Bioresource Technology 100 (2009) 6290–6294

Contents lists available at ScienceDirect

Bioresource Technology

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

Start-up procedures and analysis of heavy metals inhibition on methanogenic activity in EGSB reactor

I. Colussi, A. Cortesi *, L. Della Vedova, V. Gallo, F.K. Cano Robles

Department of Chemical, Environmental and Raw Materials Engineering (DICAMP), University of Trieste, P.le Europa 1, 34127 Trieste, Italy

ARTICLE INFO

Article history:
Received 3 March 2009
Received in revised form 15 July 2009
Accepted 18 July 2009
Available online 12 August 2009

Keywords:
Anaerobic digestion
EGSB
Heavy metals
Methanogenic inhibition

ABSTRACT

The effectiveness of operating an industrial UASB reactor, treating wastewater from the beer industry, with flows containing heavy metals was evaluated. A pilot-scale UASB reactor, already used to simulate the industrial reactor, was unsuccessfully employed. An easy start-up was obtained arranging it as an EGSB reactor. Considerations about this modification are reported. The effects of Cu(II), Ni(II) and Cr(III) ions on the anaerobic activity were analyzed by measurements of methane production rate and COD removal. The employed biomass was the sludge of the industrial UASB reactor, while a solution of ethanol and sodium acetate with COD of 3000 mg/L and a heavy metal concentration of 50 mg/L were continuously fed. Experimental results proved higher biomass sensitivity for copper and much slighter for nickel and chromium. Moreover, copper inhibition has been demonstrated to be less significant if a metal-free feed was provided to the system before copper addition.

1. Introduction

Anaerobic digestion is a process widely used for the decomposition of organic matter. It has been mainly employed for reducing sludge volumes in wastewater treatment plants, but also for the direct removal of organics from a high loaded wastewater. The more significant advantage of this process is that methane can be recovered as a by-product of the digestion.

According to the mass balance, methane gas accounting to 0.31–0.35 m^3 can be theoretically recovered from the digestion of 1 kg of COD (Chemical Oxygen Demand) (Pérez et al., 1997). However, the actual production of methane depends on pH and temperature changes and may be reduced by the presence of sulphates and other inhibitory or toxic substances in the influent feed (Pérez-García et al., 2005).

Several technologies have been employed which utilize anaerobic process for the wastewater treatment.

The up-flow anaerobic sludge blanket (UASB) technology was developed on the late 1970s in the Netherlands (Lettinga et al., 1980; Seghezzo et al., 1998), and nowadays it is employed for the treatment of industrial as well as domestic wastewaters (Kato et al., 1994a; Lettinga, 1996; Franklin, 2001; Tchobanoglous et al., 2003).

Critical elements of an UASB reactor are the influent distribution system, the gas solids separator and the effluent withdrawal design.

Above the sludge blanket, the reactor has a three-phase separator which separates the solid particles from the liquid and gas, allowing liquid and gas to leave the system separately. The three-phase separator consists of a series of upside–down "V" shaped baffles.

For developing sludge having good characteristics during primary start-up from flocculent inoculum sludge, organic loading rate and sludge loading rate should be in the range of 2.0–4.5 kg COD/m^3 d and 0.1–0.25 kg COD/kg VSS d, respectively (Ghangrekar et al., 2005). The pH should be maintained near 7.0 and a recommended COD:N:P ratio during start-up is 300:5:1 and during steady state could be 600:5:1 (Annachhatre and Amatya, 2000).

The up-flow velocity should be controlled to avoid wash out of the sludge. Also, it is recommended to work with a solids concentration greater than 6 g TSS/L for anaerobic digestion (Tchobanoglous et al., 2003).

A faster upward-flow rate is designed for the wastewater passing through the sludge bed of an expanded granular sludge bed (EGSB) (Kato et al., 1994b). The increased flux permits partial expansion (fluidization) of the granular sludge bed, improving wastewater/sludge contact as well as enhancing segregation of small inactive suspended particles from the sludge bed. The increased flow velocity is either accomplished by utilizing tall reactors, or by incorporating an effluent recycle (or both). The possibility of inducing granulation by switching from UASB to EGSB means that the up-flow velocity is apparently the key to granulation on domestic sewage.

Other equipments to be provided are for measurement of pH, temperature, influent flow rate, and gas production rate (Álvarez et al., 2006).

* Corresponding author. Tel.: +39 40 5583755; fax: +39 40 569823.
E-mail address: angelo.cortesi@dicamp.units.it (A. Cortesi).

0960-8524/$ - see front matter
doi:10.1016/j.biortech.2009.07.041

Anaerobic metabolism has shown to be strongly affected by the presence of metals (Mrafkova et al., 2003; Hullebusch van et al., 2004). Unlike many other toxic substances, heavy metals are not biodegradable and can accumulate to potentially toxic concentrations (Sterritt and Lester, 1980). The toxic effect of heavy metals is attributed to disruption of enzyme function and structure by binding of the metals with thiol and other groups on protein molecules or by replacing naturally occurring metals in enzyme prosthetic groups (Vallee and Ulner, 1972). A complete description of the factors controlling heavy metal inhibition is reported in a recent review (Chen et al., 2008).

Different metal toxicity values are reported in the literature: Lin and Chen (1999) demonstrated that the relative toxicity of metals follows the scale: Cu(II) > Cr(VI) > Cd(II) = Zn(II) > Ni(II) >> Pb(II), whereas in the study made by Codina et al. (1998), it was showed that the relative toxicity of metals in an anaerobic sludge toxicity bioassay was Zn(II) > Cr(VI) > Cu(II) > Cd(II) > Ni(II) > Pb(II).

