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An optical biosensing film for biochemical oxygen demand determination in seawater with an automatic flow sampling system

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Abstract
An on-line roboticized apparatus, including an optical biosensing film with an automatic flow sampling system, has been developed for biochemical oxygen demand (BOD) determination of seawater. The sensing film employed in the apparatus consisted of an organically modified silicate (ORMOSIL) film embedded with tri(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) perchlorate. Three species of microorganism cultivated from seawater were immobilized in an ORMOSIL-polyvinyl alcohol matrix. Possible factors affecting BOD determination were studied, including sampling frequency, temperature, pH and sodium chloride concentration. Based on measurements of the linear fluctuant coefficients and the reproducibility of its response to seawater, the BOD apparatus showed the advantages of high veracity and short response time. Generally, the linear fluctuant coefficient (R^2) in the BOD range 0.2–40 mg l^{-1} was 0.9945 when using a glucose/glutamate (GGA) BOD standard solution. A reproducible response for the BOD sensing film of within ±2.8% could be obtained in the 2 mg l^{-1} GGA solution. The BOD apparatus was applied to the BOD determination of seawater, and the values estimated by this biosensing apparatus correlated well with those determined by the conventional 5 day BOD (BOD_5) test.

Keywords: biochemical oxygen demand, sensing film, BOD apparatus, sol–gel, ormosils

(Some figures in this article are in colour only in the electronic version)

Introduction

BOD is a widely used parameter for the determination of biodegradable organic compounds in wastewater and effluents. The classical conventional BOD method is the 5 day BOD test (BOD_5) [1]. The BOD_5 method needs 5 days incubation at 20 ± 1 °C in the dark, since biochemical oxidation is a slow process. Although BOD_5 is a good indicator of the concentration of organic pollutants in water, it is time consuming and not suitable for *in situ* measurement or on-line monitoring. Furthermore, it usually requires experience and skill to obtain reproducible results. Thus, it would be beneficial to find a method that could circumvent the weaknesses of the conventional method, and several biosensor methods

have been developed as an alternative for BOD measurement [2–14]. Up to now, most of these biosensors have been based on the immobilization of a microbial layer on an amperometric oxygen electrode [2–9]. However, these still have limitations such as (a) the depletion of oxygen during BOD measurement using a sensor based on the Clark electrode; and (b) the microorganisms immobilized in current BOD sensors cannot be applied to samples containing a higher concentration of salt, such as seawater. It has been reported that fibre-optic chemical sensors possess great potential for providing real-time, on-line or *in situ* detection with high sensitivity and stability [15–20]. During the past decade, some consideration has been given to fibre optical chemical sensors for the determination of oxygen, because of their rapid performance, no oxygen consumption and less toxicity [10–14].

Although most of the BOD sensors previously reported have been designed for long-term use, and even commercialized, it seems that the performance of these sensors remains unsatisfactory for the on-line environmental monitoring of seawater, since the rapid and very steady measurement of BOD is necessary in the marine environment. We previously designed a homemade sensor for BOD measurement in seawater, and the characteristics of the sensing film and the parameters for BOD determination were studied and optimized [14, 21]. However, the apparatus was composed of disjunct units, which made it inconvenient or even unsuitable for outdoor application. In this study, we have developed and assembled an on-line automatic apparatus for the BOD determination of seawater based on our previous research results [21]. In the automatic apparatus, we specially designed a time-controlled detection cell where a BOD sensing film composed of an oxygen sensing layer covering a biosensing layer of immobilized microorganisms from seawater was used. A computer was employed in this apparatus to control parameters including the sampling program, the detection process, data processing and data transference. In addition, some effect factors (including temperature, pH and the sodium chloride concentration in the sample), and response characteristics of the sensing film (including response time, reproducibility and linear range) were evaluated and discussed. The whole process for the BOD determination of a seawater sample could be completed in 20 min.

Experimental details

Chemicals and materials

Tetramethoxysilane (TMOS) and polyvinyl acetate (PVA) were purchased from Aldrich (Milwaukee, WI, USA). Dimethyldimethoxysilane (DiMe-DMOS) was purchased from Fluka AG (Buchs, Switzerland). $Ru(ph_2phen)_3(ClO_4)_2$ [ph_2phen = 4,7-diphenyl-1,10-phenanthroline], used as an oxygen-sensing indicator, was synthesized and purified in the laboratory of the Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University. Glucose/glutamate (GGA) solution was prepared by adding 0.0750 g glucose and 0.0750 g L-glutamic acid to 100 ml phosphate buffer solution (pH 7.8), and this was used as the standard BOD solution (1000 ± 185 mg l^{-1}) [22]. All other chemicals were of analytical grade without further purification and distilled water was used throughout. The seawater samples were taken from the area around Dalian (Liaoning Province, China).

