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Impact of preozonation on biogas potential of PVC microplastics-containing waste sludge

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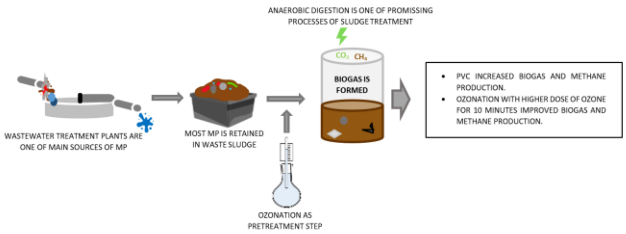
Graphical abstract



Abstract

Plastic pollution is increasing and plastic waste usually ends in environment. Microplastics (MP) as insoluble and anthropogenic micropollutant is ubiquitous and its concentration is expected to increase in the environment. One of important sources are wastewater treatment plants, where most of MP end in waste sludge. Promising technology for stabilization of waste sludge and reducing the volume and odor is anaerobic digestion, where anaerobic microorganisms digest organic matter and form biogas. The aim of this work was to evaluate inhibition on formed biogas and methane yield with and without ozonation of contaminated waste sludge with Polyvinylchloride (PVC). The inhibition of anaerobic microorganisms was determined by OxiTop® method, where biogas production was measured in terms of increased pressure (hPa). PVC increased biogas production up to 27% followed by increased CH_4 production (up to 18%). Ozonation as a sludge pretreatment method, could inhibit or increase CH_4 yield, depending on ozone dose (3.54 g h^{-1}; lower dose or 3.99 g h^{-1}; higher dose) and time of exposure to ozone (from 10 to 20 min). Higher dose of ozone with 10 minutes of ozonation, showed as the most efficient and improved biogas production up to 15% and CH_4 production up to 14%.

Keywords: Biogas production, methane yield, microplastics, ozonation, waste sludge, wastewater treatment plants

1. Introduction

Plastic has become an extremely popular material especially due to its low density, low cost and other physicochemical properties. In recent years, plastic pollution is increasing, since plastic, after usage, usually ends up as garbage in the environment, where could negatively impact on the life quality of people and animals (Zhang, 2020). It is a material with a wide spectrum of use and is also used in nearly all industrial processes (Frias and Nash, 2019). The main disadvantage of plastic is its low biodegradability. When left in environment, it gradually breaks into smaller particles which could be ingested by organisms and through food chain ends up in humans (Zhang *et al.,* 2020b).

Microplastics (MPs) are synthetic, solid polymers that are insoluble and as anthropogenic micropollutant found in aquatic ecosystems, wastewater in air and practically everywhere in the environment. In general, MPs are mainly defined as particles smaller than 5 mm and particles smaller than 1 µm as nanoplastics (NP) (Blair *et al.,* 2019; Padervand *et al.,* 2020; Sun *et al.,* 2019). Their concentration is expected to increase in the following decades because of the increased use of plastic products (Peterson and Hubbart, 2021; Yang *et al.,* 2015). MPs are capable of adsorbing other long-lasting pollutants (Padervand *et al.,* 2020). Furthermore, additives that are added to MP during production are released when it ends in the environment, therefore MP also contributes to spreading other micropollutants in the environment (Sun *et al.,* 2019).

All MP particles in the environment can be differentiated by size, density, chemical structure and shape. According to source, MP could be divided into primary or secondary (Duis and Coors, 2016; Xu *et al.,* 2019). Primary is intentionally engineered in small sizes, while secondary degrades on small particles because of mechanical, chemical or physical impacts and is more commonly found in nature (Auta et al., 2017; Jaikumar *et al.,* 2019). It mostly originates from cosmetics, hair color and nail polish, insect repellants, cleaning agents, clothes, sandblasting mediums and even some medicine, while secondary breaks down from larger particles (Auta *et al.,* 2017).

