Energy recovery of antibiotic-contaminated waste sludge

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Abstract
Purpose of the study was to determine the effect of ozonation as a method to eliminate inhibitory effects on biogas formation during anaerobic stabilization of antibiotic-contaminated sludge. By using direct ozonation of sludge, partial antibiotic structure disintegration was achieved, therefore removing inhibitory effects, and enhancing biogas formation beyond the baseline of non-contaminated sludge. It was confirmed that ozone dose of 36 mg O_3 g_{VSS}^{-1} not only eliminates any inhibition of biogas production (400 mg L^{-1} of antibiotic), but also enhances biogas production by 68%.

Keywords
Anaerobic stabilization, biogas, antibiotic, ozonation, sewage sludge.

Introduction
Anaerobic digestion is a highly efficient technology to treat a variety of organic waste from solid waste to wastewater and especially the sewage sludge. This is low energy-intense technology as well as it does not generate a lot of residual waste [1]. Anaerobic stabilization is converting waste sludge into biogas, a renewable fuel generating green electricity, and the stabilized solid residue which could be used as fertilizer in agriculture [2], part of the circular economy cycle.

The use of waste sludge from wastewater treatment plants pretreated with anaerobic stabilization is gaining in importance, both in terms of improving the quality of agricultural soils as well as materializing the principles of circular economy. On the other hand, this method of treatment and subsequent use of processed sludge carries the risk of spreading resistance genes into the environment [3]. Study reports that although the half-life of sulfamethoxazole (20 mg kg^{-1}) as one of the most widely used veterinary antibiotics, in the matrix of anaerobically stabilized sludge was only 7 days, the resistance genes were developed in that time.

Antibiotics in the animal sludge do have an inhibitory effect on the process of anaerobic stabilization. The Spielmeyer study [4] showed an acceleration of anaerobic degradation in the case of colistin by 14%, but in all other cases (tertacyclines and sulfonamides) inhibition stopped biogas formation almost completely (93% reduction). The same study also finds only minor structural changes of the molecules in the process, which does not necessarily mean that the actual biological activity of the molecules and thus their impact on the environment was removed.

Speaking of the circular economy and gaining energy, presence of antibiotics in the sludge that undergoes anaerobic stabilization has therefore two folds negative effects; antibiotics reduce the biogas gain [5] and pose a threat to spread resistance genes in the environment [6]. The aim of our study was to assess the impact of ozonation pretretament of antibiotic-contaminated waste sewage sludge to biogas production and methane gain in anaerobic stabilisation process.

Material and Methods
Ozonation of antibiotics-contaminated municipal waste was accomplished by using aerobic activated sludge from a municipal sewage treatment plant; part of it was contaminated with antibiotics (400 mg L^{-1}) and subsequently ozonated. Non-contaminated activated sludge was also ozonated. In this way, four samples were obtained: untreated sludge, ozonated sludge, contaminated sludge and contaminated-ozonated sludge.

Tiamulin, Amoxicillin and Levofloxacin were used to measure the effect that ozonation of the waste antibiotic-contaminated sludge has to the biogas production. Tiamulin is environmentally stable veterinary antibiotic, type of the diterpene pleuromutilin. For Tiamulin, there is data available about biodegradability and degradation products after ozonation [7]. Another one was a biodegradable β-lactam Amoxicillin and next alternative to benchmark was a non-biodegradable fluoroquinolone Levofloxacin. All these antibiotics do contain several functional groups (amine nitrogen, sulfur, carbon-carbon double bond, activated aromatic ring), which are susceptible to reactions with ozone. In the ozonation experiments, the semi-batch system was used (Figure 1).

A biogas production inhibition test was performed using all samples. This way a comparison of biogas production between individual samples was possible, providing data on effect of ozone and antibiotics on biogas production. The aerobic sludge was prepared before use by purging with air at room temperature (T= 20±2 ºC) for two days. After this preparation step, the dry matter content (VSS) of the sludge was determined by filtering 20 mL of a well-homogenized sludge suspension and drying to constant weight at 105 ºC. Contamination of aerobic sludge by antibiotics was accomplished by adding substance to sludge suspension and shaking on a laboratory.

