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Demonstration study of biofilm reactor based rapid biochemical oxygen demand determination of surface water

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ABSTRACT

Application investigations of rapid biochemical oxygen demand (BOD) online analyzer for surface water in Wuxi, China were carried out since 2013. The analyzer adopted a novel working principle, that is, the oxygen concentration of the sample to be tested was regarded as a reference, and the oxygen consumption by the biofilm reactor (BFR) was calculated according to the difference between the reference and sample effluent from BFR. The BFR was fabricated *via* a cultivation process using naturally occurring microbial seeds from in site surface water. This analytical principle was first presented and clearly clarified, and the impact of microbial endogenous respiration to the measured values was also proposed and analyzed. The improved analyzers were equipped in three application sites with significant differences in BOD concentration, for the purpose of evaluating the feasibility and applicability of the proposed method. This study revealed that the online analyzer could continually operate over 30 days without human intervention and additional chemical reagent consumption. The obtained rapid BOD trend line showed that this analyzer could track the fluctuation of the biodegradable organic compound level timely and accurately. The innovative analytical method, as well as the outstanding adaptation and well accuracy rating, provided the highlights for wide applications in the future.

1. Introduction

Taihu Lake is located in Yangtze River delta, China, and it is an important drinking water source feeding 60 million people in the Eastern China [1]. In recent years, its aquatic environment is becoming more and more concerning, which is mainly depended on the increasing organic pollutions and blue-green algae bloom [2]. Establishing an effectively available multi-parameter water quality automated monitoring stations and closely monitoring of the safety of water quality of Taihu Lake are a meaningful work related to people's livelihood. The organics are ever-changing, and biochemical oxygen demand (BOD) is usually used to measure the water quality of the degree of biodegradable organic pollution [3]. The standard BOD assay costs 5 day (BOD_5) and it also needs numerous fussy procedures. Importantly, this assay fails to meet the requirement of process control [4]. A rapid BOD monitoring method is needed in water quality automated monitoring system for the purpose of timely information feedback [5].

Scientific researches devoted in rapid BOD studies have been lasted for over 30 years since the first BOD biosensor developed by Karube et al. in 1977 [6]. Consequently, a number of commercial rapid BOD analyzers came out, such as BOD 2000 developed by Nisshin Denki & Central Kagaku Co. Ltd., Japan [7], BIOX-1010 put forward by STIP Isco GmbH, Germany [8], HABS series BOD analyzer developed by KORBI Co. Ltd., Korea [9], and LAR BioMonitor contributed by LAR Process Analysers AG, Germany [10]. However, as can be seen from the real time data disseminated by the national surface water automated monitoring system supported by the China Environmental Monitor Station, all of 103 automated water quality monitor stations are not equipped with a rapid BOD analyzer without exception [11]. BOD parameter is a necessary item for surface water monitoring in the comprehensive estimation of water quality [12], hence, BOD_5 assay was compelled to carry out in laboratory to make up the absence of a rapid BOD analyzer in these automated water quality monitoring stations. The flourishing development of rapid BOD determination methods in lab shows a sharp contrast to their field applications in a BOD analyzer. In the rapid BOD studies, a great many methods have been developed such as BOD biosensors based on immobilized microorganisms covered on an oxygen detection sensor [13–15], mediator BOD methods relied on a mediator as an electron transfer acceptor [16], and microbial fuel cell BOD methods with electroactive bacteria [17]. These methods mostly focus on microorganism selection, new method establishment, and performance of laboratorial sample measurement. However, few of them experience long term onsite application [7,8,18]. In fact, the online

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applicability studies of those developed methods applied to real samples are eagerly needed to promote the current scientific research level as routine parameters [19,20]. On the contrary, there are few available reports or cases of the field BOD application now, which definitely reflect the conflict between the developed methods and their application prospects. To the best of our knowledge on rapid BOD application, daily maintenance is one of the most important factors that limited their application besides the practicability of the methods themselves [21,22]. To say the least, many laboratories are provided with rapid BOD analyzers, but fail to use. The activity preservation of the microbial seeds is a thorny scientific problem when the analyzer is in standby, which needs attentive care and uninterrupted supply of nutrition [7]. Beyond that, daily maintenances also reflect in the aspect of reagent consumption/replenishment for the onsite application. Take the BOD-2000 online analyzer for example, the usage of phosphate buffer solution (PBS) increases the maintenance cost and risk of secondary pollution. In conclusion, few of developed online analyzers are still available now in China, no matter what the types or manufacturers are.