One of significant sources of MPs are wastewater treatment plants (WWTPs) (Zhang *et al.,* 2020b). They importantly contribute to releasing MP in the environment (Kang *et al.,* 2018; Sun *et al.,* 2019). MP could reach WWTPs through household wastewater or rainwater and could by the effluent from WWTP continue its path into the environment (Ngo *et al.,* 2019). Despite a large percentage of MPs being removed while treating wastewater, a great quantity of MP is still running into rivers, lakes and oceans since every day, a great volume of wastewater is treated (Sol *et al.,* 2020). Many studies were carried out that focused on removal efficiency of MP from WWTPs (Sun *et al.,* 2019). Results showed that efficiency depends on the type of WWTP and in most cases reach above 90% but it could reach even up to 99.9% (Sun *et al.,* 2019; Talvitie *et al.,* 2017). Studies show that the percent of removed MP is not dependent only on the type of waste treatment process, but also on the type of MP (Wu *et al.,* 2021). MPs are removed in different phases during water treatment, but it should be noted, that WWTP were not designed to remove MP. In pretreatment, floating particles and larger solid particles are removed, but the overall removal of MP remains relatively low (Yang *et al.,* 2015). However, the largest part of MP is removed in primary treatment (Wu *et al.,* 2021). In this phase, MP are removed by using flotation to gather particles on the surface, or by having the particles merge with heavier solid particles where they fall to the bottom and are then removed (Sun *et al.,* 2019). Secondary, biological treatment usually removes less MP than primary treatment (Yang *et al.,* 2015). The highest amount of MP, even up to 98%, remains in the sludge, also after different sludge treatments as lime stabilization and anaerobic digestion (Mahon *et al.,* 2017; Sun *et al.,* 2019). This is why it is important to research the impact of MP on treatment processes of sludge (Corradini *et al.,* 2019; Sun *et al.,* 2019). Figure 1 shows removal efficiency of MP after each treating phase in WWTP.

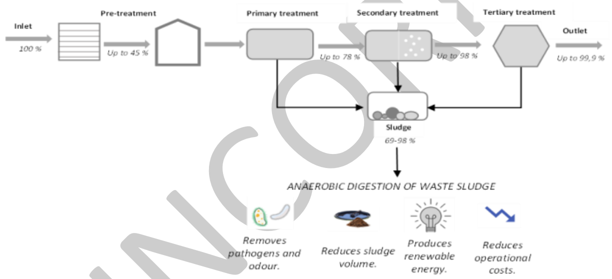


Figure 1. Removal efficiency of MP in WWTP and advantages of anaerobic digestion of waste sludge (Sun *et al.,* 2019).

In general, we differentiate between many different types of MPs, mainly polyethylene (PE), polystyrene (PS), polypropylene (PP), polyacrylamide, polyester, and polyethylene terephthalate (Liu *et al.,* 2021). Polyvinylchloride (PVC) is also among the most common MPs. There is still limited knowledge about exact concentration of MPs in wastewater or waste sludge because there are still no appropriate and standardized methodology prescribed for MP or NP extraction and further analyses. Researchers used different methods to collect, treat, separate, identify and quantify MP (Hurley, 2018). Since they used different methods and also units and size limit of detecting MP, it is difficult to compare results between different studies and fully understand MP removal and its effects on further technology processes.

Waste sludge consists of solid, semi-solid and liquid residues. It is formed during the treatment of sewage in WWTP. Sludge management poses major environmental, technical, financial and regulatory challenges. Usually, sludge is removed by incineration or disposal (Seiple *et al.,* 2017). Sludge removal usually represents 50% of the total operating costs of a municipal sewage treatment plant. Waste sludge could be used for multiple reasons, while it contains organic and inorganic components. It could be used for soil amendment, incinerated or used in the industrial production of brick, asphalt or concrete (Capodaglio and Callegari, 2018). It is also gaining ground in the process of anaerobic digestion as a source of volatile fatty acids (VFA) (Seiple *et al.,* 2020; Owusu-Agyeman *et al.,* 2020).