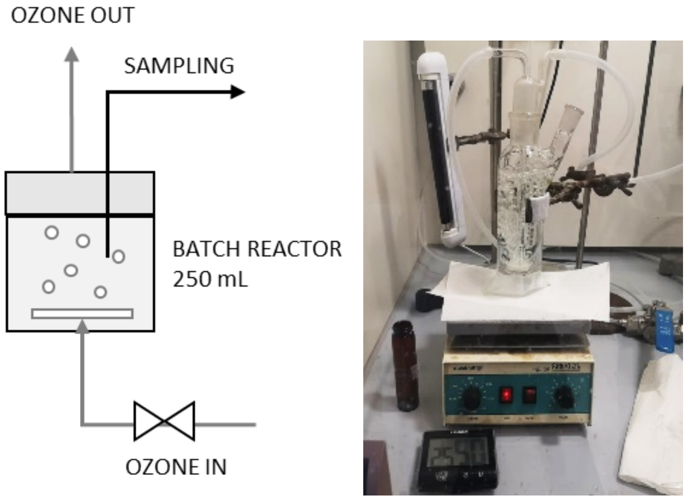

Figure 1: Set-up for semi-batch ozonation of antibiotics contaminated sludge.

Ozonation was accomplished by purging 200 mL of the sludge suspension (7.0±0.2 g_{vss} L^{-1}) with ozone in a 250 mL glass laboratory reactor (bubble column) for 20 minutes. The reactor was placed on the magnetic stirrer (600 rpm) and ozone was purged into the reactor via a porous glass frit. Experiments were performed under following conditions: pressure of the ozone generator was 0.5 bar, the gas flow was 30 L h^{-1}, the nominal concentration of ozone in the gas phase was 0.1 g L^{-1} and an overall system capacity of ozone production was 3 g h^{-1} (Figure 1). Ozone dose in experiment increased with time and it was 36.0 mg_{ozone} $mg^{-1}{}_{substance}$.

To measure biogas produced for all types of sludge samples (untreated, ozonated, contaminated, contaminated-ozonated), method ISO 11734, 2004 was used (Method for the determination of ultimate biodegradability of complex organic substrates and biogas production). In scope of this method, contaminated sludge as a test substance is mixed with anaerobic sludge microorganisms (total volume of 100 mL) and kept at constant temperature (37 ±1 °C) in a sealed vessel (250 mL) under mixing and in dark for a certain number of days. Pressure in the vessels increases as the biogas is produced (CH_4 and CO_2) and was measured by OxiTop system (WTW Germany, 2008). The curve of anaerobic degradation is plotted in terms of increasing gas volume (ΔV, mL) against time (t, days). At the end of the experiment, 2.5 mL of 6 M NaOH solution was injected into the rubber sleeve of the reaction vessel, absorbing carbon dioxide in the gaseous phase. Based on the pressure before and after the NaOH addition, volume of CH_4 and CO_2 gases were then calculated as per general gas equation.

Results and Discussion

Experiments confirmed that ozonation effectively eliminates any inhibitory effects that investigated antibiotics have to biogas production. By ozonizing contaminated sludge, we simultaneously increase the biodegradability of antibiotics and increase the amount of biogas due to the solubilisation of biological sludge (Figure 2 a-c). In case of Tiamulin and Amoxicillin contamination, overall biogas gain was larger for 68 % (dose of 36 mg_{ozone} g_{vss}^{-1}), and in case of levofloxacin for 55% (dose of 43 mg_{ozone} g_{vss}^{-1}). Ozonation not only eliminates all inhibition induced by antibiotics contamination, but it also improves overall biogas gain (Figure 2). According to the study of Zhen et al. [8], the optimal dose of ozone for soluble solubilisation is between 0.05 and 0.5 g of_{ozone} g_{vss}^{-1} substance depending on the properties of the sludge and other parameters of the pretreatment method. In our study, improved biogas productions were achieved with comparable doses, from 0.046 to 0.070 g_{ozone} g_{vss}^{-1}. Reducing this dose did not yield better results in terms of both reducing inhibition and increasing the amount of biogas.

