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Effect of membrane wettability on membrane fouling and chemical durability of SPG membranes used in a microbubble-aerated biofilm reactor

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ABSTRACT

Shirasu porous glass (SPG) membranes have been applied for microbubble aeration in aerobic wastewater treatment successfully. In the present study, both hydrophilic and hydrophobic SPG membranes were used for microbubble aeration in a biofilm reactor with online chemical cleaning, and their membrane fouling and chemical durability were determined to be strongly membrane wettability dependent during a long-term operation. The fouling layer formed on the surface of both membranes was attributed to organic fouling mainly, and the hydrophobic membrane showed a stronger resistance to the organic fouling. The severe chemical corrosion of the hydrophilic membrane due to exposure to the alkaline solution used for chemical cleaning was observed, and as a result, its median pore diameter and porosity increased significantly. On the other hand, the pore structure of the hydrophobic membrane changed slightly when exposed to the alkaline solution, suggesting its strong alkali-resistance due to the non-wetting surface; but its surface hydrophobic groups could be oxidized, making membrane surface more wettable. The hydrophobic membrane also showed more efficient performance in the respects of oxygen transfer, contaminant removal and energy-saving. Therefore, the hydrophobic membrane seems more appropriate to be applied for microbubble aeration in aerobic wastewater treatment.

1. Introduction

Microbubbles provide the enhanced gas–liquid mass transfer due to their useful characteristics, including large gas–liquid interfacial area, long residence time in the liquid phase and fast dissolution rate. In recent years, microbubble technologies have drawn great attention due to their wide applications in many fields of science and technology, including wastewater treatment [1]. Most reported applications of microbubble technologies for wastewater treatment focus on physical–chemical treatment processes at present and the enhancement of ozone and oxygen gas–liquid mass transfer in microbubble aeration has been confirmed [2–6].

The aerobic biological treatment process is commonly utilized for wastewater treatment where the contaminant digestion depends on the available dissolved oxygen (DO). The fast oxygen supply rate is required to promote the aerobic biochemical reaction because of oxygen feed limitation. Therefore, a highly efficient oxygen supplier and more useful aerobic wastewater treatment system are expected. Some microbubble aerators have been developed for aerobic wastewater treatment to increase oxygen transfer rate [7]. However, almost all microbubble aerators cause a damage to activated sludge, resulting in broken sludge flocs and poor sludge settleability [7,8], so that it is difficult to apply microbubble aeration in the activated sludge-based bioreactors. On the other hand, microbubble aeration has been applied successfully in a biofilm reactor using a Shirasu porous glass (SPG) membrane system, where the oxygen utilization efficiency was achieved as high as close to 100%, much higher than that in conventional aeration processes [9].

SPG membrane is a kind of porous glass membrane which is prepared based on phase separation and subsequent acid leaching [10]. SPG membranes find many applications as a dispersion medium in both membrane emulsification [11–13] and gas dispersion process [14–18] for the formation of uniformly sized droplets, and microbubbles. Briefly, a dispersed phase is permeated into a continuous phase through the uniform pores of a SPG membrane: in the gas–liquid dispersion system, the gas phase is forced through the porous membrane into the continuous liquid phase and uniform-sized microbubbles are formed from the inner surface

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of the membrane. In this dispersion process, microbubble formation mainly consists of the following three processes: (1) microbubble formation across the pore; (2) microbubble growth; and (3) microbubble detachment. The prominent advantage of this technique is that the resultant bubble size and void fraction are mainly determined by the membrane pore size and membrane area, respectively. This indicates that bubble size and void fraction can be optimized for a large-scale application. The SPG membrane surface is inherently hydrophilic due to the presence of hydroxyl groups such as silanol groups. On the other hand, the surface of SPG membranes can be hydrophobized by chemical modification with organosilane compounds. The microbubble generation and the gas–liquid mass transfer are proven to be influenced by SPG membrane wettability. The larger microbubbles with a broad diameter distribution would be generated from a hydrophobic SPG membrane, compared to a hydrophilic SPG membrane with the same pore diameter [16]. In addition, the resistance to gas mass transfer in a hydrophilic SPG membrane is much stronger than that of a hydrophobic SPG membrane because of the presence of water in the pores [19].

Membrane fouling is one of the main problems in many membrane applications. For inorganic membranes used in wastewater treatment, inorganic deposition, organics adsorption and biofilm growth are considered to be responsible for membrane fouling [20–23]. When SPG membranes were used for oil emulsification or demulsification process, the membrane fouling was observed as a consequence of the accumulation of oil drops on the membrane surface and inside the pores [24,25]. SPG membrane fouling caused by the protein adsorption was also reported [26]. When a hydrophilic SPG membrane was used for microbubble aeration in a biofilm reactor, the external membrane fouling was observed, which would deteriorate microbubble generation and oxygen mass transfer [27]. The thermal treatment is recommended for off-line membrane cleaning by the manufacturer, which was confirmed to be effective to remove organic foulants [27]. Moreover, the periodic chemical cleaning is needed to control the development of SPG membrane fouling. Although chemical cleaning is considered to be an integral part of a membrane process operation, it may damage the membrane material due to limited membrane resistance to chemical corrosion, resulting in reduced membrane performance and lifetime [28,29]. The chemical resistance of SPG membranes is still poor understood, especially when a chemical membrane cleaning is employed during a long-term operation. It is expected that membrane fouling and chemical durability of a SPG membrane should be influenced by its surface properties such as wettability, but this is still unclear.

