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Peroxidation enhances the biogas production in the anaerobic digestion of biosolids

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Abstract

During the anaerobic digestion of wastewater treatment sludge, commonly called biosolids, an energy rich biogas is formed which is now considered as renewable energy source and widely used for the production of heat and/or electricity. Pre-treatment methods, which achieve a transformation of refractory COD into readily available and soluble BOD, have the potential to enhance the biogas-production. This paper studies several peroxidation techniques for this purpose: the well-known Fenton peroxidation and novel reactions involving peroxymonosulphate (POMS) and dimethyldioxirane (DMDO).

The results of the treatments show a considerable increase of COD and BOD in the sludge water, and an increase of the BOD/COD ratio. The biogas production was moreover seen to increase significantly. A maximum increase of 75% was measured with Fenton, while the POMS treatment increased the biogas production by a factor of nearly 2, against an even higher 2.5 for the DMDO treatment. The methane content of the biogas remained between 65 and 70%, thus maintaining its heating value.

Keywords: Anaerobic digestion; Biogas; Biosolids; Peroxidation; Biogas yield

1. Introduction

Waste activated sludge (WAS) processes have the inherent drawback of producing huge amounts of sludge to be treated. Anaerobic digestion is widely used as a treatment step because it offers several advantages. A large amount of organic dry solids (ODS) is decomposed and transformed into biogas, thus causing a reduction of the sludge quantity by 25–30%. Moreover, part of the pathogenic organisms is destroyed and the sludge is stabilised by reducing the organic material, which serves as food for the micro-organisms. The produced biogas contains 65–75 vol% of methane and has a high calorific value: it can thus be energetically valorised in the production of electricity or heat. This energy is moreover recognised as a form of renewable energy in most European countries. It is thus beneficial to produce as much biogas as possible.

The anaerobic digestion of organic material basically occurs in three steps: hydrolysis, acidogenesis (fermentation) and methanogenesis [1]. In the hydrolysis step, insoluble organic material and higher molecular compounds such as lipids, polysaccharides, proteins, fats and nucleic acids are transformed in soluble organic materials. These smaller molecules are further broken down during the acidogenesis. The final products of this step are acetate, hydrogen and carbon dioxide. These molecules are the precursors of the methanogenesis. In this step, two groups of methanogenic organisms are involved into the methane production. One group splits acetate into methane and carbon dioxide; the second group uses hydrogen as electron donor and carbon dioxide as electron acceptor to produce methane.

In the anaerobic digestion of WAS, the rate limiting step is the hydrolysis reaction [2,3]. Pre-treatment methods that achieve a significant breakdown of refractory COD into readily available

Abbreviations: BOD, biological oxygen demand [mg O_2/l]; COD, chemical oxygen demand [mg O_2/l]; DMDO, dimethyldioxirane; DS, dry solids; MDS, mineral dry solids; ODS, organic dry solids; POMS, peroxymonosulphate; WAS, waste activated sludge

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and soluble BOD hence have the potential to enhance the biogas production. Several methods have been studied in literature with respect hereto, including mechanical, thermal, chemical, ultrasonic and/or combined sludge pre-treatment.

The use of ultrasound was intensively studied in literature. Dewil et al. [4] showed an increase in soluble COD when disintegrating sludge with ultrasound. Bougrier et al. [5] observed an increase of the biogas production by about 50% when using ultrasonic disintegration and by about 60% for thermal treatment. Lafitte-Trouqué and Forster [6] also used ultrasound for disintegrating the WAS. They measured a slight increase in biogas production during mesophilic as well as thermophilic sludge digestion. Show et al. [7] measured an overall increase of 22% in the methane production. Park et al. [8] used a thermochemical treatment and noticed a significantly improved biogas production. Kim et al. [9] made a comparison of several methods. They concluded that a combination of heat and an adaptation of the pH to 12, gave the best results (increase in methane production exceeding 34.3%). An oxidative treatment using ozone was used by Bougrier et al. [5]. They noticed an increase in biogas production of 25%. The methane content of the produced biogas did moreover remain constant.

