Sensing and Bio-Sensing Research 8 (2016) 8–13

Contents lists available at ScienceDirect

Sensing and Bio-Sensing Research

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

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

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ARTICLE INFO

Article history:
Received 25 November 2015
Received in revised form 24 February 2016
Accepted 25 February 2016

Keywords:
Biofilm reactor
Biochemical oxygen demand (BOD)
Application demonstration
Online analysis

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.

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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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http://dx.doi.org/10.1016/j.sbsr.2016.02.007
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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

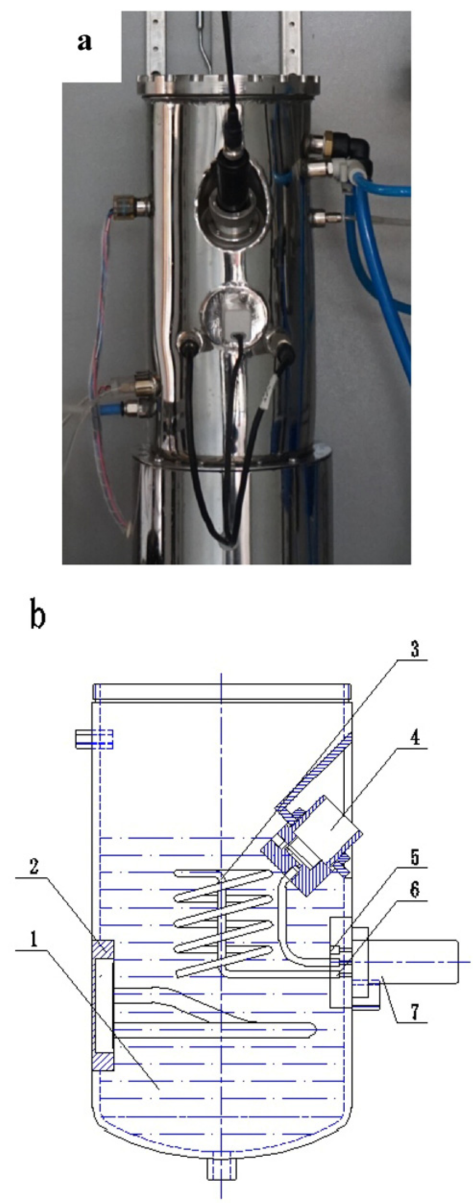

Fig. 1. Optical photo of the thermostatic chamber (a), and its schematic diagram of the waterway structure (b). 1, real sample; 2, heating rod; 3, BFR; 4, DO probe; 5, sample injection path; 6, sample injection *via* BFR path, 7, triple value.

flow paths were designed for the purpose of injecting sample into the DO probe by different ways (*via* BFR or injection directly). Such a design obviously simplified and shortened the waterway structure and provided a reliable temperature of the biological reaction in the BFR. Specifically, the real sample was pumped to the thermostatic chamber for air-saturation and heating. Next, the sample was pumped to the DO sensor directly, providing a background oxygen concentration. Alternatively, the sample was injected into the DO probe *via* BFR by switching a triple valve, providing the oxygen concentration of the sample effluent from BFR. The oxygen consumption was calculated and used for BFR-BOD quantification. The BFR was washed with the residual sample in high speed before waste discharge. The BFR was stored with the last sample in it until next measurement.