One of the most promising technologies for stabilization of waste sludge, efficient for reducing the volume of sludge and reducing odor is anaerobic digestion to produce CH_4 and CO_2 (Ma *et al.,* 2018; Zhang *et al.,* 2020a). However, it was discovered, that anaerobic digestion could lower the presence of MP, significantly (Mahon *et al.,* 2017). Some type of MPs, (PVC), could leach Bisphenol-A, that could inhibit the process of anaerobic digestion (Wei *et al.,* 2019).

Ozonation as one of the advanced oxidation processes (AOPs) is a promising method for treatment of waste sludge (Ashauer, 2016; Scholle *et al.,* 2021). Two different reaction mechanisms are important in degradation. The first one is direct reaction with molecular O_3 and the second is indirect reaction of hydroxyl radicals produced by the decomposition of O_3. It reacts with compounds which consist of electron-rich parts, such as olefins, deprotonated amines and activated aromatics. Normally, organic matter and micropollutants are not mineralized but converted into smaller and structurally related substances that are more biodegradable and less toxic. In the case of waste sludge treatment, ozonation lead to solubilisation of cells, make them more available to anaerobic microorganisms (Dogruel *et al.,* 2020).

The aim of this work was to evaluate inhibition of waste sludge, contaminated with PVC microplastics on biogas production in anaerobic digestion. Waste sludge, which inhibition is evaluated, is formed during biological treatment of municipal wastewater. Different concentrations of PVC were added and biogas and CH_4 production with and without ozonation as possible pretreatment to improve biogas production were studied.

2. Instruments, materials and methods

2.1. Samples of MPs

PVC with density of 1.39 g cm^{-3} in various concentrations was used to evaluate the impact on biogas production. It has been selected since it is one of the most common MPs found in sludge (Alimi *et al.,* 2018). Impact on biogas and CH_4 yield with and without ozonation of waste sludge as pretreatment method was evaluated. PVC particles were industrial origin, obtained from a plastic injection molding company and cut by hand on smaller particles. We sieved them and particles, smaller than 1 mm were used for experiments.

2.2. Contamination of waste sludge by MPs

Aerobic and anaerobic sludge were collected from municipal wastewater treatment plant aimed to treat mainly domestic wastewater. Anaerobic sludge was collected through pipelines, entering in digester at WWTP. It was collected into wide-necked bottle, made from material, that can expand, according to ISO 11734:1995. Aerobic sludge was collected from aeration tank from WWTP. It was collected in three different positions of aerobic tank in depth 1.00-1.5 m from surface of water with telescopic rod while aerating, to ensure mixing of sludge. To determine biogas potential of waste aerobic sludge, it was mixed with anaerobic sludge in the ratio 1:1 (%v/v). In every measuring system, 50 mL of aerobic anaerobic sludge was added. Average concentration of aerobic sludge was 4.8 ± 1.3 g_{TSS} L^{-1}. Concentration of anaerobic sludge was kept constant in all experiments (1.5 ± 0.1 g_{TSS} L^{-1}). To remove residual organic compounds, aerobic sludge was left at room temperature (22 ± 2 °C) and purging with air for two days. Anaerobic sludge was conditioned at 37 ± 2 °C for two days. By filtering both types of sludge samples through black ribbon and drying at 105 ± 2 °C to constant mass, total suspended solids were determined (g_{TSS} L^{-1}).

Two different set of experiments to measure biogas production and methane yield were conducted. In the first set of experiments biogas production was measured after ozonation of aerobic sludge as pretreatment, where four different samples were compared: i) non-ozonated aerobic sludge, ii) non-ozonated contaminated aerobic sludge with known concentration of PVC, iii) ozonated non-contaminated aerobic sludge and iv) ozonated contaminated aerobic sludge with known concentration of PVC. In the second set of experiments where anaerobic sludge was directly used in anaerobic digestion without ozonation as pretreatment, two different samples were compared: i) anaerobic sludge without added PVC (control sample) and ii) anaerobic sludge with known concentration of PVC. For each experiment, two parallels were run. 0.1-10 g L^{-1} of PVC was added in sludge samples.

