Renewable Energy 96 (2016) 1078–1085

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Effect of ultrasonic and ozonation pretreatment on methane production potential of raw molasses wastewater

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ARTICLE INFO

Article history:
Received 19 August 2015
Received in revised form
20 November 2015
Accepted 23 November 2015
Available online 10 December 2015

Keywords:
Ultrasonic
Ozonation
Anaerobic digestion
Molasses wastewater
Methane enhancement

ABSTRACT

Ozonation and sonication were applied to baker's yeast wastewater with high molasses content, under various operation conditions, in order to study the effect of them on COD (Chemical Oxygen Demand) removal and on methane enhancement. The ozonation treatment resulted in a significant reduction of the COD content; the COD removal was up to 38% after a reaction time of 5 h. Moreover, a remarkable decolorization was observed, at 20 min of ozonation. The effect of sonication on the physical characteristics of the wastewater was negligible and resulted in an increase of the COD value. The anaerobic experiment was carried out in 18 batch reactors at 37 °C. The most efficient pretreatment method was sonication in a continuous mode, since it presented the highest methane production equal to 441.6 LCH4/kgVS. It was found that this method was also effective on COD removal, when sonication is followed by anaerobic digestion. The ozonation as a pretreatment method affected negatively biomethanation, as it resulted in significant reduction of methane production compared to the samples without pretreatment. The findings of the present study proved that the sonication of molasses wastewater followed by anaerobic digestion is an efficient solution, capable of treating this type of wastewater.

1. Introduction

Molasses represents a by-product of sugar manufacturing and it is used as raw material in several industrial applications such as bioethanol production, baker's yeast fermentation etc. Molasses is made up from 10 to 15% minerals, 15–20% non sugar organic substances, 45–50% residual sugars, such as glucose, fructose and sucrose, and about 20% water [1,2]. During the baker's yeast fermentation process, a great part of the non-sugar substances is not assimilated by the yeasts, and it is released unaltered in the processing water. These compounds make up the effluent wastewater from the yeast production procedure [1].

The dark brown colored effluent from baker's yeast industry is generated in large quantities: 10–15 L of wastewater is produced per L of product. The main characteristics of the effluent are the high concentration of total Kjeldahl nitrogen, COD (chemical oxygen demand), BOD (biological oxygen demand), sulphate and trimethylglycine, the low levels of readily degradable acids and sugars, as well as the presence of highly colored melanoidin and phenolic substances [2–4]. Therefore, the wastewater produced by this process is highly polluted, and it is vital that it is treated before being discharged into the receiving water bodies, aiming to prevent significant environmental problems [2].

Several processes have been employed for the treatment of the molasses-based wastewater including anaerobic, aerobic as well as physico-chemical methods. Anaerobic treatment constitutes the most often used technique, as it is associated to energy recovery in the form of biogas and over 80% BOD reduction [5]. However the utilization of anaerobic processes for the treatment of molasses wastewater is often restricted due to the presence of a high content of non-biodegradable organic materials in the effluent, and only a partial decomposition of the organic fraction occurs under anaerobic digestion [6]. Therefore, combination of other processes with anaerobic digestion is required, aiming to the implementation of an integrated treatment scheme for the efficient degradation of

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http://dx.doi.org/10.1016/j.renene.2015.11.060
0960-1481/

biorefractories [7]. Towards this target, pretreatment methods, prior to anaerobic digestion, could be beneficial in favoring the anaerobic digestion potential of molasses wastewater and enhancing the methane production rate. Several pretreatment methods can be used to improve the biodegradability of sludge and wastewater including alkali, acid and thermal processes [8–10].

In addition to more conventional pretreatment methods the potential of advanced oxidation technologies, such as sonication and ozonation, is investigated for enhancing the biodegradability and simultaneously reducing the organic and inorganic content of wastewaters with high biorefractories content [11].

High-power ultrasound at frequencies between 20 and 100 kHz is an efficient method for wastewater treatment due to cavitation phenomena and the formation of high intensity bubbles [12,13]. The energy waves, generated by the application of ultrasound irradiation to a liquid medium, are propagated by the alternation of compression (high pressure) and rarefraction (low pressure). At sufficiently high-power densities, the attractive forces are overcome by the rarefraction cycle and bubbles are formed [14]. These bubbles grow, expand and finally collapse, leading to the establishment of high local temperatures (up to 5000 K) and pressures (up to 180 MPa). Furthermore, high shearing phenomena are generated in the liquid phase, while radicals including $OH^{\cdot}$, OH_2, and $H^{\cdot}$ may be formed [15]. During wastewater treatment processes, a cavitation bubble may function as a micro reactor in which organic bonds may break down. In addition, $H^{\cdot}$ and $OH^{\cdot}$ radicals can react with specific pollutants in the bulk of the solution, resulting to additional reduction of organic loading [16].

