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A systematic study of enhanced ozone mass transfer for ultrasonic-assisted PTFE hollow fiber membrane aeration process

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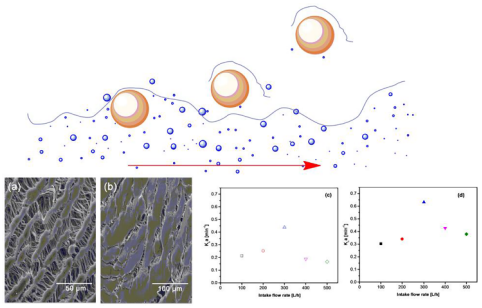
HIGHLIGHTS

- The K_La value of hydrophobic PTFE membrane aeration was affected by pressure.
- The K_La value could be significantly improved by ultrasonic.
- Ultrasonic cavitation bubbles could cause the periodical replacement of local liquid.
- The mineralization of SMP in O_3/Ultrasonic process followed the ·OH pathway.

GRAPHIC ABSTRACT

Ozone mass transfer based on hydrophobic PTFE membrane aeration depends on pressure, and the transfer efficiency could be markedly improved with the assistance of ultrasonic.



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ABSTRACT

The ozone mass transfer efficiency based on deionized water of both the PTFE hollow fiber membrane aeration and ultrasonic-assisted PTFE hollow fiber membrane aeration processes have been studied and described by mass transfer coefficient (K_La). Bubble size distributions were also investigated via an image-technology to analyze mass transfer processes. All the PTFE hollow fiber membranes were hydrophobic and had an asymmetrical structure. Results showed that the maximum value of K_La (0.438 min^{-1}) was obtained at an intake flow rate of 300 L/h with $1^{\#}$ membrane (0.22 μm) in single membrane aeration system. This gas-liquid mass transfer was strongly dependent on pressure. After the introduction of ultrasonic power, the K_La value reached 0.632 min^{-1} with an ultrasonic power of 1000 W. This enhancement was related to the periodical replacement of local liquid at the interface between the bulk solution and the liquid with high concentration of ozone. The degradation of sulfonated phenolic resin (SMP) confirms that its mineralization was promoted by the enhanced gas-liquid mass transfer of ozone and the generation of ·OH in the bulk solution.

1. Introduction

As an effective and environment-friendly oxidant, ozone has been extensively studied and successfully applied to water/wastewater treatment field and ozone-based processes [1]. Almost all conventional ozonation processes suffer from drawbacks, such as a relatively low solubility [2] and high energy consumption (around 10 Kw/Kg O_3) [3], which result in a slow, incomplete reaction or a high processing cost.

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Thus, an effective approach that could provide potential advantage for enhanced gas-liquid mass transfer efficiency of ozone is imperative [4,5]. A straightforward method is to increase the contact area of ozone–liquid. Therefore, scholars have focused on micro-bubble aeration and relevant reinforcement techniques [6,7].

Ozone aeration is a membrane process that exhibits superior characteristics, especially large interfacial area [8] and operational flexibility [9]. In this process, the mass transfer efficiency of ozone depends on the properties of both membranes and liquid phase, since membrane acts as a medium that separates two phase and the main resistance existing in the liquid film [10,11]. Controlling the liquid phase in practical application seems impossible. Hence, a suitable membrane that could optimize the gas–liquid contact must be developed. PTFE (polytetrafluorethylene) hollow fiber membrane, with the exceptional capability of both PTFE and hollow fiber membrane, could be regarded as an ideal material for membrane aeration. This type of membrane exhibits superior hydrophobicity and ozone durability among common polymer membranes that ozone resistance follows the order of PTFE > PVDF (polyvinylidenefluoride) > ETFE (ethylene-tetrafluoronitrile) > PE (polyethylene) > PVF (polyvinylfluoride) [2,12]. Compared with tube and flat sheet, hollow fiber membrane is more suitable as a gas–liquid contactor due to its high porosity, and this property which could render a higher mass transfer coefficient [2,13]. Nonetheless, mass transfer efficiency of this technology remains limited because of the presence of underused ozone in most processes [13]. Ozone molecules that are diffused into the living environment could cause great harm to the nose, throat, eyes, trachea, and lungs of humans [14–17]. Therefore, controlling the off gas containing ozone is necessary [14].

In the past decades, O_3/ultrasonic processes were studied by several groups [18] and a great success has been achieved in degradation of pollutants, such as 4-chloro 2-aminophenol (4C2AP) [19], 1,4-dioxane [20], dye [21], et al. Of technical importance, this approach does not require the addition of chemical substances. Ultrasonic assistance improved removal rate of model pollutants, and this reinforcement was mainly ascribed to the formation of hydroxyl radicals (HO·), which was fabricated via ozonolysis under ultrasonic in bulk solution [20–22]. Ultrasonic power could accelerate the ozone–liquid mass transfer compared with single aeration, which was no conflict with the aforementioned opinion that more hydroxyl radicals (HO·) were generated in its presence. This hybrid technology has also been applied to sludge reduction [23,24]. Thus far, limited studies have focused on ozone mass transfer processes based on PTFE hollow fiber membrane aeration. Moreover, the enhancement mechanism of ultrasonic-assisted PTFE hollow fiber membrane aeration process has not been identified.