2.3. Ozonation as pretreatment of waste aerobic sludge

In 100 mL of aerobic sludge with known concentration of PVC (1 g L^{-1}) was added in 250 mL glass ozone batch reactor and purged with ozone for 10 or 20 minutes with mixture of oxygen and ozone containing lower (c=118 g Nm^{-3}) and higher (c=133 g Nm^{-3}) ozone concentrations. For ozonation, Wedeco H16 system was used, with operating pressure 0.5 bar and gas flow 30 L h^{-1} resulting in ozone production of 3.54 g h^{-1} (0.059 g min^{-1}; lower dose) and 3.99 g h^{-1} (0.067 g min^{-1}; higher dose). pH was measured during ozonation of PVC in tap water, using pH meter Iskra MA 5740 (Iskra, Slovenia). pH remained in the range from 7.00-8.00 (± 0.01) during 120 min ozonation.

2.4. Biogas production

The inhibition of anaerobic microorganisms was determined by modified standard procedure (SIST EN ISO 11734:1999), OxiTop® method, where biogas production was measured in terms of increased pressure (hPa) in a closed system (Figure 2). Glass bottles were filled up to 100 mL with mixture of aerobic sludge (50 mL; non-ozonated aerobic sludge, non-ozonated contaminated aerobic sludge with known concentration of PVC, ozonated non-contaminated aerobic sludge and ozonated contaminated aerobic sludge with known concentration of PVC), anaerobic sludge (maintaining fixed concentration of 1.5 g_{vs} L^{-1}), 0.5 mL of glucose as a substrate (c = 0.833 mol L^{-1}), 2 mL of buffer solution for maintaining constant pH, PVC, sized < 1 mm in concentrations, ranging from 0.1 to 10 g L^{-1} was added and also control samples without added PVC were run in order to evaluate the impact of PVC on methane yield and biogas production. Biogas production, in sealed 250 mL glass bottles was measured at constant temperature 37 ± 1 °C for 8 days. When biogas composed mainly of methane and CO_2, is produced, pressure increases. On the 7th day of experiment, 2 mL of NaOH (6.0 M) was added in every bottle through side rubber of the glass bottle to absorb formed CO_2 and remained pressure was only due to the methane. With difference in pressures, percentage of gases were calculated. PVC particles after experiment were collected and stored at room temperature until FTIR analysis. All biogas measurement experiments were run in duplicates (n=2). Standard deviations of biogas measurement results varied from ±0% to ±12%.

Figure 2. Steps of OxiTop® method for determination of biogas production and methane yield.

2.5. FTIR analysis

PVC particles before and after anaerobic digestion experiments were analysed by Fourier transform infrared spectroscopy (FTIR) using IR Spectrometer Spectrum BX FTIR Perkin-Elmer, to determine effects of oxidation and biogas production on particles composition. (Xu *et al.,* 2019b). PVC particles were obtained from bottles after ending of experiments and were air dried for 2 days until constant mass before FTIR analysis.

3. Results and discussion

3.1. The impact of PVC on methane yield and biogas production

The aim of the work was to evaluate impact of ozonation as pretreatment of PVC contaminated waste aerobic sludge on biogas and methane production due to the applied dose of ozone. Concurrently, impact of PVC contaminated anaerobic sludge without any pretretament on biogas and methane production was investigated. Comparison was made after adding NaOH on the 7th day of experiment to evaluate ratio of CO_2 and CH_4 in biogas.

It was assumed, that biogas consists only of CH_4 and CO_2. Figure 3 shows percentage (Vol.%) of formed CH_4 and CO_2 in the control sample, and in samples containing different concentrations of PVC added to anaerobic sludge. In the control sample ration of CH_4/ CO_2 was comparable to other authors. In the study of Zhang and Wang (2021), methane content reached around 45% of methane after 8 days. According to the standard procedure, biogas in the control sample containing only glucose as a substrate should contain 50% of CH_4 and 50% of the CO_2. In our case, 45±9 % of CH_4 was produced and results are in accordance with the requirements of the standard method. With PVC added to aerobic sludge from 49±2% (0.1 g L^{-1}) to 63±0% (1 g L^{-1}) of methane was produced.