Ultrasound technology has been used for the treatment of several types of wastewater, such as chlorophenolics, high fat dairy wastewater, herbicide wastewater and wastewater containing textile dyes [17–21]. Nevertheless, ultrasound irradiation has found application as a pretreatment method for the enhancement of biodegradability of wastewater with a high biorefractories content, such as olive mill or distilleries wastewater, ahead of biological treatment carried out by anaerobic digestion or by fungi [7,22,23]. Moreover, ultrasound technology was efficiently used in waste activated sludge to improve the biodegradability of the organic compounds [24] and for the enhancement of methane production when ultrasound technology was used prior to anaerobic digestion in the sludge [25].

Ozonation constitutes a promising method for the polishing of secondary effluents, due to its potential of degrading detrimental organic contaminants. Hence, it has been used for the removal of a large number of compounds such as pesticides, organochlorides, phenolic substances and dyes [26,27]. Moreover, ozonation has shown high COD removal on anaerobically treated molasses wastewater followed by aerobic treatment and therefore can be considered as an excellent way for COD removal [28].

However, limited efforts have been reported on the utilization of advanced oxidation processes for the enhancement of anaerobic digestion potential of wastewater with a high content of substances with low or even negligible biodegradability such as wastewater from the baker's yeast manufacturing with a high concentration of melanoidins.

The objectives of this work were the examination of the effect of ultrasound irradiation and ozonation on the anaerobic biodegradability and methane production rate of molasses wastewater, the investigation of the reduction potential of COD content and decolorization capacity of raw molasses effluents due to these processes, and the determination of the optimum experimental conditions for the achievement of an integrated process with the highest efficiency for the treatment of molasses wastewater. The objectives of this work are illustrated in Fig. 1.

2. Materials and methods

2.1. Ozonation and sonication experiments

Wastewater samples were collected from the effluent of a baker's yeast industrial plant. About 10 L of samples were collected in plastic bottles, and they were transferred to the laboratory for further analysis or treatment; samples were stored at 4 °C, prior to their usage.

Ozonation experiments took place at room temperature, in a 2 L bubble flow plexi-glass reactor, under various reaction times, ranging from 5 up to 300 min. The gas flow rate was adjusted at 4 L/min, the inlet ozone concentration was approximately 8.3 mg O_3/L gas, while ozone was produced by an ozone generator.

An ultrasonic homogenizer (SONOPLUS HD3400, BANDELIN, Germany) was used for the sonication experiments and the pretreatment of the samples. During sonication experiment, 500 mL of sample were added in a glass beaker and were treated at different conditions; sample temperature was monitored and was maintained at 25 °C using an ice bath. The operation conditions examined included: ultrasound power 400 W, ultrasound frequency 20 kHz, amplitude of the ultrasound waves 90% and 50%, contact time 30, 60, 90, 120 min, continuous or intermitted operation mode (pulsation time on–0.5 s, off-1 sec). In addition, SDS (Dodecyl hydrogen sulfate sodium salt, Merck) was added, at concentrations of 50 and 100 mg/L, in order to examine the effect of an anionic surfactant on reduction of organics concentration and on the enhancement of biodegradation potential.

2.2. Anaerobic biodegradation potential

A batch assay was carried out to determine the anaerobic biodegradation potential of different samples of pretreated wastewater, corresponding to the biochemical methane potential (BMP). The experimental setup for the determination of the BMP test consisted in 1 L glass bottles representing bench scale anaerobic reactors. The working volume of each glass bottle was 500 mL; in each reactor, an appropriate volume of anaerobic sludge was added in order to obtain a sludge: substrate ratio of 2:1 v/v. Anaerobic sludge was collected from the full scale anaerobic digester of the wastewater treatment plant of the baker's yeast industry. Each sample was carried out in three replicates in order to receive representative results.

Nevertheless, control reactors containing only sludge and water in the desired ratio were prepared aiming to the estimation of the background methane production due to organic matter content of the sludge itself. After inoculation of the sludge and the substrate in each reactor, the glass bottles were flushed with nitrogen gas to ensure anaerobic conditions, sealed with screw cap GL45, and finally were placed in an incubator operating at 37 ± 1 °C. Once per day the reactors were vigorously mixed by hand. All the reactors were operated for 35 days until no further biogas production was observed.

2.3. Analytical methods

Total and soluble COD content in each sample were determined by the Hach-Lange cuvette tests, along with a spectrophotometer (DR-2800). Soluble COD was determined by filtering the sample through a 0.45 μm filter. Total and volatile solids analysis carried out according to standard methods of analysis [29]. The pH of the samples was measured using a portable pH-meter (Nahita, model 902/4). The absorbance spectrum of each sample was measured by a UV–Vis spectrophotometer (Helios Alpha, Thermo Electron Corporation) at wavelengths from 200 to 800 nm, using quartz cells