3. Results and discussion

3.1. Analytical principle generation

The oxygen concentration of the air saturated real sample solution was used as a reference ($[O_2]_{\text{Sample}}$), and the total oxygen consumption by the BFR ($[\Delta O_2]_{\text{Total}}$) was obtained by calculating the oxygen concentration difference between $[O_2]_{\text{Sample}}$ and the oxygen concentration of sample effluent from the BFR ($[O_2]_{\text{Sample Effluent-BFR}}$) (Eq. (1)). The $[\Delta O_2]_{\text{Total}}$ was one of the factors used for the BOD quantification of real sample. When calibrated, a known GGA stock standard was added into the real sample. At this time, the $[O_2]_{\text{Sample Effluent-BFR}}$ was used as a reference, and the difference between $[O_2]_{\text{Sample Effluent-BFR}}$ and $[O_2]_{\text{Sample-GGA Effluent-BFR}}$ was caused by the added GGA standard and it was defined as $[\Delta O_2]_{\text{GGA}}$ (Eq. (2)). The analytical sensitivity (k) was easily calculated by comparing $[\Delta O_2]_{\text{GGA}}$ with its BOD_5 concentrations (Eq. (3)). Hence, the real sample's BOD value could be expressed in Eq. (4).

$$\Delta[O_2]_{\text{Total}} = [O_2]_{\text{Sample}} - [O_2]_{\text{Sample Effluent-BFR}} \tag{1}$$

$$\Delta[O_2]_{\text{GGA}} = [O_2]_{\text{Sample Effluent-BFR}} - [O_2]_{\text{Sample-GGA Effluent-BFR}} \tag{2}$$

$$k = \frac{[\Delta O_2]_{\text{GGA}}}{[BOD_5]_{\text{GGA}}} \tag{3}$$

$$[\text{BFR}-\text{BOD}]_{\text{Sample}} = \frac{\Delta[O_2]_{\text{Total}}}{k} \tag{4}$$

Actually, the $[\Delta O_2]_{\text{Total}}$ was regarded of comprising of the oxygen deletions by the microbial endogenous respiration without organic compounds supplying ($[\Delta O_2]_{\text{Endogenous}}$) and exogenous respiration with organic compounds supplying ($[\Delta O_2]_{\text{Exogenous}}$) (Eq. (5)). $[\Delta O_2]_{\text{Endogenous}}$ might be roughly estimated by calculating the oxygen concentration difference of a blank solution ($[O_2]_{\text{Blank}}$) and blank effluent from the BFR ($[O_2]_{\text{Blank Effluent-BFR}}$) theoretically (Eq. (6)).

$$\Delta[O_2]_{\text{Total}} = \Delta[O_2]_{\text{Endogenous}} + \Delta[O_2]_{\text{Exogenous}} \tag{5}$$

$$\Delta[O_2]_{\text{Endogenous}} = [O_2]_{\text{Blank}} - [O_2]_{\text{Blank Effluent-BFR}} \tag{6}$$

Buffer system has always been used as a blank in rapid BOD biosensor system since this analytical method was primarily developed by Karube in 1977 [6], and it was regarded as necessary in rapid BOD biosensor method for providing both biocompatible environment and background in calculation of oxygen consumption. In our previous study, PBS was successfully replaced by tap water, and the long term stability validated that this natively cultivated BFR could acclimatize itself to this harsh working conditions [25]. However, as reported in our previous study, both the organic compounds in tap water and the buffer concentration were sure to result in a deviation [26]. Anyway, neither buffer system nor tap water was a qualified blank strictly. However, tap water instead of conventional PBS in rapid BOD application extremely facilitated the services of operation and maintenance *in situ*. Therefore, tap water would be used as blank and the influence of $[\Delta O_2]_{\text{Endogenous}}$ to the determined BOD would be detailedly discussed hereinafter.

3.2. Onsite application

The application sites were located in Wuxi, China, namely, Shazhu water quality automated monitoring station (E120°13′46.4″, N31°23′57.8″), Shangxian River Wetland Park water quality automated monitoring station (E120°18′51.5″, N31°28′31.9″), and Liangtang River Wetland Park water quality automated monitoring station (E120°19′01.0″, N31°30′54.8″), respectively [26]. The online BOD analyzers were integrated in the monitoring station together with other water quality parameters such as conductivity, turbidity, chlorophyll a, pH, DO, ammonia nitrogen, total nitrogen, total phosphorus, and permanganate index (COD_{Mn}). The experimental BOD profile was also available for insiders by means of remote access service.