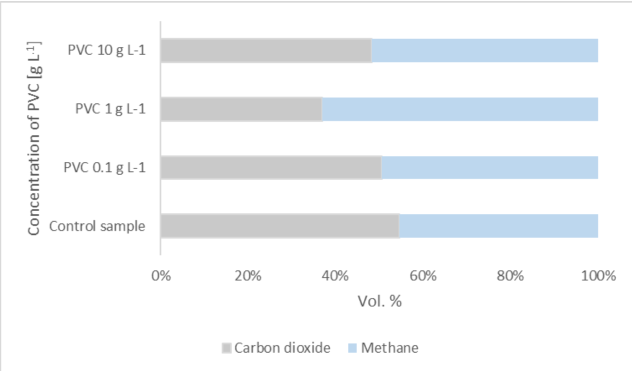


Figure 3. Percentage of formed CH_4 and CO_2 based on concentration of added PVC, compared with control sample.

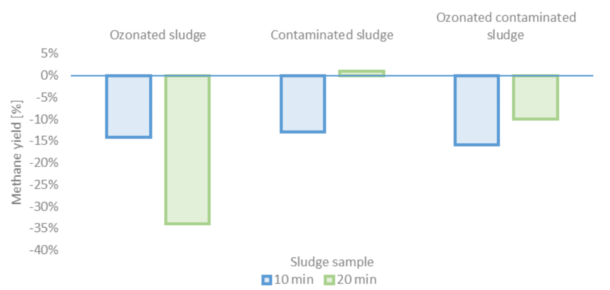


Figure 4. Methane yields of PVC-contaminated (1 g L^{-1}) and ozonated sludge at lower ozone dose 3.54 g h^{-1} (10 and 20 min) in comparison to control sample.

As it is seen on Figure 3, added PVC increases CH_4 production, compared to control sample. In this experiment, only anaerobic sludge was added and ozonation was not included as pretreatment step. Lower concentrations of PVC (0.1-1 g L^{-1}) increased CH_4 production up to 18%, while higher concentrations (10 g L^{-1}) increased CH_4 production less, only up to 7%. Also, cumulative biogas production was higher in the systems with added PVC in comparison to control sample and reached up to 27% more biogas with concentration 1 g L^{-1} of added PVC, while lower and higher concentrations of PVC added increased biogas production up to 17%. It was not possible to correlate amount of PVC added and biogas production potential, but it can be concluded, that PVC MP has significant impact on biogas production and methane yield, due to deviation to control samples, where PVC was not present. Since PVC could contain different compounds such as additives, plasticizers or colorants and stabilizers we could assume, that these compounds could be released during anaerobic digestion and could have noticeable impact on biogas and methane production. Since selected PVC with higher density of 1.39 g cm^{-3}, contain less additives, according to Material safety date sheet (MSDS), and since methane and biogas production are the lowest at higher concentrations of PVC added to sludge, it could be assumed, that higher concentrations of PVC could be releasing more compounds and inhibiting both, methane and biogas production.

3.2. The impact of ozonation of PVC-contaminated sludge on methane yield and biogas production

Biogas production and CH_4 production were also compared prior and after ozonation of aerobic sludge. Results of biogas and CH_4 production with aerobic sludge, contaminated aerobic sludge with PVC, ozonated aerobic sludge and aerobic sludge contaminated with PVC were compared. In Figures 4 and 5, CH_4 yields are presented. As it is seen in Figure 4, when lower dose of ozone (3.54 g h^{-1}) was used, the CH_4 yield was reduced in comparison to control sample. In 10 minutes of ozonation 0.59 g of ozone was introduced, while in 20 minutes its amount reached 1.18 g. Up to 14% less CH_4 was produced in ozonated aerobic sludge and up to 16% less when PVC-contaminated aerobic sludge was ozonated. Longer time of ozonation (20 minutes) even increased reduction of CH_4 yield. Compared with control sample, ozonated aerobic sludge produced up to 34% less CH_4, the same was also noticed in the system with ozonated contaminated aerobic sludge (up to 10%). It could be assumed, that at lower dose of ozone, more compounds, that could reduce methane production, remained in the mixture in comparison to system, where higher dose of ozone was applied. On the other hand, higher dose of ozone could destroy or deactivate compounds, that inhibits methane yields and thus promotes methane production.

