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ENHANCEMENT BIOGAS PRODUCTION OF CANNED MAIZE PRODUCTION SLUDGE BY OZONE AND MICROWAVE PRETREATMENTS

S. Beszédes, S. Kertész, Zsuzsanna László, G. Szabó, Cecilia Hodúr

University of Szeged, Faculty of Engineering, Department of Mechanical and Process Engineering HU-6725, Szeged, Moszkvai krt 5-7, HUNGARY

SUMMARY

The aim of the most of cases in the sludge management technologies is only the volume reduction. But nowadays requires of biomass based energy sources have led to the utilization of organic content of sludge for biogas producing. The production of canned maize produces high volume of waste water and sewage sludge, with high starch-content, high chemical and biological oxygen demand. Thermal, chemical, biological and mechanical processes and their different combinations have been studied as possible pretreatment to accelerate sludge hydrolysis. In our work the effect of microwave and ozone pre-treatment on biogas production and biodegradability of canned maize production sludge were examined and the energy balance of the processes using different sludge pre-treatments were determined. It was found, that the ozone treatment decreased the chemical oxygen demand, while the biological oxygen demand, and the biodegradability increased. Microwave pre-treatments could enhance biodegradability and the organic content was became more water soluble and accessible for microorganisms. The combination of microwave and ozone treatment also increased the biodegradability, related to the ozone treatment alone. The investigation of biogas production showed that all type of pre-treatment enhance the methane-production: the 30 min ozone treatment and the 5 min 250W microwave treatment resulted positive energy balance.

Keywords: Sewage sludge, microwave pre-treatment, ozone, biogas, biodegradability

INTRODUCTION

The most branch of food industry, for instance the dairy industry, the meat industry and the cannery industry has a considerable wastewater output. The sewage sludge is the residue of the primary, secondary or tertiary wastewater technologies. Depending on the processed raw material the sludge may be rich in carbohydrates, lipids or proteins. In most cases the main structure of municipal and food industrial sewage sludge consists of extracellular polymeric substance (polysaccharides, proteins, lipids, nucleic acids), multivalent cations, other organic and inorganic matter and microbial cells which compose a special flock structure [1]. This agglomerated complex flock structure is resistance to a direct anaerobic degradation since cell walls and polymeric conformation present physical and chemical barriers for microbial and enzymatic degradation. The aim of sewage sludge treatment technologies is to reduce the mass of it or to modify to be able for further utilization. Nowadays the commonly used methods for sludge treatment are digestion, dewatering, incineration or using in agriculture. The anaerobic digestion is an appropriate technique for the treatment of sludge before the final disposal and it is used worldwide as the oldest and most important process for sludge stabilization.

The biogas producing fermentation is resulted by four major steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the rate limiting step of sludge degradation. During hydrolysis both solubilization of particulate matter and biological degradation of organic components can occur. Thermal, chemical, biological and mechanical processes and their different combinations have been studied as possible pre-treatment accelerating sludge hydrolysis [2, 3]. Thermal, chemical, biological and mechanical processes and their different combinations have been studied as a possible pre-treatment to accelerate sludge hydrolysis. These pre-treatment cause lysis or degradation of sludge cells, therefore the organic matter become more accessible to anaerobic microorganisms. It causes increased methane production and decreased the digestion time. Efficiency of the pre-treatment is commonly evaluated by means of biodegradability or biogas production.

Ozonation is considered as a promising pre-oxidation process to control of the levels of organic pollutants in water, because the ozone is a strong oxidant and a potent disinfecting agent. The compounds with large molecular size may decompose to smaller molecules. In consequence of ozone treatment the organic matter may become more accessible to microorganisms [4]. This may improve the overall digestion process rate and the degree of sludge degradation thus reduces anaerobic digester retention time and increases methane production rates.

Microwave heating is used as a popular alternative to conventional heating mainly due to considerable reaction time reducing and so-called non-thermal microwave effects.

Due to high water content the sewage sludge can absorb microwave energy efficiency [5]. The microwave irradiation has thermal and athermal effect. The thermal effect can be attributed heat generation in the matter due to rotation of dipole molecules or ionic conduction and in many case these two mechanisms have been experienced simultaneously. The intensive microwave heat generation and the different dielectric properties of compounds of cell wall lead to a rapid disruption of extracellular polymer network and residue cells of sludge [6]. However the cell liquor and extracellular organic matter within polymeric network can release into the soluble phase, hereby increase the ratio of accessible and biodegradable component [7].

