Chemical Engineering Journal 231 (2013) 206–213

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Disintegration and acidification of MBR sludge under alkaline conditions

Hongguang Yu, Zhiwei Wang *, Qiaoying Wang *, Zhichao Wu, Jinxing Ma

State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China

HIGHLIGHTS

- Alkaline pH values greatly enhanced disintegration and VFA production of MBR sludge.
- The optimal condition for VFA production was under pH 11.0 and digestion time 4 d.
- High pH stimulated organic matter transfer from the inner to the outer of microbes.
- Bound EPS were involved in organic matter transformation and VFA production.

ARTICLE INFO

Article history:
Received 16 January 2013
Received in revised form 1 July 2013
Accepted 7 July 2013
Available online 16 July 2013

Keywords:
Membrane bioreactor
Sludge disintegration
Sludge acidification
Waste activated sludge
Wastewater treatment

ABSTRACT

The effects of alkaline treatment on sludge disintegration and acidification under anaerobic conditions were investigated in order to explore potential use of waste activated sludge (WAS) discharged from membrane bioreactors (MBRs). During the 12-day anaerobic digestion process, it was observed that volatile fatty acids (VFAs) production was greatly improved by alkaline treatment. The optimal conditions for VFA production of MBR sludge were under pH 11.0 and digestion time 4 d, and specific VFA production could reach about 219.7 mg COD/g VSS. Compositions of VFAs at pH 11.0 showed that acetic acid was the most prevalent product. Meanwhile, test results indicated that sludge hydrolysis and nutrient release were enhanced at alkaline pH values. Alkaline treatment stimulated organic matter (e.g., proteins and carbohydrates) to penetrate through cell membranes, transferring from the inner to the outer of microbes. It was also found that bound extracellular polymeric substances (EPS) played an important role in mass transfer and VFA production during sludge disintegration and acidification.

1. Introduction

Membrane bioreactor (MBR) processes have been drawing more and more attention for wastewater treatment during the past decades. Thousands of MBR plants are currently in operation over the world [1]. Moreover, the MBR market has been expanding at an average annual growth rate of approximately 10.9%, immensely faster than other advanced wastewater treatment technologies [2]. Compared with conventional activated sludge (CAS) processes, waste activated sludge (WAS) yield is lower in MBR processes [3]. However, with the dramatic increase of MBR plants, the treatment and disposal of excess sludge of MBRs still remains difficult.

For WAS treatment, anaerobic digestion is widely applied for reduction, resource recovery and detoxification. Three stages, i.e., disintegration (hydrolysis), acidification, and methane production, are included in the process. Disintegration and acidification can change particulate organic substances into soluble carbon compounds, especially volatile fatty acids (VFAs) [4]. Acidification is an important step prior to fuel gas production, and the produced VFAs can be further partially converted to H_2 or CH_4 in anaerobic digesters. In addition, VFAs, without further conversion to fuel gases, can be directly used as carbon source for biological nitrogen and phosphorous removal [5,6]. In this way, wastewater treatment plants (WWTPs) can resolve the shortage of carbon source and disposal of excess sludge simultaneously in a feasible and economical way.

VFA production can be affected by a series of factors, including pH [7–9], temperature [10,11], sludge type [12], C/N ratio [13,14], and solids retention time (SRT) [15]. Previous researches seem to reach a consensus that sludge digestion can be significantly affected by pH values [7–9], and VFA production is enhanced under alkaline conditions. However, sludge samples in above-mentioned studies, regardless of primary or secondary sludge, were all collected from CAS processes. To date, information on the use of MBR sludge for VFA production has been very limited. Compared to CAS systems, sludge characteristics in MBRs are greatly varied due to the fact that MBRs always adopt long SRT and low food/microorganisms (F/M) operation. Generally speaking, MBR sludge contains high biomass concentration and relatively low content of organic matter, which is less biodegradable [16]. It is necessary

* Corresponding authors. Tel./fax: +86 (21)65980400.
E-mail addresses: zwwang@tongji.edu.cn (Z. Wang), wqy-tj@163.com (Q. Wang).

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http://dx.doi.org/10.1016/j.cej.2013.07.012

to explore potential economical treatment pathways for MBR sludge.

The purpose of this work is, therefore, to explore possible method for MBR sludge treatment. The effects of alkaline treatment on sludge disintegration and acidification for VFA production were investigated. Soluble chemical oxygen demand (SCOD) production, biomass reduction, nitrogen and phosphorous release, distribution and transformation of proteins and carbohydrates under different pH values were evaluated to in order to gain an overall understanding on the anaerobic treatment of WAS from MBRs. In addition, the VFA-production mechanisms were further discussed.

2. Materials and methods

2.1. MBR sludge

The sludge used in this study was collected from the aeration tank of a full-scale submerged MBR for municipal wastewater treatment. The operating conditions of this MBR plant were as follows: food/microorganisms (F/M) was 0.07 kg COD/(kg MLSS d), hydraulic retention time (HRT) was 4.1 h, and solids retention time (SRT) was 20 d. The sludge characteristics are listed in Table 1. As shown in Table 1, SCOD in the sludge accounted for only 0.2% of the total COD, indicating that the majority of organic matter was in particulate form. Meanwhile, proteins and carbohydrates were the two major types of organic components in sludge, which accounted for 54.8% and 22.0% of the volatile suspended solids (VSS), respectively.