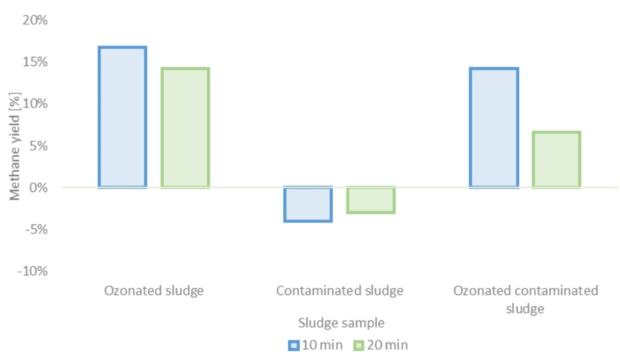


Figure 5. Methane yields of PVC-contaminated (1 g L^{-1}) and ozonated sludge at higher dose 3.99 g h^{-1} (10 and 20 min) in comparison to control sample.

Higher doses of ozone (3.99 g h^{-1}) increased CH_4 production as it can be seen in Figure 5. In comparison to control sample, ozonation at higher dose of ozone for 10 minutes produced more CH_4 than longer ozonation under the same conditions for 20 minutes. When higher dose of ozone was used, up to 17% more CH_4 was produced with 10 minutes ozonation of sludge, while ozonation of contaminated sludge reached a bit less, up to 14% more CH_4 in comparison with control sample. Ozonation for 20 minutes, produced 14% more CH_4, while ozonation of contaminated sludge reached up to 7%.

Lower dose of ozone was not as efficient as higher dose of ozone when CH_4 production is considered and it seems, that added PVC inhibited production of CH_4, compared with control samples. In Figure 6, the cumulative biogas production is presented for all conducted experiments at lower (3.545 g h^{-1}) and higher (3.99 g h^{-1}) dose of ozone with 10 or 20 minutes ozonation of PVC contaminated (c = 1 g L^{-1}) aerobic sludge. As it can be seen in Figure 7, lower dose of ozone inhibited biogas production. Longer time of ozonation even increased biogas inhibition of contaminated and non-contaminated sludge. Higher dose of ozone increased biogas production of sludge and contaminated sludge in comparison with control sample.

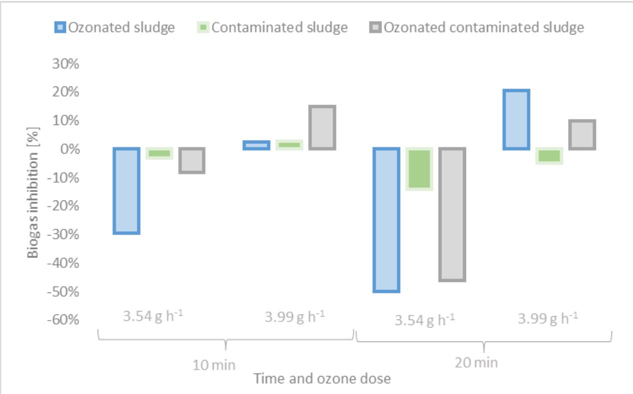


Figure 6. Biogas inhibition according to time of ozonation and dose of ozone of contaminated and ozonated sludge in comparison to control sample.

Results of some studies demonstrated that leachates from MP particles affected and increased the activity of some microorganisms and thus could impact the activities of microorganisms, producing biogas. Study of Wei and co-authors (2019) demonstrated, that one of the reasons for inhibition of methane production is BPA leaching from PVC. Since ozonation at lower dose (3.54 g h^{-1}) inhibited methane and biogas production and inhibition of methane was higher with 10 minutes ozonation than with 20 minutes ozonation, it could be assumed, that lower dose was too low to improve methane yield and that longer time of ozonation at lower dose could be more effective, as inhibition was decreasing after 20 minutes.

