolone moiety, tertiary amine of piperazine moiety

100 %

biodegradability

0 %



Antibiotics are **mostly environmentally persistent molecules, with low biodegradability**, therefore conventional biological treatment is not sufficient

BASELINE DATA

Aerobic conditions, water solutions of antibiotics

Tiamulin

- Has a low biodegradability (**17 % in 41 days at 400 mg L⁻¹** and **40 % in 41 days at 100 mg L⁻¹**)
- Measured at non-toxic concentration;
30min EC50 : 691 ± 261 mg L⁻¹

Levofloksacin

- Is non-biodegradable (**8 % in 41 days at 100 mg L⁻¹**), structure of the molecule does not have weak points to allow for hydrolysis
- Measured at non-toxic concentration;
30min EC50 : 1.115 ± 298 mg L⁻¹

Amoksicilin

- Is biodegradable (**100 % in 41 days at 100 mg L⁻¹**), β -lactam ring, able to hydrolyze
- Measured at non-toxic concentration;
30min EC50 : 1.026 ± 276 mg L⁻¹.

Use of animal sludge, pre-treated with anaerobic stabilization

- **Inhibitory effect on anaerobic digestion;** tetracyclines and sulfonamides up to -93% (Spielmeyer et al. 2018).
- Anaerobic stabilized sludge - **presence of resistance genes.**
- Ozonation - **skip the level of hydrolysis, improve biogas production.**

BIODEGRADATION IS INHIBITED – molecules are passing biological treatment unchanged and /or biogas production is inhibited

Anaerobic conditions

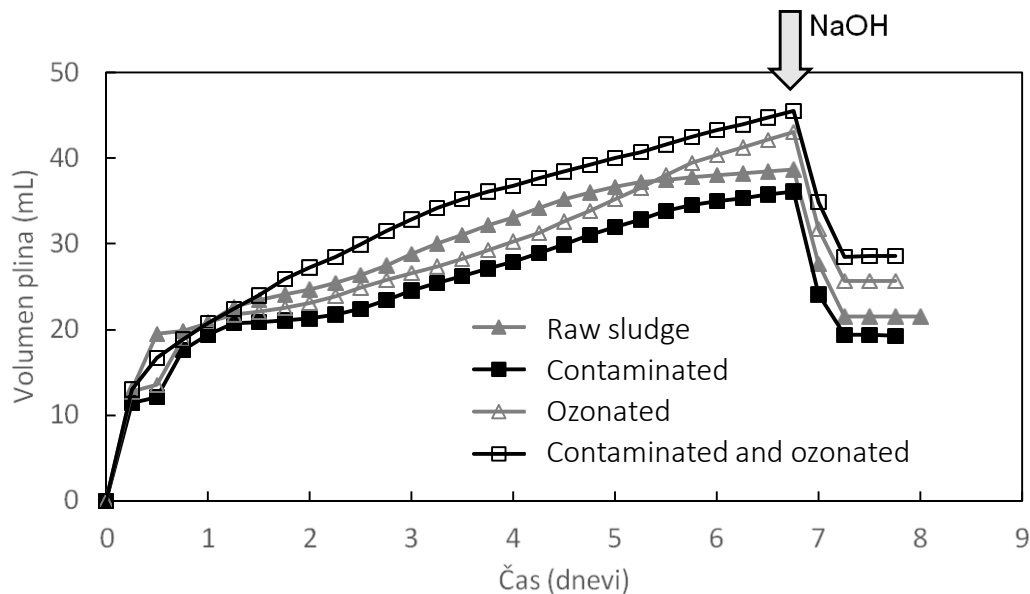
400 mg L⁻¹, inhibitions of biogas production:

- tiamulin 8 % (14 % CH₄)
- levofloxacin 27 % (44 % CH₄)
- amoxicillin 30 % (45 % CH₄)