2.2. Batch digestion experiments

Six identical lab-scale anaerobic digesters, were operated at constant temperature (25 ± 1 °C). The reactors were made of plexiglass and the working volume of each was 4 L. Twenty-four liters of MBR sludge was divided equally into the 6 reactors, and no inoculums were added. Each reactor was mechanically stirred at a speed of 50 rpm to maintain homogenous mixing, and kept sealed during the experiments. From reactors 1–5, the pH was maintained at 8.0, 9.0, 10.0, 11.0 and 12.0, respectively, which was adjusted by adding 2 mol/L sodium hydroxide (NaOH) during the whole experiment. The reactor 6, in which the pH was not adjusted, was set as the control test. After start-up, sludge samples were collected from the reactors periodically for the analyses of VFAs, COD, total suspended solids (TSS), volatile suspended solids (VSS), carbohydrate, protein, ammonia nitrogen (NH_4^+-N) and soluble ortho-phospate (PO_4^{3-}-P). Fermentation time of the experiments was set at 12 d. The experiments were conducted in duplicate, and one way analysis of variance (ANOVA) at the 0.05 level was used to analyze the data.

2.3. Extraction of organic matter

In order to investigate the variations and distributions of organic matter during the disintegration and acidification of MBR sludge, organic matter of biomass was divided into three parts, i.e., dissolved organic matter (DOM), bound extracellular polymeric substances (EPS) and intracellular polymeric substances (IPS). Bound EPS was extracted with a modified thermal treatment method [17,18]. The extraction procedures were conducted as follows. After taken from the reactors, sludge samples were immediately centrifuged at 6000 rpm for 10 min. The supernatant was filtered through a glass fiber syringe filter (Membrane Solutions LLC., 1.0 μm pore size). The organic matter in the filtrate was regarded as DOM. The bottom sediments were re-suspended to their original volume with a phosphate-buffered saline (PBS [0.790% NaCl, 0.020% KCl, 0.142% Na_2HPO_4 and 0.024% KH_2PO_4]). The mixed liquor was then subject to heat treatment (60 °C, 1 h) and centrifuged again at 6000 rpm for 15 min. The bulk solution was filtered with the aforementioned glass fiber syringe filter, and the organic matter in the filtrate represented bound EPS. The residues were the pellet fraction of mixed liquors, in which the organic matter was IPS.

2.4. Analytical methods

The analyses of COD, TSS, VSS, NH_4^+-N and PO_4^{3-}-P were conducted in accordance with Chinese NEPA standard methods [19]. Capillary suction time was tested by a capillary suction timer (Model 304M CST, Triton Electronics Ltd., England). Carbohydrate was determined by the Anthrone method [20] with glucose as the standard reference, and proteins was measured by the modified Lowry method [21] with bovine serum albumin (BSA) as the standard reference.

To analyze VFA, 3% H_3PO_4 was added into the DOM samples to adjust the pH to approximately 4.0, and then the liquor was put in a 1.5 mL gas chromatography (GC) vial. The compositions of VFA were determined using gas chromatography (Agilent 6890N GC) equipped with flame ionization detector (FID) and DB-WAXetr column (30 m × 530 μm × 1 μm). Nitrogen was the carrier gas and make-up gas, of which the flowrate was 6.4 mL/min and 25.0 mL/min, respectively. The injection port and the detector were maintained at 200 and 220 °C, respectively. The oven of GC was set to begin at 55 °C and to remain the status for 1 min, then to increase at a rate of 30 °C/min to 110 °C, to hold at 110 °C for an additional 1 min, then to increase at a rate of 10 °C/min to 200 °C, then immediately to increase at a rate of 30 °C/min to 220 °C, and to hold at 220 °C for an additional 1 min. The sample injection volume was 1.0 μL.

3. Results and discussion

3.1. VFA production

Fig. 1 illustrates the effect of alkaline pH on total VFA production during the experiments. In this study, six VFAs, i.e., acetic, propionic, iso-butyric, *n*-butyric, iso-valeric, and *n*-valeric acids, were calculated on basis of COD via multiplying their concentration by 1.07, 1.51, 1.82, 1.82, 2.04 and 2.04, respectively, and total VFAs are the sum of all the individual VFAs. In the raw sludge, the initial total VFAs was 8.1 ± 1.9 mg COD/L (data not shown in Fig. 1), and acetic acid was the only composition of VFAs. As shown in Fig. 1, during the 12-day digestion, total VFA concentrations in reactors 1–5 were higher than that of the control test, but the changing patterns of VFA concentrations were different. VFA accumulated with time at strong alkaline pH values (pH 11.0 and pH 12.0); however,

Table 1
Characteristics of the MBR sludge.[a]

Parameter	Content
pH	7.0 ± 0.1
Capillary suction time (s)	18 ± 2
Total suspended solids (mg/L)	11,748 ± 647
Volatile suspended solids (mg/L)	7090 ± 326
Total COD (mg/L)	11,576 ± 723
SCOD (mg/L)	28 ± 4
Total proteins (mg/L)	3886 ± 46
Total carbohydrates (mg/L)	1561 ± 25
NH_4^+-N (mg/L)	3.7 ± 0.3
PO_4^{3-}-P (mg/L)	6.3 ± 3.0

[a] The data were tested in duplicate and given as mean value ± standard deviation.