MATERIALS AND METHODS

The non pre-treated maize canning sludge originated from DEKO Food Cannery, Debrecen, Hungary. The initial chemical oxygen demand of sludge was 136 kg/m^3. Chemical oxygen demand (COD) was measured before and after the treatments according to the dichromate standard method in COD tests with an ET 108 digester Lovibond PC Checkit photometer. Before sCOD determination the samples were centrifuged for 20 minutes at 6000 RCF. The separation of water soluble phase a 0,45 μm pore size disc filter (Millipore) was used. The biochemical oxygen demand measurements were carried out in a respirometric BOD meter (BOI Oxidirect, Lovibond, Germany), at 20 °C. Biodegradability during 5 days (BD_5%) was calculated by the expression

$$BD_5\% = (BOD_5/COD_0) \times 100$$

The ozone treatments were evaluated in continuously mixed solutions diluted to 6 % dry matter content. Ozone was generated from oxygen (Linde 3.0) by a flow type ozone generator (Ozomatic Modular 4, Wedeco Ltd., Germany) operating via a silent electric discharge, and the ozone-containing gas (flow rate 1.0 dm^3/min) was bubbled through 180 ml of solution in a batch reactor through a ceramic diffuser. The ozone concentration in the feed gas was 32 mg/l, which was measured at 254 nm with a UV spectrophotometer (WPA Lightwave S2000) the contact time was 30 and 60 min, the flow rate of bubbling gas was 1 $dm^3 min^{-1}$.

The microwave treatments were performed in a Labotron 500 (Buchner Ltd) professional microwave equipment, at 250 and 500 W microwave power. For the measurements 200 g sludge sample was diluted with 200 ml distilled water in a PTFE vessel, then it was irradiated for 5 or 10 minutes. In the case of acidic and microwave pre-treatment the pH was adjusted to pH 2 with 1 M HCl. After the treatment the pH was adjusted to pH 7.2 with 1M NaOH.

Biogas production tests were performed in batch mode under mesophilic conditions, at 30°C for 30 day, in an anaerobic digester with pressure measuring head

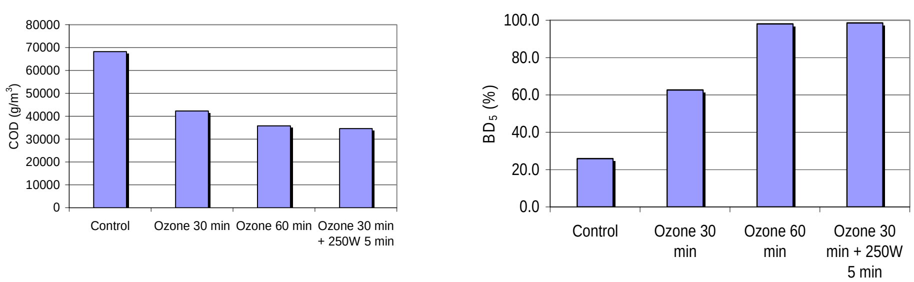
(Oxitop Control AN12 measurement system), (WTW Gmbh, Germany). The digesters were inoculated with anaerobic sludge from a municipal wastewater treatment plant (Hódmezővásárhely, Hungary). The composition of produced biogas was measured by gas chromatographic and mass spectrometric method (Agilent 6890N-5976 GC-MS).The net energy product (NEP) of processes with microwave pre-treatments can be calculated by the equation:

$$NEP = q_{comb} \times m_{methane} - P_m \times \tau$$

where NEP is the net energy product [J], q_{comb} is the combustion heat [J/kg] of methane, $m_{methane}$ the mass of the produced methane [kg], P_m the power of microwave magnetron [W], τ the time of treatment [s].

RESULTS AND DISCUSSION

In the first series of measurements the chemical and biological oxygen demand were measured (Figure 1.).



(a) (b)

Figure 1. Changes of COD (a) and biodegradability BD_5 (b) of sludge after treatments

It was found, that the ozone treatments and the combined ozone and microwave treatment decreased the COD, while the biodegradability (BD_5) increased. After 30 min ozone pre-treatment the microwave irradiation caused as about same COD decreasing as the 60 min ozone treatment. At the same time the process time of the combined treatment was less time consuming. Calculating the biodegradability it was found, that the treatments increased it. The combination of microwave and ozone treatment also increased the biodegradability close to 100%.

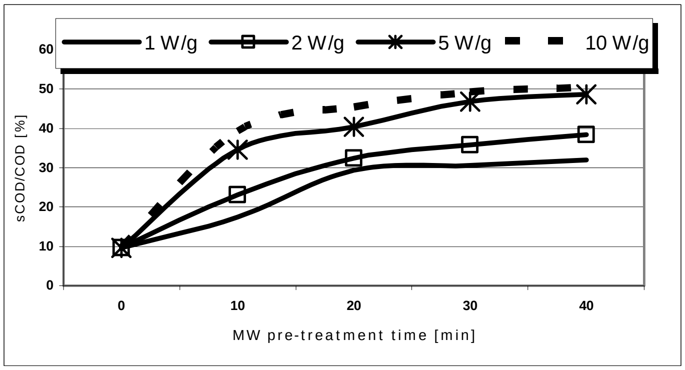


Figure 2. The effect of microwave pre-treatments on solubilization (sCOD/COD ratio) of organic matter content of sludge

It was found that the microwave pre-treatment could increase the quantity of water-soluble part of organic matter. The efficiency of increased microwave power level was slighter than the difference by biodegradability. Enhancing of biodegradability may be linked to solubilization of organic matter which was indicated by the increased sCOD/COD ratio.