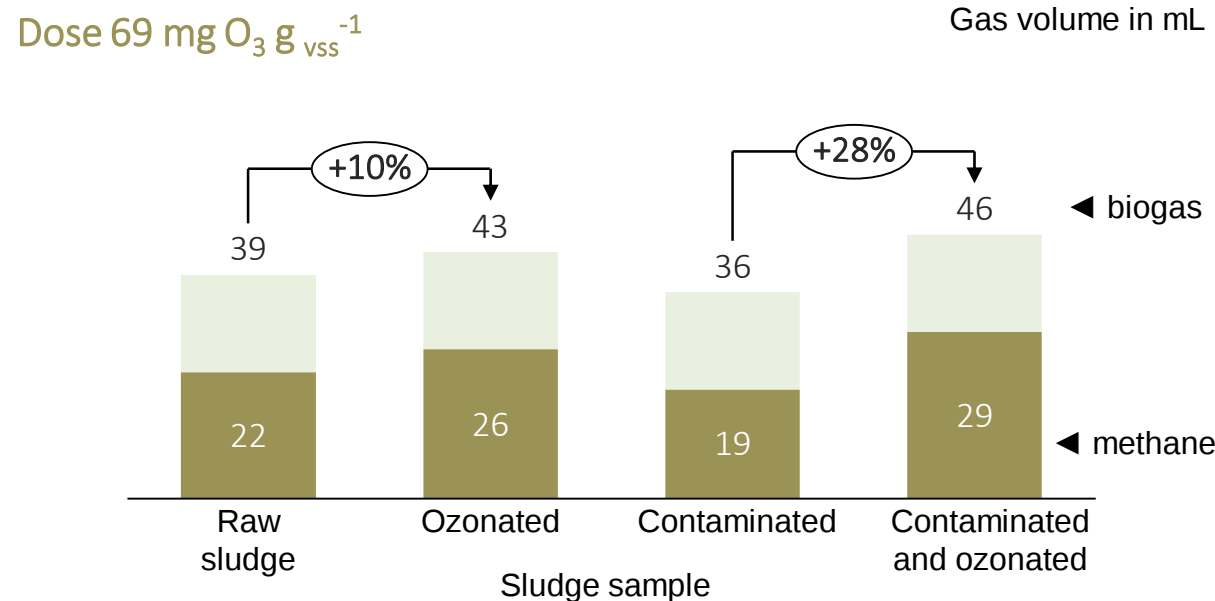


TIAMULIN

Ozonation of contaminated sludge



Biogas production for a raw sludge and ozonated sludge, sludge contaminated with 400 mg L^{-1} tiamulin and ozonated contaminated sludge, dose $69 \text{ mg O}_3 \text{ g}_{\text{vss}}^{-1}$



