Bioresource Technology 152 (2014) 101–106

Contents lists available at ScienceDirect

Bioresource Technology

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

Effects of suspended titanium dioxide nanoparticles on cake layer formation in submerged membrane bioreactor

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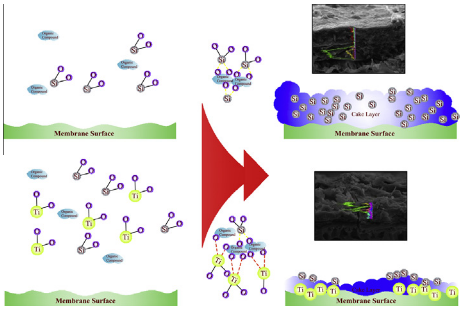
HIGHLIGHTS

- Effects of suspended TiO_2 nanoparticles on cake layer formation in MBR were studied.
- TiO_2 NPs aggravated membrane pore blocking but postponed cake layer fouling.
- TiO_2 NPs affected the distribution of the organic and the inorganic in cake layer.
- Line-analysis and dot map of EDX were firstly used to identify cake layer structure.
- Element distribution of cross-section cake layer, especially inner, was disclosed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 September 2013
Received in revised form 30 October 2013
Accepted 2 November 2013
Available online 12 November 2013

Keywords:
Membrane bioreactor
Titanium dioxide nanoparticles
Cake layer
Membrane fouling

ABSTRACT

Effects of the suspended titanium dioxide nanoparticles (TiO_2 NPs, 50 mg/L) on the cake layer formation in a submerged MBR were systematically investigated. With nanometer sizes, TiO_2 NPs were found to aggravate membrane pore blocking but postpone cake layer fouling. TiO_2 NPs showed obvious effects on the structure and the distribution of the organic and the inorganic compounds in cake layer. Concentrations of fatty acids and cholesterol in the cake layer increased due to the acute response of bacteria to the toxicity of TiO_2 NPs. Line-analysis and dot map of energy-dispersive X-ray were also carried out. Since TiO_2 NPs inhibited the interactions between the inorganic and the organic compounds, the inorganic compounds (especially SiO_2) were prevented from depositing onto the membrane surface. Thus, the postponed cake layer fouling was due to the changing features of the complexes on the membrane surface caused by TiO_2 NPs.

1. Introduction

With the rapid development and application of nanotechnology, nanoparticles (NPs) are now widely applied in industrial products (Nel et al., 2006). Particularly, titanium dioxide nanoparticles (TiO_2 NPs) have been widely used in catalysts, sunscreens, cosmetics and coatings (Kim and Van der Bruggen, 2010; Lu et al., 2008; Mu and Chen, 2011; Zhao and Chen, 2011; Zheng et al., 2011). However, these extensive applications of TiO_2 NPs inevitably induce their environmental release (Zhao and Chen, 2011; Zheng et al., 2011). Recently, TiO_2 NPs have been found to be present in air, soil,

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http://dx.doi.org/10.1016/j.biortech.2013.11.006

sewage as well as sludge from wastewater treatment processes (Zheng et al., 2011). Thus their potential health and environmental effects have attracted great concerns (Lu et al., 2008; Zhang et al., 2012). Concerns have also been raised about the toxicity of TiO_2 NPs in human and organisms at mg/L (Kalive et al., 2012). Currently their potential effects on certain bacteria in the activated sludge of wastewater treatment plants (WWTPs) have been considered and studied. Zhao and Chen (2011) reported that TiO_2 NPs improved the decomposition of protein and polysaccharide to small molecule organic compounds and promoted the growth of photosynthetic bacteria during hydrogen production from waste activated sludge. Zheng et al. (2011) showed that 50 mg/L of TiO_2 NPs significantly decreased total nitrogen (TN) removal efficiency after long-term exposure, but they had no chronic effect on biological phosphorus removal. Hence, TiO_2 NPs might influence the microbial activity in membrane bioreactors (MBRs).

As the major obstacle for MBR application, membrane fouling is mainly attributed to cake layer formation on the membrane surface (Guo et al., 2012; Johir et al., 2013; Meng et al., 2007, 2009; Wang and Wu, 2009). Foulants in cake layer can be classified into two categories: the organic and the inorganic (Meng et al., 2007). Organic compounds, such as soluble microbial products (SMP) and extracellular polymeric substances (EPS), have aroused a wide concern in cake layer formation. Chen et al. (2006) reported that α-polysaccharide was an important contributor to the initial cake layer formation. Protein and β-polysaccharide built up the remaining part of the cake layer. Regarding inorganic compounds, they play an important role in cake layer formation through crystallization and particulate fouling (Guo et al., 2012; Wang and Wu, 2009). Meng et al. (2009) also pointed out that inorganic compounds of wastewater were in close relation with the formation of precipitation and cake layer. Generally, the inorganic fouling could be irreversible and more difficult to be eliminated even by chemical cleaning (Guo et al., 2012).