In this study membrane fouling of hydrophilic and hydrophobic SPG membranes used for microbubble aeration in a biofilm reactor was observed and characterized after a long-term operation, to investigate the effect of surface wettability on membrane fouling. In addition, the sodium hypochlorite solution and the hydrochloric acid solution were used for online chemical cleaning during the long-term operation. Then surface properties and pore structure of both SPG membranes employed were observed and characterized after a frequent exposure to these chemical solutions to compare their chemical durability.

2. Materials and methods

2.1. SPG membranes

Two types of tubular SPG membranes obtained from SPG Technology Co., Ltd. (Miyazaki, Japan) were used in this study, including a hydrophilic membrane (PJ-500-006N) with the pore size of 0.6 μm and the contact angle of 27°, and a hydrophobic membrane (PJ-500-006U) with pore size of 0.6 μm and the contact angle of 107°. The SPG membrane is prepared by phase separation of the mother glass in the Na_2O–CaO–MgO–Al_2O_3–B_2O_3–SiO_2 system, which can separate into an acid-insoluble (silica-rich) phase and an acid-soluble (borate-rich) phase. The SPG membrane contains SiO_2 of about 70 wt%, Al_2O_3 of 10–15 wt%, and other components [14]. The detailed preparation procedure of SPG membranes has been described elsewhere [10]. The hydrophobic SPG membrane is prepared by surface chemical modification with organosilane compounds.

2.2. Experimental set-up

Fig. 1 depicts schematic of a biofilm reactor with a SPG membrane microbubble aeration system. The new hydrophilic or hydrophobic membrane was used to generate air microbubbles for aeration. The gas–liquid dispersion system consisted of air as the dispersed gaseous phase and the mixed liquor in the reactor as the continuous water phase. A continuous water phase was flowed inside the membrane at a velocity of 0.73–1.08 m/s, corresponding to a Reynolds number range of 1.01×10^4 to 1.49×10^4, while the compressed air was introduced on the outside and forced through the membrane pores to form microbubbles in the water phase. The air flux was controlled at a range of 1.15×10^{-3} $m^3/(m^2\ s)$ to 1.51×10^{-3} $m^3/(m^2\ s)$. The diameter range of most generated microbubbles in clean water was determined as 20–60 μm under these conditions, based on microscope observation and measurement [4]. The average microbubble diameters were determined statistically as 31.1 μm for the hydrophilic membrane and 41.7 μm for the hydrophobic membrane, respectively.

The reactor was a transparent plexiglass tank with a diameter of 250 mm and a depth of 600 mm. The work volume of the reactor was 15 L. The commercial polypropylene ball filled with porous polyurethane cubes with the volume of 3.2 cm^3 and the pore size of about 1.5 mm (Shengxing, China), were used as carriers in the reactor to support biofilm growth. The diameter of these balls was 8.0 cm and the carrier filling was about 27% in the reactor.

2.3. Experimental procedure

The activated sludge from a municipal wastewater treatment plant was used as a microbial biomass inoculum for seeding the reactor at an approximate concentration of 0.8 g/L during the start-up period to promote biofilm formation on the carriers. A usual air distributor was used at this stage to aerate the reactor and a synthetic wastewater was fed into the reactor at an organic loading rate of 0.41 kgCOD/(m^3 d). Glucose, starch, peptone, NH_4Cl and KH_2PO_4 were the main constituents in the synthetic wastewater to provide carbon, nitrogen and phosphorus sources [30]. Synthetic wastewater was prepared daily and kept in a refrigerator to avoid degradation. The start-up of the reactor was considered to be completed when the biofilm biomass on the carriers reached up to 0.8 g/L. After that, microbubble aeration using the hydrophilic or hydrophobic SPG membrane was applied for the following long-term operation.

The synthetic wastewater mentioned above was treated in the microbubble-aerated biofilm reactor and the operating conditions were identical for both types of the membranes used during the long-term operation, as shown in Table 1. The synthetic wastewater had an average chemical oxygen demand (COD) of 385.7 mg/L. Feed wastewater was pumped to the reactor continuously and the effluent from the bottom of the reactor was controlled by a valve. The reactor was operated at room temperature.

Two chemical solutions, including the sodium hypochlorite solution (1000 mg/L, pH > 11) and the hydrochloric acid solution (0.5 mol/L), and water, were successively circulated inside the