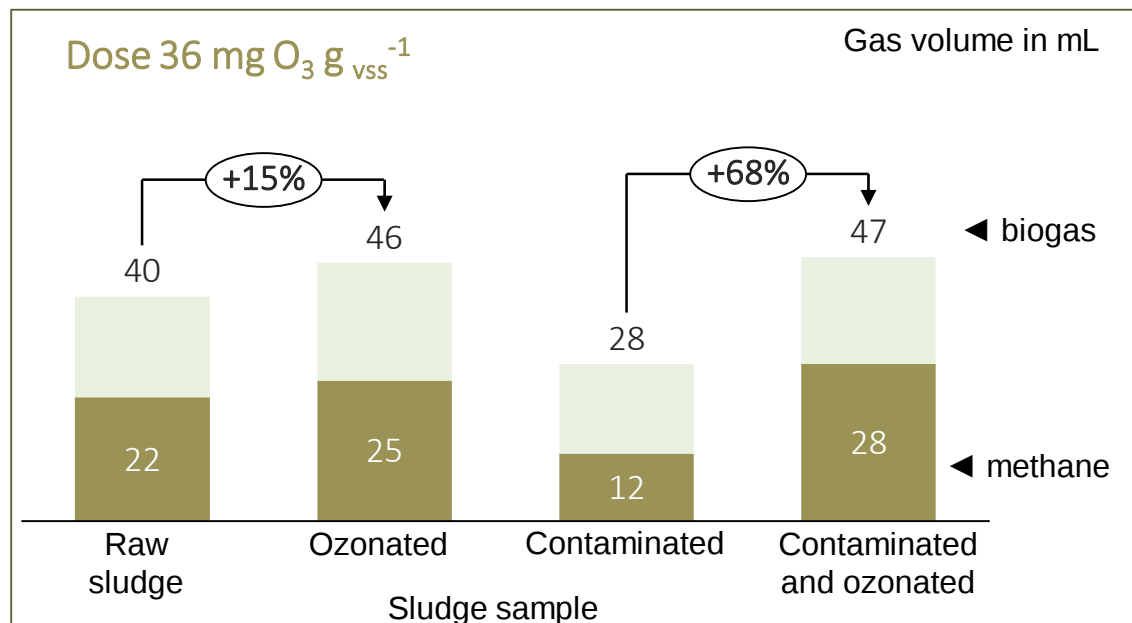
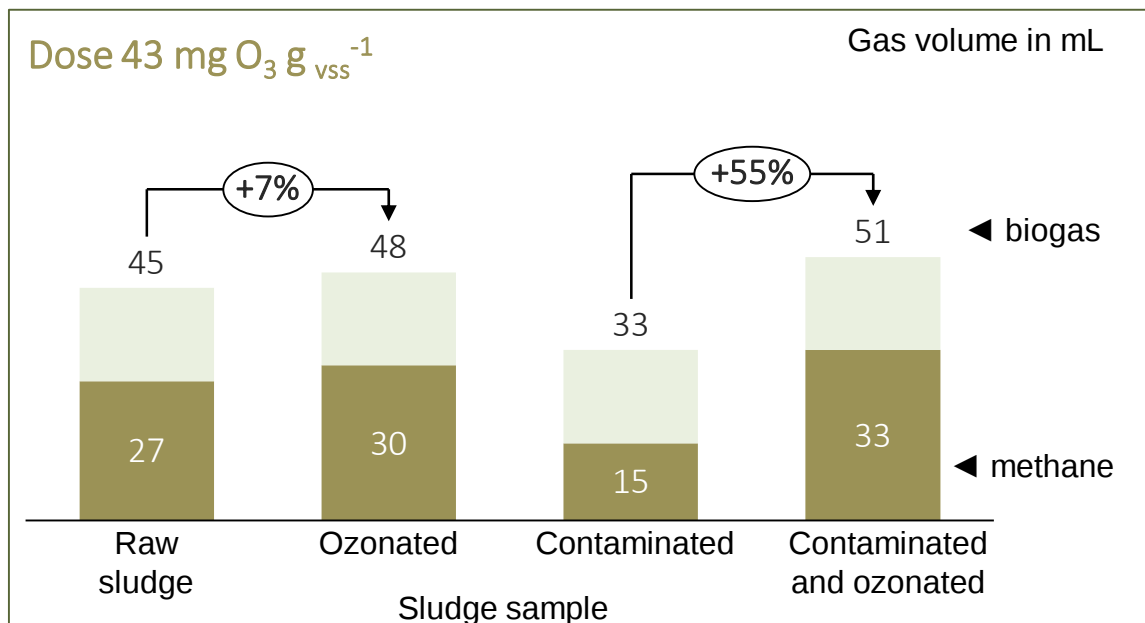
The impact of single step ozonation of antibiotics-contaminated waste sludge to biogas production. Chemosphere. 2021, 271, 1-8.

Ozone and antibiotics in waste water and sludge. Ozone: science & engineering. 2020, 42 (2), 128-135.



LEVOFLOXACIN in AMOXICILLIN

Ozonation of contaminated sludge



The impact of single step ozonation of antibiotics-contaminated waste sludge to biogas production. Chemosphere. 2021, 271, 1-8.



Ozone as an element of circular economy: gaining energy from bio-waste, while eliminating spread of antibiotics contamination

- **Ozonation might be a key technique of circular economy** when gaining energy from waste sludge, while simultaneously considering broader environmental sustainability.
- In case of antibiotics contaminated sludge (400 mg L^{-1}), ozonation (dose of $36 \text{ mg O}_3 \text{ g vss}^{-1}$) **not only eliminates any inhibition of biogas production, but also enhances biogas production (by 68%)**.
- Gained excess biogas however does not compensate for cost of ozone used.
- In terms of sustainability it is important, **that ozonation eliminates the spread of antibiotic resistance genes in the environment**, when anaerobically stabilized sludge is applied to agriculture soils.