In the next series of experiments the biogas production was measured. Gas chromatographic and mass spectrometric measurements showed that after 30 days fermentation the fermenter contains CO_2 and CH_4 gas. The non pre-treated sludge was used as control sample. The microwave treatments alone had no significant effect on the biogas production, while the ozone treatments enhanced it (Figure 3.).

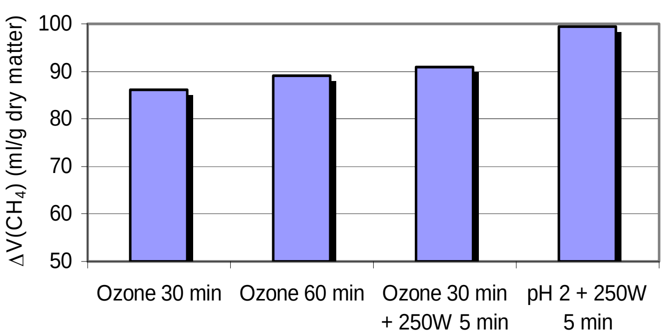


Figure 3. The difference of methane production of pre-treated and control sample

The results show, that all type of pre-treatment enhance the methane-production related to control (18,0 ml/g dry matter). There was no significant difference between the biogas production of 60 min and the combined microwave-ozone pre-treatments. At the same time the microwave treatment carried out at an acidic pH (pH=2) resulted higher methane production.

Initial specific biogas production rate ($dm^3\ kg^{-1}day^{-1}$) was calculated as the slope of the straight line fitting the values of biogas produced during the initial 10 days of the test [7], and summarized in the following table (Table I.).

Table I. The parameters of biodegradability after different pre-treatments

Pretreatment	Treatment time [min]	BD5% (BOD5/COD)×100	Initial biogas production rate [cm3 g–1day–1]
Untreated	-	26	1.037
Ozone	30	63	3.77
Ozone	60	94	7.40
Ozone + MW	30+5	96	9.52
MW (pH=2)	5	95	25.75

The results show that all of the treatments enhance the initial specific biogas production rate. Applying the combined MW/ozone treatment the increasing is tenfold; however the acidic microwave treatment enhances the initial biogas product rate about to 25 fold.

More different results can be obtained by calculating the energy balance of the treatments. The results show, that the 30 min ozone treatment and the 5 min microwave treatment at acidic pH have energy increase, while 60 min ozone treatment or combined ozone and MW treatments need more energy than that of the plus can be obtained from methane production (Figure 4).

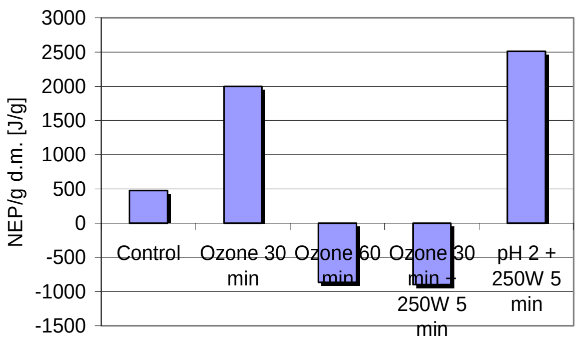


Figure 4. Energy balance of the treatments

Therefore, differently from the biodegradability and the biogas product, from energetically aspect the 30 min ozone and the microwave pre-treatment at a lower pH carried out were more profitable, because of the high energy demand of long-time treatments.

CONCLUSION

Our results shown, that the microwave irradiation is successfully adjustable and utilizable technique in sewage sludge handling. Applying of microwave pre-treatment the solubility of organic matter content increased and therefore the aerobic biodegradable enhanced and however the biogas product of sludge increased to. The MW treatment of acidic sludge solution resulted higher biodegradability and enhanced biogas production. The ozone pre-treatment and the combined ozone-microwave treatments also increased the biodegradability and the biogas and methane production. However, taking into consideration the procession time, the energetical benefits of the pre-treatments are not so unambiguous, only short-time ozone- or MW-treatment resulted net energy production. On the basis of our experiments, the ozone pre-treatment is appropriate for decrease the organic content of canning sludge, make the organic component of sludge more accessible for anaerobic degradation and thereby increase the biogas production.

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