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Peroxidation enhances the biogas production in the anaerobic digestion of biosolids

Raf Dewil [a,*], Lise Appels [b], Jan Baeyens [c], Jan Degrève [d]

[a] Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
[b] Department of Chemical Engineering, Associated Faculty of Industrial and Biosciences, Catholic University of Leuven, Campus De Nayer, J. De Nayerlaan 5, 2680 Sint-Katelijne-Waver, Belgium
[c] School of Engineering, University of Birmingham, Edgbaston, Birmingham, United Kingdom
[d] Department of Chemical Engineering, Catholic University of Leuven, Willem De Croylaan 46, 3001 Heverlee, Belgium

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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

* Corresponding author. Tel.: +32 3 2653569; fax: +32 3 2653225.
E-mail address: raf.dewil@skynet.be (R. Dewil).

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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®.

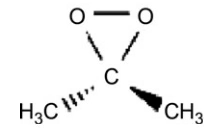

Fig. 1. Structure of dimethyldioxirane.

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