Besides the innovative analytical method, several effective technical improvements and optimized designs were also considered in this application demonstration. The inner diameter of the BFR expanded from previous 2.0 to 3.0 mm. Although such a dilatation weakened the biodegradation efficiency, a good performance in reducing hydraulic resistance in the BFR was obtained. A multistage sand filter device was introduced, where most of the large particles and algae were filtered. The inlet of the BFR was equipped with a metal net (500 mesh) to further prohibit small particles into the BFR, and the intercepted crud was backwashed with the gas–liquid mixture with high pressure after each measurement. Even so, high speed pulsing rinse (~50 mL min^{-1}) in both positive and negative directions was needed in preventing from the sludge deposition on the inner wall of BFR. Besides, ubiquitous biofilm was one of the most headaches in the aspect of cleaning the thermostatic chamber. The biofilm might result in a negative analytical deviation due to its self-biodegradation in the thermostatic chamber, and the aggregated extracellular slime substance was apt to clog the plug flow system. Therefore, the air bubbles powered acrylonitrile butadiene styrene cubes (approximately $4 \times 4 \times 4$ mm) were introduced into the chamber for erasing the biofilm around its inner wall while aeration. The self-cleaning of the thermostatic chamber was proceeded simultaneously with each measurement, which obviously improved the accuracy and stability in long term operation. The cleaning results were satisfactory concluded from an optical photograph (Fig. S2, Supplementary material) together with the one-month continual operation data (data not shown). These improvements seemed not to be of the core technologies of BOD measurement, but were of practical value in field application. In fact, some advanced BOD methods or instruments ultimately failed in application more or less due to their thoughtless designs.

3.2.1. Influence of $[\Delta O_2]_{\text{Endogenous}}$

Apparently, $[\Delta O_2]_{\text{Endogenous}}$ depended on the length of BFR (microbial population amounts), the reaction temperature and sample injection rate. Compared to previous parameter optimization, we decreased the BFR length from 105 to 75 cm, expanded the BFR inner diameter from 2 to 3 mm, decreased the bioreaction temperature from 37 to 30 °C, and increased the sample injection rate from 2.0 to 3.5 mL min^{-1}. In this condition, the linear range of this method is from 1 to 20 mg L^{-1}. It takes about 90 s for the sample flowing through the BFR. With these optimization, tap water was used as blank solution, and the ratio of $[\Delta O_2]_{\text{Endogenous}}$ and $[\Delta O_2]_{\text{Total}}$ was estimated in this application study with three kinds of surface water with great difference. The tests were carried out during a week within 3 repeated measurements each day. The analytical results were illustrated in Fig. 2. Obviously, the $[\Delta O_2]_{\text{Endogenous}}/[\Delta O_2]_{\text{Total}}$ ratios were different among each sites. For the Taihu Lake site, the $[\Delta O_2]_{\text{Endogenous}}/[\Delta O_2]_{\text{Total}}$ ratio was as high as nearly 40%.

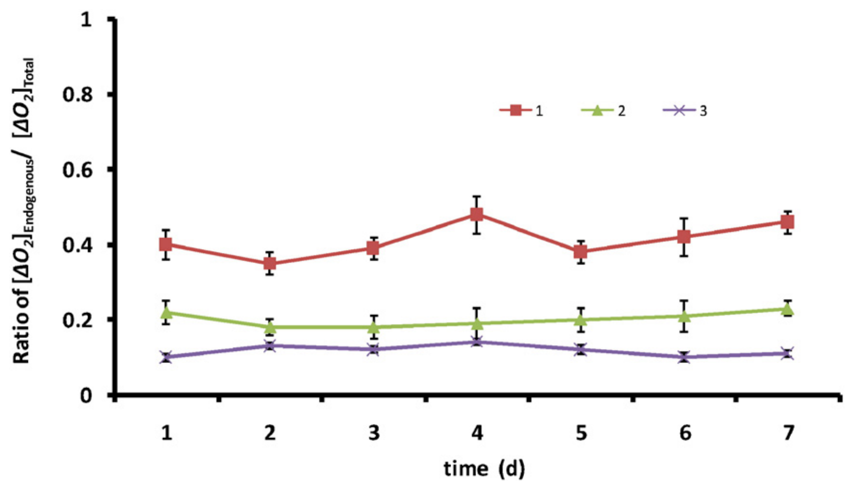

Fig. 2. Microbial endogenous respiration proportion in total oxygen consumption in the three application sites. Application site: 1, Taihu Lake; 2, Shangxian River Wetland Park; and 3, Liangtang River Wetland Park.