Vigorous development of the domestic analytical instruments and reaching the world-class level are a long-term strategic plan in China. Our research group has been devoted into practical BOD studies over eighteen years with the financial supports from Chinese government [23–30]. In our previous studies, we proposed a novel flow-through biofilm reactor (BFR), which was fabricated *via* a cultivation process using naturally occurring microbial seeds from in site surface water. We achieved online BOD measurements utilizing the biodegradation actions to organics of the biofilm, which needs tap water as blank instead of conventional PBS [25]. The further field application was also carried out in Taihu Lake previously [26]. Of course, this method was not completely free of maintenances due to the regular tap water supply. However, further researches brought us new knowledge on this BFR. The BFR could maintain a satisfied activity without washing with blank solution in long term real sample measurements. This remarkable environmental adaptive ability and high efficiency in biodegradation make us propose an improved BOD monitoring method here, which consumes nothing in the process of measurement except the sample itself. The novel analytical principle was expounded here and the long-term field application in Taihu Lake, as well as two inland rivers in Wuxi City, was carried out.

2. Materials and methods

2.1. Standards

The glucose and glutamic acid (GGA) synthetic sample ($BOD_5 = 1880 \pm 150$ mg O_2 L^{-1}) is usually used for BOD_5 standard, and it was prepared with 1.50 g glucose and 1.50 g glutamic acid in 1 L according to the American Public Health Association (APHA) standard methods [4]. It was used for the system calibration.

2.2. Preparation of biofilm reactor

The tubular BFR ($\varphi = 3.0$ mm) was prepared according to our previous studies [24]. Basically, the glass tube was treated with HF/NH_4F (1.7%/2.3%, w/w) solution, followed by thorough washing with water to obtain a rough inner surface. Air-saturated real sample with added nutrients was continually 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 dissolved oxygen (DO) probe to an injected GGA 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 GGA solution in two consecutive time intervals. The resultant BFR was thoroughly washed and filled in the real water sample and stored at room temperature before use.

2.3. System operation

The demonstrated BOD online analyzer was developed by Changchun Institute of Applied Chemistry (Chinese Academy of Sciences) and fabricated by Jilin Grand Analysis Technology Co., Ltd. according to our previous studies (Fig. S1, Supplementary material). DO probe with an Au working electrode ($\varphi = 0.8$ mm) covered by the Teflon membrane (Orbisphere 2956A) was used for current signal measurements, and it was performed under a constant applied potential of −700 mV *vs* Ag/AgCl (0.1 M KCl), controlled by an integrated electrochemical set-up. All the current signals were calibrated into oxygen concentration in principle of commercial DO meters [27]. The optical photo of the thermostatic chamber and its schematic diagram of working area were illustrated in Fig. 1. The BFR and DO probe were immersed in the thermostatic chamber, which consisted of a series of auxiliary sensors such as temperature sensor, liquid level sensor and devices such as overflow port, heating rod and aerator. The real sample was filled in the chamber and used as the medium for heating. Two subaqueous

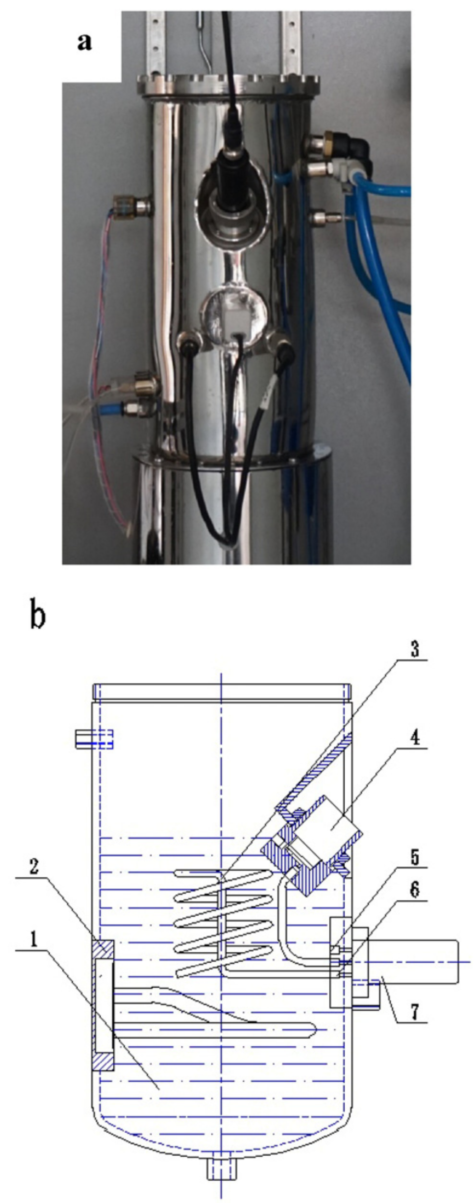

Fig. 1. Optical photo of the thermostatic chamber (a), and its schematic diagram of the waterway structure (b). 1, real sample; 2, heating rod; 3, BFR; 4, DO probe; 5, sample injection path; 6, sample injection *via* BFR path, 7, triple value.