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Crater formation on anaerobic granular sludge

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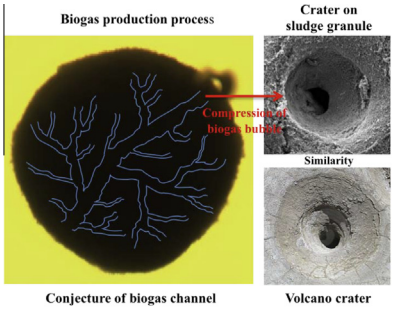
HIGHLIGHTS

- Crater results from a balance between mechanical resistance and Laplace compression.
- Crater's diameter is related to the size of principal gas channel.
- Mechanical strength of granule and Laplace compression of bubble are close in order of magnitude.
- Small channels in a granule serve as transportation of substrate and microbubbles.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic granular sludge plays an important role in high-rate anaerobic reactors for the improvement of wastewater treatment efficiency. The structure of granules is closely related to the mass transfer process and anaerobic biodegradation process. The current work aims at gaining an insight into the mechanism of crater formation during biogas production and then deepening the understanding of complex granule structure. The crater results mainly from the compression of biogas bubble and is relevant to the size of gas pore to some extent. The exerted compression pressure on a granule is estimated by the Young–Laplace equation and compared favorably with the mechanical strength of granule measured by penetrometer. As porous materials, extremely small channels at nano- and micro-scale are well developed inside of sludge granule in favor of substrate transportation and biogas production.

1. Introduction

Through progressive evolution in the past four decades, anaerobic treatment of organic wastewater becomes a quite mature technology nowadays, which not only reduces the organic pollution but also recovers biogas as a renewable clean energy [1–3]. Especially, high-rate anaerobic reactors based on anaerobic granular sludge, such as internal circulation (IC) reactor, expanded granular sludge bed (EGSB) reactor, greatly shorten the hydraulic retention time and improve the treatment efficiency simultaneously. To date, there are considerable studies on the anaerobic granular sludge. A part of them mainly focused on the mechanism of nucleation [4], granulation [5–7] and disruption [8]. Another part was devoted to physicochemical characteristics [9], such as morphology [10], porosity and permeability [11,12], settleability [13], extracellular polymer substances (EPS) [14] and so on.

The structure of anaerobic granular sludge plays an important role in the mass transfer and biodegradation process inside of the granules. However, the interior structure of CH_4-producing anaerobic granules received limited attentions up to now. In the early 1990s, a multi-layered microbial architecture was initially

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proposed for the structure of anaerobic granules [15,16]. But some other authors found that the granules were homogenous without a multi-layered structure [17,18], as well as a cluster structure revealed in anaerobic aggregates from an EGSB reactor fed with ethanol [19]. These contradictive observations were due to the properties of different substrates in wastewater [20,21]. The microbial structures were largely determined by the kinetics of substrate degradation [22]. Afterward, advanced analysis techniques such as fluorescent *in situ* hybridization (FISH) and confocal laser scanning microscopy (CLSM) were applied to explore the internal structure of anaerobic granule [23,24].

As a porous matter, pores, channels and cavities exist in granules and facilitate the transport of nutrients and metabolites. Pores were commonly observed on the granule surface. Channels play a role of bridge to connect outside pores and inside cavities. In the previous works, a cascade structure of channel distribution was proposed in which fine channels gradually converged into bigger ones [25]. In the core of anaerobic granules, a large number of cavities were visible [26] and their forms were similar to the honeycomb appearance [27]. These cavities were probably the interior gas vents for biogas production. In addition to CH_4-producing granule, such pores, channels and cavities exist also in anaerobic H_2-producing granules [28], Anammox granules [29] and aerobic granules [30]. These works revealed the complex interior structure of granules. Nevertheless, the knowledge about granule structure is still deficient, especially in the form of pore for biogas production.