Meanwhile, this ratio was merely 10% for the Liangtang River Wetland Park site. The ratio represented the analytical error for each site. Even so, only a fraction of analytical error in accuracy was brought in the Taihu Lake onsite monitoring. The comparison studies on $[\Delta O_2]_{Endogenous}$ effect to determine BOD were further studied (Fig. S3, Supplementary material). Definitely, the monitoring trends were consistent with or without consideration of $[\Delta O_2]_{Endogenous}$. Discriminatively, the data were somewhat higher compared to those calculated by deducting $[\Delta O_2]_{Endogenous}$. However, such an analytical error was never a decisive factor for onsite monitoring. First, BOD is a rough water quality parameter. The BOD_5 assay with an analytical error less than 25% is universally acceptable, and sometimes it is even greater for surface water assay. Second, surface water with BOD level less than 3 mg L^{-1} is considered to accord with the first/second level according to the environmental quality standard of surface water. Take the Taihu Lake site as an example, the average analytical results in a week were 1.1 and 1.7 mg L^{-1} ($n = 21$) with or without consideration of the $[\Delta O_2]_{Endogenous}$, respectively. The analytical error was around +40%, but such an analytical result was acceptable to estimate the water quality of Taihu Lake. On the other hand, the measurement error decreased drastically to +9% for the Liangtang River Wetland Park site with or without consideration of the $[\Delta O_2]_{Endogenous}$. It should be noted that the conventional BOD_5 assays of local tap water were of 0.4 ± 0.2 mg L^{-1} ($n = 5$), thus, the determined $[\Delta O_2]_{Endogenous}$ value embraced a positive deviation itself. From the viewpoint of convenience in field application, it was acceptable without respect to $[\Delta O_2]_{Endogenous}$. In short, the discussion on the deduction of $[\Delta O_2]_{Endogenous}$ was principal because of the scientificity of the proposed analytical method, and the doubt on the influence of $[\Delta O_2]_{Endogenous}$ was sufficiently clarified with scientific data obtained by different kinds of surface water.

3.2.2. Stability and accuracy evaluation

The stability and accuracy were mainly concerned on the DO sensor and BFR. The Teflon membrane covered on the DO sensor was inevitably contaminated by the microorganisms in continual operations. The contamination ultimately resulted in an unceasing growth in the determined BOD values in the methods of previously established biofilm-covered BOD biosensors [6]. However, in our proposed BFR-BOD system, the real sample solution flowed through the DO sensor first and the obtained $[O_2]_{Sample}$ was used as a reference, with the step of real sample solution flowed through the BFR and DO sensor in sequence followed. Hence, the influence of dirty DO sensor was deducted completely. The further experiments also demonstrated this principle. The $[O_2]_{Sample}$ decreased from 7.62 to 6.16 mg L^{-1} after 19 days' operation in the Liangtang River Wetland Park site, however, the measured BFR-BOD values showed a maximum +15.2% error to BOD_5, which was essentially the same as results of preliminary stage (Table 1). Even so, periodic maintenance to the Teflon membrane was necessary for the reason of keeping an expectant analytical range.