Recently, the use of Fenton peroxidation was proposed for enhancing the dewaterability of WAS by Neyens et al. [10]. In a later work [11], these authors concluded that this improvement was caused by the disintegration of extracellular polymeric substances (EPS) and a breakdown of cell walls, thus releasing intracellular water. It was also seen that the amount of soluble COD and BOD in the sludge water increased considerably. These observations suggested that a Fenton pre-treatment could possibly enhance the anaerobic digestion of the WAS. In this paper, this assumption was intensively studied. For the full working mechanism of the Fenton peroxidation reaction, the reader is referred to Neyens and Baeyens [12].

Some alternative peroxidation methods were additionally considered, including the oxidation using peroxymonosulphate (POMS) and dimethyldioxirane (DMDO).

The POMS ion (SO_5^{2-}) is a derivate of hydrogen peroxide (one H-atom is replaced by a SO_3-group). Its standard oxidation/reduction potential is 1.44 V [13]. The reaction rates are three to four times faster than for H_2O_2 for all nucleophilic reactions [14].

The main reaction scheme [14] for the oxidation of nucleophilic components by POMS is:

$$^{-}SO_3\text{-}OOH + Nu \rightarrow SO_4^{2-} + NuOH^{+}$$

Nu hereby stands for the nucleophilic part of the molecule or radical.

POMS is used in numerous industrial processes because of its oxidative capacity, and has applications as bleaching agent, disinfectant and oxidant in organic synthesis. In wastewater treatment, POMS is used for the oxidation of hydrogen sulphide and other reduced sulphur compounds [15]. The use of POMS in sludge handling is novel.

The compound can be used in its acid form (H_2SO_5) or as salt ($NaHSO_5$ or $KHSO_5$). Because of their instability, these compounds however cannot be stored. The active component $KHSO_5$ is therefore incorporated in the triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, which is stable under ambient conditions and is commercially available under the brand names Oxone®, Caroat® and Curox®.

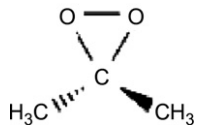

Fig. 1. Structure of dimethyldioxirane.

Dimethyldioxirane is a very powerful oxidising agent, which can be used for the transfer of oxygen and for the oxidation of persistent organic molecules. It is part of the group of cyclic peroxides and is an isomer of carbonyloxides [16]. Its structure is shown in Fig. 1.

DMDO is used in several industrial processes such as the sterilisation of medical equipment and as chlorine-free bleaching agent in the paper industry. It is furthermore used for the decontamination of chemical and biochemical weapons used in modern warfare [17].

This paper studies the biogas production when treating sludge with these oxidation techniques prior to digestion. The rate of release of BOD and COD in the sludge water was measured and the biogas production of treated and untreated sludge was examined on lab scale.

2. Experimental lay-out and procedures

2.1. Sludge

For the experiments sludge samples were taken from the full scale WWTP of Deurne-Schijnpoort (Belgium). The samples were taken directly from the secondary clarifier. No primary sedimentation is present. The sludge was collected and settled in the laboratory for about 4 h prior to the treatment.

During digestion the sludge was seeded with digested sludge obtained from the same WWTP. The three peroxidation treatments were applied (Fenton reaction, POMS and DMDO, i.e. the acetone-catalysed POMS-reaction).

The Fenton treatment was performed in a batch reactor, containing 2 l of sludge at ambient temperature and pressure. The pH of the sludge was firstly adjusted to 3 using H_2SO_4. The Fe^{2+}-catalyst was thereafter added under the form of $FeSO_4$, using a ratio of 0.07 g Fe^{2+} per gram of H_2O_2 added. This ratio was determined by Neyens et al. [10] to be the optimum concentration for uses with WAS. The H_2O_2 was thereafter added in the given amount from a solution containing 390 g H_2O_2/l solution. The mixture was stirred gently during reaction. The oxidation releases reaction gases (mostly CO_2, H_2O and small organic molecules) and the time of reaction was considered as the time until the gas production stopped. This time is about 60 min. After the reaction, the sludge mixture was neutralised using $Ca(OH)_2$.

