



Short communication

Field application of a biofilm reactor based BOD prototype in Taihu Lake, China

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ABSTRACT

A tubular biofilm reactor (BFR) based online biochemical oxygen demand prototype was applied in Taihu Lake, China. Municipal tap water was used instead of conventional phosphate buffer as blank solution to avoid phosphate pollution. The background organic compounds in municipal tap water were taken into account and they were validated to result in negative deviation to accuracy. The microbial endogenous respiration was experimentally validated to be sensitive to salt ionic strength, and municipal tap water as blank was thought to generate positive deviation to accuracy. The system was continuously operated over 2 months without man intervention, and the automated monitoring data agreed well with that of the conventional BOD₅ methods. The BFR resisted the frequent measurements with samples of high turbidity, and the BOD monitoring data indicated the index of biodegradable organic compounds of Taihu Lake was accorded with the second class described in the environmental quality standard of surface water. Analyzed together with permanganate index on site, Taihu Lake was revealed to be of good capacity of self cleaning. Importantly, field application study of new BOD method made it more objective in evaluating its applicability, and could provide practical information and useful improvements in the process of commercializing.

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1. Introduction

With the urban construction, economic construction and development and population growth, the water pollution problem has intensified and become a hot topic [1]. Recent years, the huge outbreaks of algae in China's inland lakes and coastal area have seriously imperiled local residents. Water pollution problem has become a bottleneck constraining economic growth in China. In order to rapidly gain the information of water qualities, protect water source and prevent pollution, it is imperative to establish a general and efficient system for water quality monitoring [2]. Normally, the water quality parameters such as pH, dissolved oxygen (DO), oxygen demand (OD), total organic carbon (TOC), conductivity, nitrogen and phosphorus related parameters are the most commonly being monitored [3]. These monitor units are integrated with peripheral sampling, washing and filtering system, forming an automated water quality monitoring station [3]. Among these parameters, OD usually includes chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Further in surface water quality evaluation, permanganate index, namely COD_{Mn}, is extensively applied [4]. The difference between COD_{Mn} and BOD is essentially determined by "oxidant" used in the two methods: permanganate or microorganisms [5]. Undoubtedly,

BOD determination has been the most preferred mean for environmental estimation because it simulates the biodegradation process of the aggregate organic pollutants in natural conditions, providing useful information for biological and environmental impact assessment.

BOD is a necessary item in the monitoring of surface water quality [4]. The standard method for estimating biological oxygen demand is 5-day BOD assay (BOD₅) [6]. Obviously, the 5-day incubation is a fatal disadvantage in routine monitoring, resulting hysteric feedback [7]. Rapid BOD methods based on biosensors [8–10], mediators [11,12] and biofuel cells [13,14] have been broadly lighted in the past thirty years, and some of them were commercialized. BOD-2000 analyzer utilizes a typical biosensor based BOD method developed by Nisshin Denki and Central Kagaku Co. Ltd., Japan [15]. The primary element is a biosensor, which consists of a microbial film coupled with an oxygen sensor. The output current of this oxygen sensor decreased when sample solution with biodegradable organic compounds flew through this biosensor on account of the increased microbial respiration rate. This is also the common operation principle of the biosensor based BOD analyzer and it is regarded as one of the simplest BOD determination principles to date. An online bioreactor based BOD analyzer BIOX-1010 was put forward by STIP Isco GmbH, Germany [16]. The samples were diluted and pumped into the bioreactor until a constant microbial respiration rate was obtained, and BOD was calculated according to the dilution multiples. The use of huge amount of complex microorganisms in the bioreactor brought promising in biodegradation efficiency [17].

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However, the consumption of fresh water of 720 L/day made it impractical in application. Moreover, the HABS series BOD analyzer using the mediator-less microbial fuel cell was developed by KORBI Co. Ltd., Korea [18]. Electrochemically active bacteria produced electrons during the digestion of organic contaminants in wastewater. Produced electrons were transferred from the electrochemically active bacteria to the electrodes, generating an electric current. The current generated from a microbial fuel cell was directly proportional to the amount of organic waste supplied. It was then converted to measure the BOD value. However, without rigorous maintenance, all microbial fuel cells were instable and have a limited lifespan [5]. These listed BOD analyzers well represented the development directions and great progresses of rapid BOD methods. Even so, rapid BOD analyzers were seldom integrated in automated water quality monitor station to the best of our knowledge. In most cases, rapid BOD analyzers were not widespread, and this parameter was ignored. Occasionally, rapid BOD analyzers were provided but unused. The absences of BOD parameter in estimation water quality were mainly because of the unauthentic results and complicated maintenances of the BOD analyzer [19].