It was stated that low-fouling or functional membranes using various nanoparticles (mainly TiO_2 NPs) have been developed and widely applied in membrane filtration process (Kim and Van der Bruggen, 2010). Due to photocatalytic property of TiO_2 NPs, research has been focused on fabricating nanocomposite membrane containing TiO_2 NPs to improve the properties of polymer materials, enhanced permeability and decrease fouling-resistance (Kim and Van der Bruggen, 2010; Li et al., 2009; Zhang and Yang, 2012; Zhang et al., 2011). However, there are very few studies about the potential effects of suspended TiO_2 NPs on cake layer formation in MBR.

The aim of this study was to gain insight into the effects of suspended TiO_2 NPs on cake layer formation on the membrane surface in a submerged MBR. The variations of both transmembrane pressure (TMP) and membrane resistances were measured to determine the responses of the cake layer to TiO_2 NPs. Both organic and inorganic foulants in the cake layer were also characterized via various methods, including Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), etc. In addition, the effects of the cake layer formed by TiO_2 NPs were analyzed using both dot map and line-analysis of energy-dispersive X-ray (EDX).

2. Methods

2.1. Preparation of TiO_2 NPs suspension

Commercially available TiO_2 NPs were purchased from Sigma–Aldrich. XRD analysis was conducted using a Rigaku D/Max-RB diffractometer equipped with a rotating anode and a Cu KR radiation source (Bruker,Optik GmbH, Ettlingen, Germany), and the XRD pattern of TiO_2 NPs is shown in Fig. S1 (supporting information, SI). The structure of TiO_2 NPs was visualized through the transmission electron microscopy (TEM) image using a Tecnai F20 (Philips Eletron Optics, Netherlands) with a 200 kV accelerating voltage (Fig. S2). The primary size of TiO_2 NPs in stock suspension was in the range of 20 nm, which was similar to the particle size provided by Sigma–Aldrich. The TiO_2 NPs stock suspension (100 mg/L) was prepared by adding 100 mg of TiO_2 NPs to 1 L of Milli-Q water, followed by 1 h ultrasonication (25 °C, 300 W, 40 kHz) according to the literature (Keller et al., 2010). Zheng et al. (2011) found that significant loss of bacterial viability was NP concentration-dependent after bacteria were exposed to the relatively small size of TiO_2 NPs (diameter ranged from 10 to 25 nm). TiO_2 NPs concentration of 1, 10 and 50 mg/L were chosen in our study, and showed the same result. Due to 50 mg/L TiO_2 NPs showed obvious effects on the bacterial viability, it was chosen in this study (Some results of 1 and 10 mg/L TiO_2 NPs are shown in the SI).

The influent was synthetized with tap water, containing 420 mg/L glucose, 420 mg/L corn starch, 102.75 mg/L NH_4Cl and 22 mg/L KH_2PO_4 as well as trace nutrients such as $CaCl_2$ (8 mg/L), $MgSO_4·7H_2O$ (9 mg/L), $MnSO_4·H_2O$ (3.66 mg/L) and $FeSO_4·7H_2O$ (0.55 mg/L). $NaHCO_3$ was used as a buffer to adjust the influent pH of to about 7.0.

2.2. Set-up and operation of MBRs

Two identical submerged MBRs (MBR-NPs and MBR-Blank) (3 L working volume, 20 cm × 10 cm × 25 cm of length × width × height) were used in this study. 2 L of inoculation sludge obtained from Quyang WWTP (Shanghai, China) was added in each bioreactor and then the stable biological pollutants removal (approximately 90% of both COD and ammonia nitrogen removal) was achieved before starting the experiment. MBR-NPs was initially fed with TiO_2 NPs stock suspension (100 mg/L) in order to reach the predetermined TiO_2 NPs concentration of 50 mg/L, and the operational time was recorded when MBR-NPs performance was stable (TiO_2 NPs were directly added into MBR-NPs during operation and the influent was without TiO_2 NPs). Because the concentration of TiO_2 NPs in MBR-NPs might slowly decrease due to the discharge of effluent or sludge, a certain amount of TiO_2 NPs stock suspension (100 mg/L) were supplemented every day for maintaining the initial TiO_2 NPs concentration (50 mg/L) after determining the total concentration of TiO_2 in MBR-NPs. MBR-Blank was operated as the control unit (i.e., without TiO_2 NPs addition). A hollow fiber PVDF membrane module (0.02 m^2 total surface area and 0.1 μm pore size, manufactured by Li-tree Company, Suzhou, China), was immersed in each MBR. Air (0.4 m^3/h) was continuously supplied through a perforated pipe under the membrane module. Peristaltic pump equipped with distributing pan was employed to control the influent feeding rate. Hydraulic retention time (HRT) and solids retention time (SRT) was remained at 8.0 h and 30 days for two MBRs. Mixed liquor suspended solids (MLSS) in MBR-NPs and MBR-Blank were 5170 ± 340 mg/L and 5014 ± 275 mg/L, respectively, during operation. Additionally the flux in two reactors was maintained at 45 L/(m^2 h) by an intermittent suction mode with 10 min of suction followed by 2 min relaxation. When the TMP reached 40 kPa, the membrane module was removed for physical (tap water washing) and chemical cleaning (2% NaOCl and 1% citric acid immersion for 4 h, respectively (Johir et al., 2013)) prior to the next run. The influent and effluent qualities in two MBRs were summarized in Table S1and Table S2.