Sulfonated phenolic resin (SMP) is widely used in deep-well drilling in China because of its excellent high-temperature resistant and salt-tolerant [25]. Sufficient degradation of SMP seems imperative considering strict standards and environmental awareness. However, to the best our knowledge, few studies have focused on the disadvantages of this strong polar and soluble organic matter. Herein, SMP was chosen as a target for testing ultrasonic-assisted PTFE hollow fiber membrane aeration and detecting the degradation mechanism of SMP by ozonation in the absence/presence of ultrasonic.

This work aims to provide an in-depth discussion about this hybrid technology and mainly focuses on the enhancement mechanism of ozone mass transfer based on ultrasonic-assisted micro-bubble ozonation with PTFE hollow fiber membrane. Bubble size distribution and mass transfer coefficient were investigated in terms of membrane pore size, intake flow rate, ultrasonic power and operating temperature to describe the ozone mass transfer processes in PTFE hollow fiber membrane and PTFE hollow fiber-ultrasonic coupled systems. Deionized water was used as liquid phase. Moreover, the degradation of SMP was evaluated by TOC and UV–vis analysis.

2. Experimental

2.1. Characterization of PTFE hollow fiber membranes

The PTFE hollow fiber membranes used in this study were kindly provided by DD Water Group Co. (Zhejiang Province, China). The mean pore diameter and porosity values were determined using a mercury porosimeter (AutoPore IV 9500, Micromeritics Co., Ltd., USA). Scanning electron microscope (SEM) images were obtained on an Inspect F50 microscope, and before the analysis, PTFE membranes were dried at 50 °C overnight, then cooled in liquid nitrogen and cut into pieces.

Contact angle was measured through static sessile drop method. The membranes were cut into pieces and flattened with the internal surface upwards. A droplet was placed on the internal surface of each membrane, and contact angle was measured by data physics contact angle system. Note that the evaporation of the droplet was negligible.

2.2. Experimental unit

The schematic of the experimental apparatus is shown in Fig. 1. The apparatus consists of bubble generation, shoot and ultrasonic generation system. Ozone was generated from pure oxygen by a CF-G-3–20 g generator. The aeration reactor was a plexiglass cuboid with 2.16 L capability (0.06 m × 0.06 m × 0.6 m), and 20 membranes were installed at the bottom. Each hollow fiber was 150 mm in length. One end of the membrane was fixed at the bottom of the reactor, and the other end was well-sealed to ensure that the membrane pores act as gas transfer channels. All the experiments were conducted with distilled water, and any residual ozone was removed by 2% KI solution.

In bubble generation system, ozone was introduced into the liquid phase through the PTFE hollow fiber membrane aerators. A flowmeter was used to control and measure intake flowrate. Photos of micro-bubbles were taken using a digital camera (Legria HF R706, Canon, Japan), and halogen lamps were used for brightness adjustment simultaneously. The ultrasonic probe connected with an ultrasonic generator (MS-ZDB, Handan City Meishun Machinery Co., Ltd) was fixed at the top of the reactor to contact the liquid phase.

Samples were withdrawn from the reactor at a given time and analyzed immediately. Dissolved ozone concentration was measured by indigo method [26]. The Total organic carbon (TOC) of the reaction mixture was detected using a TOC-VCPH analyzer (Shimadzu, Japan). The UV spectra of the SMP solution were recorded by UV–Visible spectrometer (UV-1900, Macy, China).

2.3. Measurement of bubble-size distribution

The diameter distributions of micro-bubbles were determined through statistical analysis.

The typical procedure is as follows: (1) a ruler was placed outside of the reactor to calibration; (2) photos were taken using a digital camera at a shutter speed of $1/60\ s^{-1}$; (3) quality photographs were chosen and analyzed using Image-Pro Plus 6.0; (4) 500 micro-bubbles were randomly selected for diameter analysis based on the ruler (Fig. S1); and (5) a distribution curve was drawn according to the statistical data.

2.4. Measurement of the apparent liquid-side volumetric mass-transfer coefficient, K_La

The apparent volumetric mass transfer coefficient, K_La, based on distilled water can be expressed as follows:

$$\frac{dc}{dt} = K_L a(Cs - C) - r \quad (1)$$

where Cs is the equilibrium concentration of ozone in deionized water, which corresponds to ozone concentration at saturation; C is the