The reaction with POMS was carried out in a reactor at ambient temperature and pressure. About 2 l of sludge was treated in the reactor. Ten grams of solid POMS triple

Table 1
Release of DS, COD and BOD into the sludge water

	Blank	Fenton 5 g H_2O_2/kg DS	Fenton 25 g H_2O_2/kg DS	Fenton 50 g H_2O_2/kg DS
DS (%)	0.08	0.15	0.44	0.65
COD (mg O_2/l)	421	787	1708	2507
BOD (mg O_2/l)	198	361	862	1403
BOD/COD	0.47	0.46	0.50	0.56
	POMS 30 g/kg DS	POMS 60 g/kg DS	DMDO 330 ml/kg DS	DMDO 660 ml/kg DS
DS (%)	0.54	0.78	0.67	0.87
COD (mg O_2/l)	1622	2131	1923	2902
BOD (mg O_2/l)	781	1192	1081	1697
BOD/COD	0.48	0.56	0.56	0.58

salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) were dissolved into 100 ml of deionised water. An appropriate amount of this solution was added to the sludge. No adaptation of the pH is necessary for this treatment. The sludge mixture was gently stirred during the reaction. After 60 min the reaction was considered complete.

DMDOs are very unstable and should be produced directly before usage. A dioxirane is formed through the reaction of POMS with a ketone [18]. In the present research, acetone is used for generating DMDO. A concise method hereto was presented by Wallace et al. [19] and was used in this study. Firstly, 4.2 g of sodium bicarbonate was added to 100 ml of deionised water at ambient temperature. Then 10 g of POMS triple salt (Oxone©) were added. Because of the vigorous off-gassing during the preparation, the POMS was added slowly to the bicarbonate solution and allowed to mix for 10 min before use. The DMDO solutions were made by adding 10 ml of acetone to the mixture. The DMDO mixture was applied to the sludge directly after adding the acetone. For the sludge experiments 21 of sludge were inserted in a reactor at ambient temperature and pressure. The appropriate amount of the DMDO mixture was added. The mixture was gently stirred during the reaction. After 60 min, the reaction was considered complete.

2.2. Digestion

The laboratory scale digesters consisted of a series of 11 batch reactors. Six hundred millilitres of the treated WAS were introduced in a reactor and seeded with 100 ml of the digested sludge. The unfilled part of the reactor was flushed with nitrogen gas to evacuate residual oxygen. The reactors were kept at a constant temperature of 37 °C in a water bath. Each reactor was connected to the top of a cylindrical glass gas collector. The gas production was measured by the downward displacement of acidified (0.05 M H_2SO_4) water at different times during digestion. The reaction was considered complete when the gas production stopped.

The methane concentration of the formed biogas was determined by scrubbing the biogas with a 5 molar NaOH-solution: all CO_2 in the gas is hereby converted into carbonate and hence removed from the gas phase. By determining the gas volume after scrubbing, the amount of methane can be measured.

The dry solids content (DS), organic dry solids content (ODS), mineral dry solids content (MDS), BOD and COD concentrations were determined according to standard analytical methods [20]. Since the presence of peroxidants affects the analyses of COD, the non-reacted peroxides were removed from the mixture prior to COD measurement using $NaHSO_3$.

For determining the release of DS, COD and BOD in the sludge water, the sludge was subjected to a lab scale centrifugation at 4400 rpm (approx. 8900 g) for 5 min. The analyses were done on the supernatant.

3. Results and discussion

3.1. Effects of pre-treatment on solubilisation of DS

After dewatering the treated sludge samples, the DS, COD and BOD of the filtrate was measured for determining the release of biodegradable solids. The results are presented in Table 1.

The values of the concerned parameters in the water phase increase with an increasing dosage of peroxide. This confirms the breakdown and release of organics into the sludge water. Moreover, the BOD/COD ratio also increases, confirming the disintegration of organic matter during treatment and the conversion of COD into BOD.