The present work aims at gaining new insight into the crater formation mechanism during biogas production and then deepening the understanding of granule structure. As the main exit channel for produced biogas, the crater formation reflects then the process of biogas production. In addition, a cavity structure like crater could induce mechanical fragility to some extent depending on the integrity of granules. Therefore, it is crucial to study the crater formation, which wasn't reported yet in the literature on account of opacity in industrial processes or even at bench scale reactors. The mechanism of crater formation might be similar to that of various craters that appear in nature and physical experiments [31–35]. A single granule was fixed in a micro-device under batch conditions to investigate the appearance and growth of biogas bubbles and to select granules actively producing biogas as well. Selected granules were examined by a scanning electron microscope (SEM). A crater could be obviously observed at the exit of gas pore. To our best knowledge, it is the first time that a crater is detected on an anaerobic granular sludge. It appeared once in a tremendous amount of SEM images but didn't attract the authors' attention [36].

2. Materials and methods

2.1. Granular sludge

Anaerobic sludge granules were sampled from an EGSB reactor treating starch wastewater and conserved in a brown glass bottle of 1 L at static condition in the laboratory. They were fed with fresh glucose and sodium bicarbonate solution everyday before subsequent experiments. The detailed substrate composition and concentration were described in the previous work [37].

2.2. Surface tension

The surface tension of biogas was measured by a dynamic tensiometer (n° Tracker, IT Concept, France). For gas phase, different proportions of methane and carbon dioxide were composed of pure methane and pure carbon dioxide to investigate the influence of methane percentage that varied in real biogas. The potential influence of trace composition in biogas, such as hydrogen and hydrogen sulfide, on the surface tension wasn't investigated in this work. For liquid phase, distilled water, glucose and sodium bicarbonate solution with different concentrations of chemical oxygen demand (COD) were respectively employed.

2.3. Mechanical resistance

The mechanical resistance measurement of a single granule against an orthogonal compression was realized by a penetrometer (n° 5569, Instron, USA), equipped with a cylindrical needle of diameter 3 mm and a force sensor in the range of 0–10 N. The displacement velocity of the needle was set at 10^{-4} m/s. Thirty randomly selected granules were sampled to compute a mean value.

2.4. Biogas production in a micro-device

An integral granule was placed in the center of a micro-device at 35 °C and fed with above-mentioned glucose and sodium bicarbonate solution that had been filtered through a 0.22 μm microfiltration membrane to remove impurities. The micro-device was a parallelepiped cellule made of transparent Plexiglas with the following dimensions: 40 mm length, 15 mm width and 3 mm height. It was horizontally placed under a stereomicroscope (Motic K700, China) equipped with an online digital camera (Moticam 3000, China). The images of the granule as well as produced biogas bubbles were regularly acquired at a fixed time interval. The average biogas production rate can be estimated, about 5×10^{-4} mL/h per granule. The granule possesses a mass ranging from 4.5 to 6.5 mg and contains 12% solid content approximately.

2.5. SEM

About fifty integral granules that actively produced biogas were selected as samples for the SEM observation. Firstly, selected granules were fixed overnight in a buffer solution of 0.1 mol/L sodium phosphate (pH 7.2) with 2.5% volume percent glutaraldehyde. Granules were then washed thrice in sodium phosphate buffer solution for 45 min, dehydrated through a graded series of ethanol solution (30%, 50%, 70%, 85% and 95% ethanol) successively once for 15 min and through 100% ethanol thrice for 45 min. Drying was achieved in a critical point dryer (BalTec, CPD 030, Finland). Granules were coated with Au in a sputter coater (BalTec, SCD 005, Finland). Finally, the specimens could be examined and photographed with a SEM (FEI, Quanta 200, USA).

2.6. Porosity

The preparation for porosity measurement was the same as that for SEM observation except for the coating step. It is worth noting that potential formation of cracks during the drying process might inevitably affect accurate measurements of pore volume. Then the sample granules were measured by a mercury porosimeter (Micromeritics, AutoPore IV 9500, USA). The pore size can be determined based on the external pressure needed to force the mercury into pores against the opposing surface tension of liquid, namely the application of Washburn's equation where the cylindrical channels were assumed. The measurable pore diameter ranges from 0.003 to 420 μm. The corresponding volume at each channel diameter can be acquired according to progressively increasing quantity of injected mercury. As dry granule samples were analyzed, a linear shrink coefficient δ was used to reduce the error [30]. It was defined by

$$\delta = 1 - D_{dry}/D_{wet} \quad (1)$$