The BFR performed a better stability as described in our previous study [24]. In the GGA standard checking tests during 2 weeks, a maximum analytical error of +10.7% and −13.3% for GGA standard of 5.6 and 3.0 mg L^{-1} was observed, respectively for the Liangtang River and Shangxian River Wetland Park site (Table S1, Supplementary material). The improved results depended on the delicate designs to a great extent. The GGA response was directly related to the analytical sensitivity, therefore, the system was artificially maintained and periodically recalibrated every two weeks. The typical sensitivities of 0.118 ± 0.007, 0.139 ± 0.009 and 0.154 ± 0.008 were obtained for the Taihu Lake, Shangxian River, and Liangtang River application site, respectively.

3.2.3. Real sample online application

The application station in Taihu Lake has been operated since March, 2013. Meanwhile, the analyzer went through six time's upgrading and reconstruction in aspects of above-mentioned detail designs, until its ultimate application in Shangxian River Wetland Park and Liangtang River Wetland Park in March, 2015. Up to now, the system could continuously and stably run at least 30 days without human intervention. In this background, the tests on field application accuracy of the proposed method and analyzer were carried out. The standard BOD_5 assay was also carried out correspondingly for comparative study. The analytical results for the three application sites were discussed respectively.

The rapid BOD monitoring data of Taihu Lake sample from April to May in 2014, combined with partial BOD_5 results, were illustrated in Fig. 3a. Generally, the BOD maintained at 1.5 mg O_2 L^{-1}, which was a relative low level for surface water and fit for the first level (level I) specified in the environmental quality standard of surface water [12]. However, great fluctuations during this study were captured by our rapid BOD analyzer and partly by BOD_5 methods. Take example

Table 1
Influence of Teflon contamination on the measured results. Data unit: mg L^{-1}.

Time	$[O_2]_{Sample}$	$[O_2]_{Sample\ Effluent\text{-}BFR}$	$[\Delta O_2]_{Total}$	BFR-BOD	BOD_5
Apr. 20, 2015	7.62	6.33	1.29	8.4	7.5
Apr. 23, 2015	7.33	5.88	1.45	9.4	9.5
Apr. 25, 2015	7.23	5.42	1.81	11.8	10.2
Apr. 30, 2015	7.05	4.56	2.49	16.2	16.0
May 4, 2015	6.88	4.88	2.00	13.0	12.8
May 6, 2015	6.42	4.44	1.98	12.9	12.0
May 9, 2015	6.16	3.92	2.24	14.5	13.8