The releases are higher for POMS and DMDO than for the classic Fenton peroxidation. Due to the exploratory objectives of the research, conditions of experiments were not varied over wide ranges of operating conditions. The comparative results

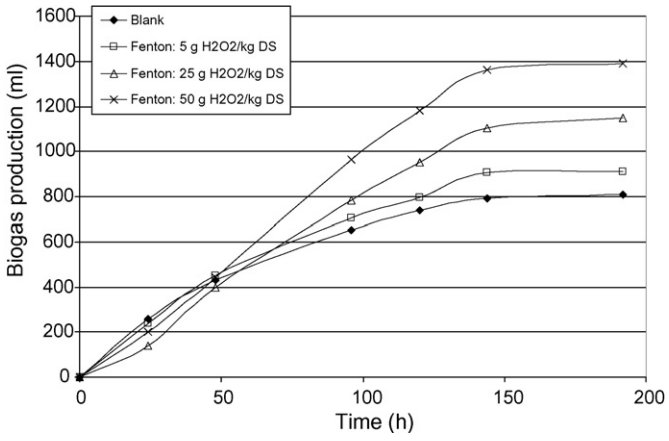

Fig. 2. Production of biogas for blank and treated sludge for Fenton peroxidation.

Table 2
Specific biogas production for Fenton

H_2O_2 doses (mg/kg DS)	%ODS before digestion (%)	%ODS after digestion (%)	ODS decrease (g)	Specific biogas production (ml/g ΔODS)
Blank	56.6	47.8	1.25	644
5	56.8	47.1	1.44	632
25	55.7	45.1	1.70	655
50	56.8	41.7	1.96	668

are hence strictly speaking only valid within the range of concentrations used and for batch conditions.

3.2. Increase in biogas production

3.2.1. The Fenton peroxidation

Since the principal aim of the study was to increase the amount of formed biogas, the sludge samples were subjected to an anaerobic digestion on lab scale. Fig. 2 presents the results of these tests when using Fenton's reagent.

The pre-treatment with the Fenton reagent positively influences the biogas formation during anaerobic digestion. The enhancement moreover increases with increasing dosage of H_2O_2. It is, however, observed that the production starts more slowly than for the untreated sample. This is in disagreement with other literature findings (e.g. Bougrier et al. [5]). The difference is rather small and can be due to presence of some non-reacted H_2O_2 affecting the anaerobic micro-organisms. This anomaly will be studied in detail in future research.

For determining the specific biogas production (mg biogas per g disintegrated ODS), the DS and ODS content of the sludge was sampled before and after digestion. The results are presented in Table 2.

The specific biogas production increases only slightly for increasing H_2O_2 dosage, but confirms that the Fenton treatment reduces refractory COD and biomass into smaller molecules, which are readily available for the anaerobic micro-organisms. The ODS decrease during digestion increases significantly with increasing H_2O_2 dosage.

No significant change in methane concentration of the biogas was observed between the blank and treated sludge samples. For all samples, the methane content remained between 65 and 70%.

3.2.2. POMS and DMDO

The results for the peroxidation with POMS and DMDO are presented in Fig. 3. Since 30 g (resp. 60 g) of POMS were used for preparing 330 ml (resp. 660 ml) of DMDO, the dosages used in the experiments are comparable.

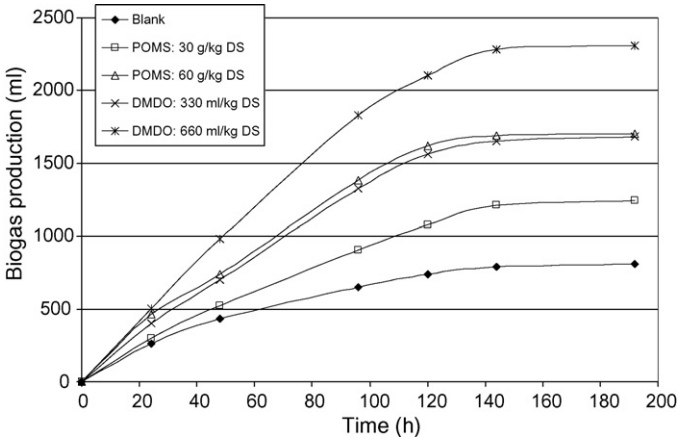

Fig. 3. Production of biogas for blank and treated sludge for peroxidation with POMS and DMDO.