Recently, we developed a tubular biofilm reactor (BFR) based reagent-free BOD determination method [20,21]. This method embraced the advantages of simplicity as biosensor based BOD method and high biodegradation capacity as biofuel cell based BOD method. Municipal tap water was used as blank to avoid secondary pollution caused by phosphate buffer [22]. Long term operational and storage stabilities were studied with standard solutions in laboratory. Excellent performances, coupled with simplicity in device, convenience in operation and minimal maintenance, made it promising in field application. Herein, field application study based on the tubular BFR-BOD system was carried out in Taihu Lake, China. As a significant drinking water source, the water quality of Taihu Lake attracted the governmental and public attentions, especially since the breakout of blue-green algae bloom in 2007. Additionally, Taihu Lake is a characteristic inland lake in China and has been widely studied in many aspects. In this study, some practical problems in field applications, such as the effects of the trace amount organic compound and salt ionic strength to measurements, were discussed.

2. Experimental section

2.1. Standard and blank solutions

An artificial wastewater (AWW) was prepared according to previous report [23]. It contains 4.25 mg L⁻¹ nitrohumic acid, 4.18 mg L⁻¹ tannic acid, 2.43 mg L⁻¹ sodium lignisulfonate, 4.70 mg L⁻¹ gum arabic, and 0.94 mg L⁻¹ sodium lauryl sulfate. The experimental BOD₅ of AWW was 3.7 mg L⁻¹. An artificial tap water was prepared by dissolving 200 mg Na₂SO₄, 200 mg CaCl₂, 200 mg KCl, 10 mg KNO₃, and 300 mg MgSO₄·7H₂O with deionized water, and diluted until its conductivity was around 340 μS cm⁻¹. The municipal tap water was collected and stored at room temperature (~20 °C) ahead.

2.2. Preparation of biofilm reactor

The BFR ($\varphi=2.0$ mm and $L=105$ cm) was prepared in accordance to our previous studies [20]. Basically, the glass tube was treated with HF/NH₄F (1.7%/2.3%, w/w) solution, followed by thorough washing with water to obtain a rough inner surface. Air-saturated Taihu Lake sample with added nutrients was continuously pumped through the etched tube at a flow rate of 0.5 mL min⁻¹ at a constant temperature of 30 °C. The status of biofilm formation was estimated by measuring the current

responses of a DO probe to an injected AWW solution at intervals. The gradually decreased current signal with increased cultivation time indicates the progressive biofilm formation process. The cultivation process was terminated when no further decrease in current signal was observed from the injections of the AWW solution in two consecutive time intervals. The resultant BFR was filled in municipal tap water and stored at room temperature before use.

2.3. System operation

The BOD online prototype was developed by Changchun Institute of Applied Chemistry (Chinese Academy of Sciences) and fabricated by Jilin Grand Analysis Co., Ltd. based on our previous studies [20,21]. DO probe with an Au working electrode ($\varphi=0.8$ mm) covered by the Teflon membrane (Orbisphere 2956A) was used and all current signal measurements were performed under a constant applied potential of -700 mV vs. Ag/AgCl (0.1 M KCl), controlled by an integrated electrochemical platform. The BFR was placed in a thermostatic chamber at a constant temperature of 30 °C, as well as the tap water and sample containers. The tap water and sample alternately flowed through the BFR at a flow rate of 2.0 mL min⁻¹, and DO of the effluent from BFR was continuously monitored. When instructed to measure, the tap water in store was transferred to the container for air-saturation and heating. Five minutes later, the air-saturated tap water was pumped through the BFR, providing a steady-state current (i_b) of the DO probe. This process lasted for 35 min, during which the sample (standard or real sample) was injected into the sample container for DO equilibrium and heating. The air-saturated sample solution was then continuously injected into the BFR by switching a triple valve while the oxygen depletion of the effluent was simultaneously indicated by the current signal decrease, achieving a new steady-state current (i_s) in 10 min. The steady-state current change ($\Delta i=i_b-i_s$) was calculated and used as the analytical signal for BOD quantification. The BFR was stored with last sample in it until next measurement.

To apply the present method, several measurement instruments were utilized to measure the quality of Taihu Lake samples and municipal tap water. The COD_{Mn} values were obtained by using a COD_{Mn} analyzer (COD-203A, Hach). Conductivity was measured using a conductivity meter (FE30K, Mettler). DO was measured using a DO meter (Model 58, YSI), and pH was measured using a pH meter (FE20K, Mettler). The BOD₅ assay was carried out according to the standard method [6].

2.4. Field application site

The application site was located in Nanquan Waterworks (Wuxi, China), namely Wuxi ShaZhu automated water quality monitoring station (E120°13'46.4", N31°23'57.8") (Fig. 1). The BOD monitoring unit was experimentally installed in the monitoring station. The water intake extended to the middle of the lake. The samples were roughly filtered by sand filtration for this unit only. The general characteristics of the inflow sample are described in Table 1. Some of these water quality indexes can be freely obtained via Internet supported by National Environment Monitoring Station [24].

3. Results and discussion

3.1. Effect of organic compounds in municipal tap water

Municipal tap water has been successfully used in our BFR based BOD system instead of PBS over the past two years [22].

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