This research addresses the feasibility of the EGSB process for treatment of industry wastewater containing chromium(III), copper(II) and nickel(II) as metal pollutants.

Purpose of the study was to evaluate the effectiveness, for an industrial UASB reactor (3000 m^3) treating wastewater from the beer industry, to operate with flows containing heavy metals, as industrial wastewater and landfill leachate.

A pilot-scale UASB reactor, designed and already used to simulate the industrial reactor for a whole year, was unsuccessfully employed: the presence of heavy metals and the consequent biomass inhibition made impossible its start-up. It was then modified and arranged as an EGSB reactor, which permitted an easy start-up and the running of tests for the study of heavy metal effects on the anaerobic digestion.

Biomass inhibition was investigated by monitoring methane gas flow and the removal of the organic matter with COD analysis.

2. Methods

The employed UASB and EGSB configurations are reported in Fig. 1.

The sludge was acquired from an industrial size (3000 m^3) UASB reactor (San Giorgio di Nogaro – Udine, Italy) treating wastewater from the beer industry.

Two start-up procedures were attempted with the UASB device obtaining scarce COD removal and negligible methane production after one month. The UASB reactor, with a useful volume of 61 L, was modified in the EGSB configuration (see dotted lines in Fig. 1) by a recycle basin to increase the average hydraulic retention time HRT from 35 to 49 h: a pH control of the recycle was implemented by using a NaOH dosing system (Seghezzo et al., 1998). The third start-up was carried out using a recycle with an effective volume of 15 L.

Macronutrients and micronutrients were continuously supplied in each start-up. The main components of the synthetic wastewater (macronutrients) were ethanol and sodium acetate. These compounds were selected because are very easy to digest by the bacteria and their metabolism to produce biogas is faster than with more complex molecules.

To ensure microorganisms growth, other micronutrients as nitrogen, iron, potassium, sulphates, phosphorus, calcium, cobalt and some trace minerals, are needed: a dosage of 5 mL of a micronutrients solution (NH_4Cl, 65 g/L; $FeCl_3$, 1.162 g/L; K_2HPO_4, 29 g/L) per Liter of synthetic wastewater was then provided.

Once more 250 mg/L of Na_2SO_4 and 0.5 g/L of $NaHCO_3$ were added. Notice that even though the sodium and sulphates are needed, the use of Na_2SO_4 contributes to diminish the COD removal efficiency, and as a consequence the biogas production: then, in the experiment, it was expected to obtain a 5% less biogas than the theoretical value.

$NaHCO_3$ was added (on the third start-up) in order to maintain a proper buffering capacity in the medium (due to the acidification observed on the start-up 1 and 2).

Experiments were carried out using the EGSB configuration of the third start-up. By means of a thermostatic jacket, temperature inside both the reactor and the recycle basin was kept constant at 37 °C (±0.1 °C). Experiments lasted for 67 days with an average hydraulic retention time (HRT) of 49 h. Feed had 3000 mg/L of COD with an average flow rate of 1.57 L/h, constant for all the experiment. The up-flow velocity was 0.05 m/h, and the Organic Loading Rate (OLR) was 1.853 kg COD/(m^3 d).

As metal pollutants $CrCl_3 \cdot 6H_2O$, $CuSO_4$ and $NiCl_2$ were used with a concentration of 50 mg/L for each metal ion.

The experiments were carried out in two phases: the first one, 26 days long, in which 43 L of activated anaerobic sludge were filled with a value of 22.2 g TSS/L, and the second one, 41 days long, with 40 L of active sludge with 36 g TSS/L. The active sludge had a 45% of TVS in both cases.

2.1. Analysis

COD concentration was measured using the colorimetric determination: influent, effluent and the liquid inside the recycle basin were analyzed. pH values were measured, by a HANNA HI6291005 pH meter, inside the reactor at different levels to locate the digestion steps. A second pH meter, ENDRESS-HAUSER LIQUISYS CPM 221, was placed inside the recycle tank for an automatic pH control by means of a NaOH 1 M solution.

Biogas was collected at the top of the reactor and it led through a sealed container filled with NaOH 1 M, to remove CO_2 from the biogas. Subsequently, the gas passed through a BRONKHORST™ Hi Tech Flow meter, certified to measure CH_4 at standard conditions (0 °C, 101.325 kPa).

To see how heavy metals inhibited the methane production, the Methanogenic Inhibition percentage (%MI) was calculated as follows:

$$\%MI = 1 - \frac{CH_{4_{w/metals}}}{CH_{4_{wout/metals}}} \cdot 100$$

where $CH_{4w/metals}$ is the minimum value of the methane rate achieved during ethanol and acetate degradation in the presence of metals and $CH_{4wout/metals}$ is the methane rate generated during nutrients supply without metals (steady state condition).

3. Results and discussion

3.1. UASB configuration: start-up 1 and 2

The first attempt to start-up the UASB reactor was with an inoculum of 16 liters of activated anaerobic sludge. The feed was composed of sugar, butyl acetate, ethanol and sodium acetate to reach an influent concentration of 10000 mg/L of COD. During 24 days of continuous operation, less than 50% of average COD removal was observed, on the final 5 days the performance dropped to 20% removal and no methane production was detected (see Fig. 2). The sugar, ethanol and sodium acetate were completely converted to fatty acids or acetate. So the pH lowered to a value near 4.5 which is completely inadequate for methanogenic bacteria.

After the pH problems on the first phase, the feed was changed and composed only of rapidly soluble COD, as ethanol and acetate, but remaining the COD near the value of 10000 mg/L.

For this second attempt to start the UASB, the pH value was the main controlled feature. Again the average COD removal was really