A significant increase in biogas production is observed for both techniques. An increasing peroxide dosage has a positive effect on the amount of biogas produced. The results for the DMDO treatment are superior: an increase by a factor 2.5 is observed for the highest dosage. In contrast to the Fenton treatment, the biogas yield increases from starting the experiment.

The specific biogas production (ml biogas per g disintegrated ODS) is presented in Table 3.

The decrease in ODS increases with increasing biogas production. The specific biogas production increases only slightly, but still its value at the highest dosage of DMDO is considerably higher.

The methane concentration of all biogas samples lied between 65 and 70%, illustrating the constant quality of produced gas.

3.2.3. Comparison of both methods

To compare the proposed treatment methods, the peroxidant dosages should be expressed in terms of the available oxygen for reaction, as shown in Table 4.

Table 3
Specific biogas production for POMS and DMDO

Treatment	%ODS before digestion (%)	%ODS after digestion (%)	ODS decrease (g)	Specific biogas production (ml/g ΔODS)
Blank	56.6	47.8	1.25	644
POMS (30 g/kg DS)	56.9	43.7	1.87	663
POMS (60 g/kg DS)	56.3	40.7	2.37	716
DMDO (330 ml/kg DS)	56.1	40.3	2.32	724
DMDO (660 ml/kg DS)	56.8	31.6	2.69	859

Table 4
Dosages of peroxidants expressed in terms of available oxygen

Peroxidant	Dosage (g)	Available O (mole/kg DS)
H_2O_2	5	0.147
	25	0.735
	50	1.471
POMS	30	0.098
	60	0.195
DMDO-mixture	330	0.098
	660	0.195

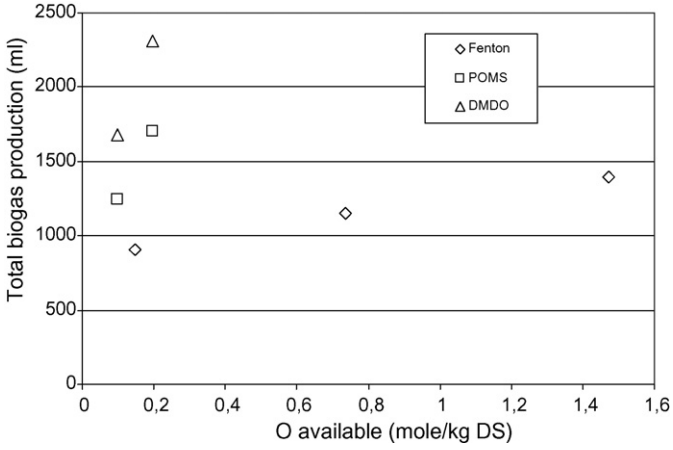

Fig. 4. Total biogas production as a function of the available oxygen for each treatment method.

Fig. 4 presents the final amount of produced biogas (after a residence time of 190 h in the digester) as a function of the available amount of oxygen added for each treatment method. The figure clearly illustrates the superiority of both alternative peroxidation methods POMS and DMDO.

4. Conclusions

The anaerobic digestion of WAS is widely used because of several advantages including the decomposition of some of the organic material, the destruction of some pathogens, the stabilisation of the sludge and the production of a high calorific biogas which can be energetically valorised. This paper studied the use of some peroxidation techniques for increasing the biogas production during digestion: classic Fenton peroxidation and peroxidation using POMS and DMDO.

The results indicate a significant increase in biogas production, which is due to the disintegration and solubilisation of organic matter during the treatment of the sludge: more organic matter is readily available for the anaerobic micro-organisms and can thus participate in the digestion.

The treatment with DMDO results in the highest biogas yield, an increase with a factor 2.5 as compared to the untreated sludge (blank). The quality of the biogas (methane content) remains constant.

These observations are very promising and will be further tested on pilot and full scale. These tests are ongoing and will be reported in a follow-up paper.

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