In terms of cost effectiveness, we have related to the data from a study by Krichevskaya et al. [9]. At a higher dose of ozone, 69 mg_{ozone} g_{vss}^{-1}, 10 mL more biogas was obtained from contaminated and subsequently ozonated sludge than from contaminated, however 52 mg of O_3 was consumed. Calculating with an average price of ozone, which is EUR 0.0339 per mg O_3, 1.76 EUR was spent for this purpose. Considering the calorific value of methane (50 MJ kg^{-1}), we thus obtained 357 J, which at the price of EUR 0.135 KWh^{-1} (Eurostat, 2020) does not mean added economic value. Ozonation of contaminated sludge does not result in a direct positive contribution to the economics of anaerobic stabilization, but it does compensate for the cost partially. On the other hand, resistance genes spread was stopped (Bosevski et al. 2019), which is a key sustainability element, not yet properly defined economically.

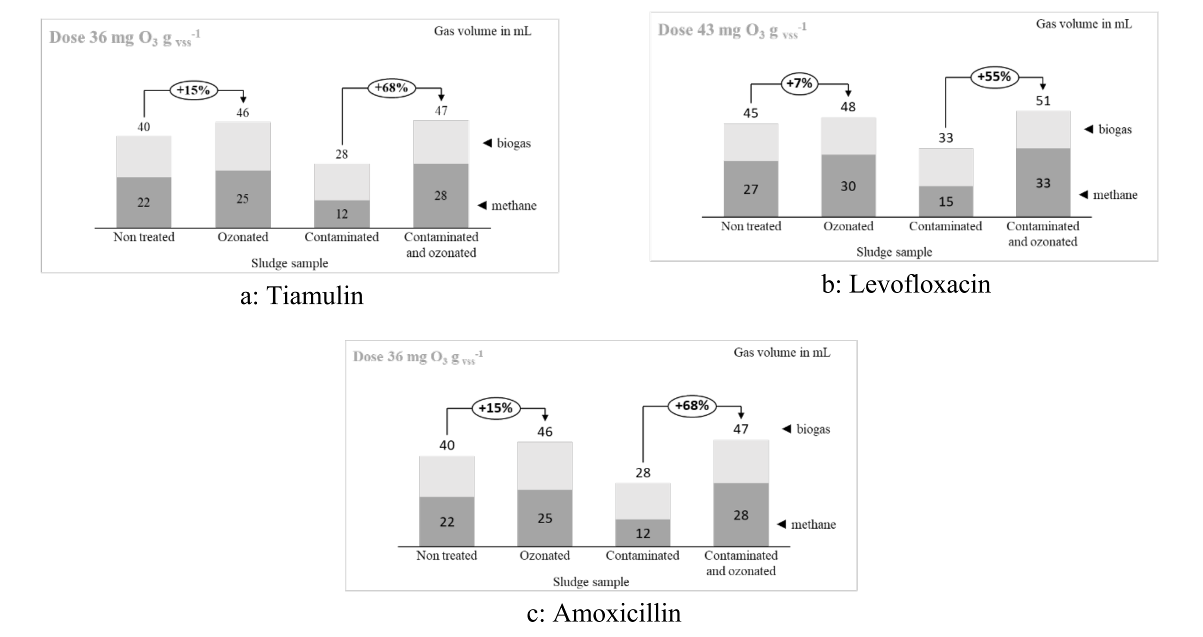

Figure 2: Biogas and methane volumes; non treated sludge sample, contaminated, ozonated, contaminated and consequently ozonated sample.

Conclusions

Ozonation might be a key technique of circular economy when gaining energy from waste sludge, while simultaneously considering broader environmental sustainability. It was confirmed, that in the case of antibiotics contaminated sludge (400 mg L^{-1}), ozonation (dose of 36 mg O_{ozone} 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.

Acknowledgments

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