Ozonation at higher dose (3.99 g h^{-1}) improved methane yield as also biogas production and it could be assumed, that when ozonating with higher dose (3.99 g h^{-1}), ozone is first affecting toxic compounds, that are leaching from PVC and after longer time (20 minutes) of ozonation starts to impact also PVC particles.

3.3. FTIR analysis

With FTIR analysis composition of non-treated, and ozonated PVC particles were identified as well as ozonated PVC particles after biogas production experiments were analysed (Figure 7).

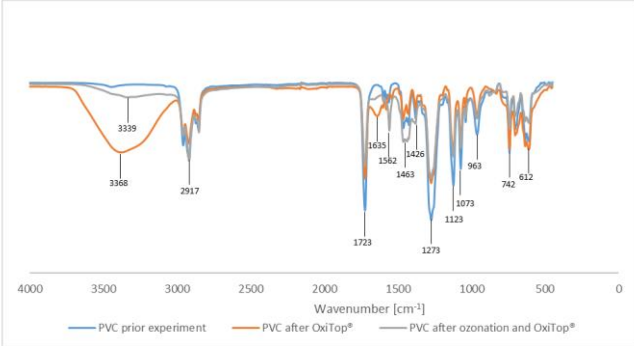


Figure 7. FTIR spectre of non-treated, ozonated and PVC particles after biogas production experiments.

As can be seen on Figure 7, it seems, that ozonation, followed by method of biogas production did not affect PVC particles spectre. The composition remained constant. Peaks from 3100 to 3700 cm^{-1}, centred between 3300-3400 cm^{-1}, present hydroxyl groups, that could be a consequence of not enough dried sample prior FTIR analysis. Mallampati with co-authors (2010) ozonated various different PVC particles with 8-36% of additives and used lower doses of ozone, from 0.27-0.45 g $h^{-1}$for 60 minutes. While ozonating PVC, that contained low % of additives, chlorine groups on the surface of PVC were replaced into hydrophilic functional groups that increased by ozonation, while vinyl chloride group decreased.

4. Conclusion

PVC present in waste sludge in general increases CH_4 production in anaerobic stabilisation. Lower concentrations of PVC increase CH_4 production more, than higher concentrations. Also, cumulative biogas production is higher, compared with control sample. It was shown, that with ozonation, as possible pretreatment of anaerobic digestion, PVC inhibits and, in some cases, increases CH_4 production and also biogas formation. Particles of MPs and compounds that are bound to particles could inhibit the growth and metabolism of some microorganisms. It could also be concluded, that ozonation could be additional step before anaerobic stabilization of waste sludge, because it improves CH_4 yield and biogas production under certain conditions, such as define time of ozonation and dose of ozone, while inhibits production of CH_4 and biogas at lower doses (3.54 g h^{-1}). It must be noted, that more research needs to be done in order to completely understand impact of ozonation on biogas production with PVC and other types of MPs contaminated waste sludge.

Main findings of the research:

- PVC increases CH_4 yield and biogas production, especially at lower concentrations of PVC (0.1 - 1 g L^{-1}) added.

- Ozonation, as a pretreatment method, could inhibit or increase CH_4 yield, depending on ozone dose and time of treatment. Higher dose of ozone (3.99 g h^{-1}) in the first 10 minutes of ozonation of PVC-contaminated aerobic sludge was the most efficient in terms of high biogas production (up to 14%) followed by improved methane yield.

- Ozonation also increase cumulative biogas production (up to 15% with 10 minutes ozonation) when higher dose of ozone (3.99 g h^{-1}) is used.

We can conclude, that PVC has impact on anaerobic digestion and consequently on methane and biogas production. It seems that PVC in general improves methane production. PVC also has impact on ozonation as pretreatment of anaerobic digestion of sludge, since it seems, that added PVC improves methane production and also biogas production, depending of characteristics of sludge and when appropriate pretreatment conditions are used. Further research will be done in order to deepen understanding of the impact of MP on biogas production and CH_4 yield.

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