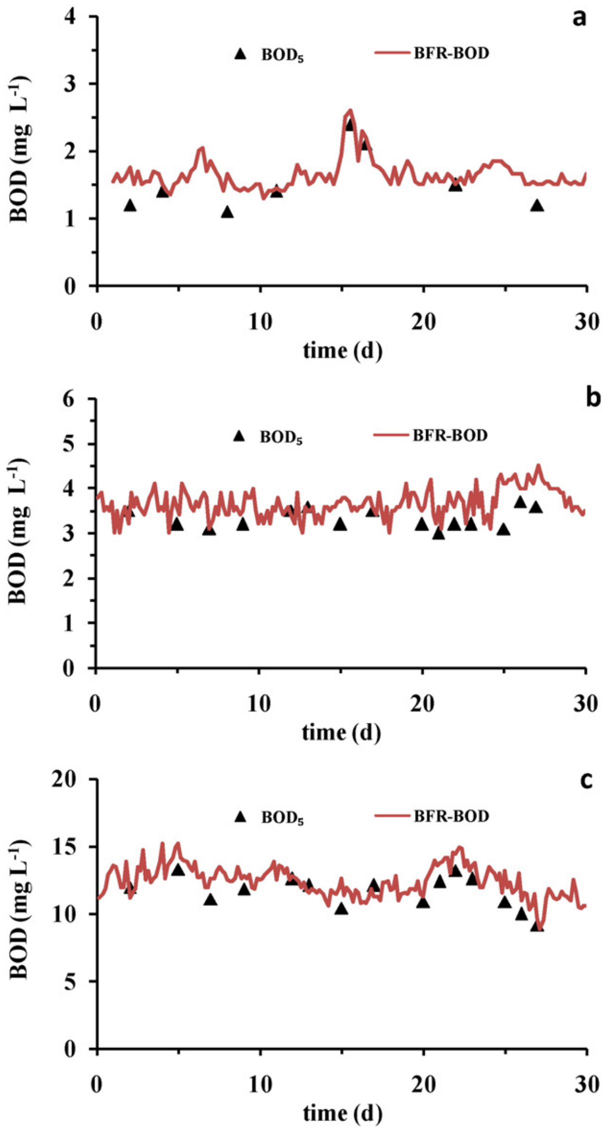

Fig. 3. Comparison studies of BFR-BOD and BOD_5 to the real samples for the three application sites. Application site: a, Taihu Lake; b, Shangxian River Wetland Park; and c, Liangtang River Wetland Park.

for the monitoring data on day 15th, the sharp increase of rapid BOD values was regarded as originating from the increased turbidity caused by heavy wind, which was near 70 NTU while the raw sample was over 800 NTU. The other parameters in this site could also verify this performance, for example, the COD_{Mn} index increased from usual 4.0 to 7.5 mg O_2 L^{-1}. Such a scene was much more obvious in late Sep. 2014, when the severe tropical storm Fung-wong transited Taihu Lake. The BOD profiles provided us sufficient evidence that the BFR based BOD analyzer could be used for biodegradable organic compounds continuously monitoring, achieving a sensitive, timely BOD early-warning for this low BOD surface water.

The Shangxian River and Liangtang River Wetland Park automated monitoring were carried out from July to August in 2015 and the results were illustrated in Fig. 3b and c, respectively. For the Shangxian River, the water quality fluctuated slightly from the results of both rapid BOD and conventional BOD_5. A mean value of 3.7 mg L^{-1} was obtained with a standard deviation of ± 0.4 mg L^{-1} ($n = 180$). The maximum analytical error was observed of $+24.6\%$ for the rapid BOD compared to BOD_5. Sharp contrast to Shangxian River, the pollution was quite serious for the Liangtang River. The average BOD exceeded 10 mg L^{-1}, which was far beyond the fifth level (level V). The Liangtang River is an urban river with unscheduled discharge of domestic and industrial wastewater. The kinds and amounts of organic pollutions fluctuated with time. Form the monitoring trend line, it could be seen that the maximum and minimum monitoring values were 14.9 and 8.8 mg L^{-1} with an analytical error of $+12.9\%$ and -4.3%, respectively. Meanwhile, the pollution was validated by other automated monitoring equipments in this site. This scene has been acquired by local government, and our online BOD analyzer would be further used for tracking the pollution source along this river.

4. Conclusions

Scientific research papers devoted into rapid BOD studies were mostly concentrated in new methods, and infrequent in field application studies. In China, this parameter attracted less attention, which can not get rid of the reason of the hysteretic instrumentation compared to other parameters. Though several kinds of rapid BOD analyzers were developed by different international manufacturers, we could hardly obtain their field application information in China. Operation and maintenance were thought to be a decisive factor regarding to the long term usage on site. Here, the oxygen concentration of the sample to be determined was used as a reference, and the oxygen consumption by the BFR was calculated according to the difference between this reference and the sample effluent from BFR. The proposed method was validated to be a feasible way in three surface water application sites and its unique feature reflected in its simplicity, near zero consumption, and easy-maintenance. Long term on site application and comparative data convinced that it was an alternative choose for BOD prediction. These onsite application data and experiences were sure to accelerate this analyzer into commercial BOD analyzer.

Acknowledgments

We acknowledge financial supports from the National Natural Science Foundation of China (No. 21305132), the Science and Technology Agency of Jilin Province (20150203020GX), and the Ministry of Science and Technology of China (No. 2013YQ17058502). The authors are grateful to the cooperation of the Environmental Protection Department of Jiangsu Province, the Environmental Protection Bureau of Wuxi City, Wuxi Environmental Monitoring Center, and the Nanquan Water Supply Factory of Wuxi City for supporting the field application study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.sbsr.2016.02.007.

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