BOD sensing film preparation

The BOD sensing film was made from a glass slide covered with an optical oxygen sensing layer and a microorganism-immobilized layer. Before preparation, the glass slide of 76 (L) × 25 (W) × 0.15 (H) mm^3, was soaked in concentrated nitric acid for 12 h, and then washed using distilled water and ethanol. The oxygen sensing layer composed of ORMOSIL immobilizing $Ru(ph_2phen)_3(ClO_4)_2$, was produced symmetrically at the middle of the glass slide with an area of 25 × 25 mm^2. The biosensing layer was made up of microorganisms from seawater immobilized in ORMOSIL-PVA. This layer tightly adhered to the oxygen sensing layer.

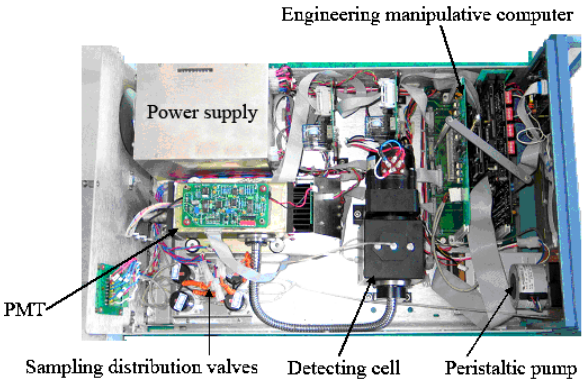
The ORMOSIL material was prepared for microbial immobilization by mixing TMOS, DiMe-DMOS as precursors and 0.01 mol l^{-1} HCl (1:1.2:1.5, v/v). The precursors were stirred at 60 °C for 1 h, and then 200 μl of a culture containing *Bacillus licheniformis, Dietzia maris* and *Marinobacter marinus* (1:2:1, w/w) at a concentration of 2.9 × 10^9 cell ml^{-1}, was mixed with 200 μl 8% (w/w) PVA and 200 μl of the prepared ORMOSIL. The mixture was then spread onto the oxygen-sensing layer to build up the BOD sensing film. The BOD sensing film was dried at room temperature for 24 h and stored in a 100 mg l^{-1} GGA solution.

Apparatus

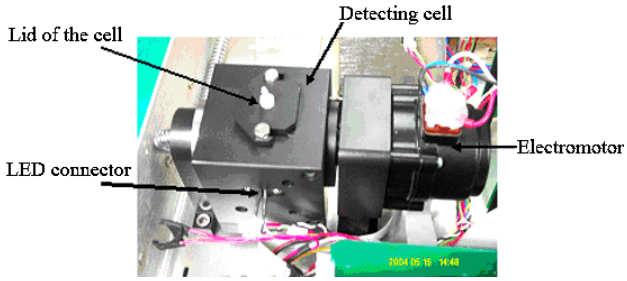
An on-line roboticized apparatus (figure 1(*a*)) was designed and developed for the BOD determination of seawater. The optical scheme and system principles of the apparatus have previously been described [25]. An optic-chemical BOD sensing film was used to measure changes in fluorescence intensity. The size of the apparatus was 60 (*L*) × 40 (*W*) × 22 (*H*) cm^3, and it was composed of (1) the sampling part, including peristaltic pump and valves to control the pumping of the recovery solution, the standard BOD solutions for calibration, and the seawater samples; (2) the controlling part, including an engineering manipulative computer and software; (3) the measurement part, including a sensing detection cell and a constant temperature controller; and (4) the light to current conversion part, including an optical fibre and a PMT (figure 1(*b*)).

Figures 1(*b*) and (*c*) show the inside configuration of the BOD apparatus. The controlling electronic circuit was composed of a computer and a driving electronic circuit. The routes of the sample and standard BOD solutions were controlled by the sampling peristaltic pump and valves. The BOD sensing film was placed in the middle of the detection cell. A pre-warming cell with a volume of 20 ml was designed and set into the bottom of the detection cell. As soon as the solution was pre-warmed to a constant temperature, the detection cell was automatically switched on by an electromotor, and the BOD measurement started. The temperature of the detection cell was kept constant using a temperature controller with a precision of ±0.2 °C. An excitation light (wavelength 475 nm) from a blue LED was

(*a*)



(*b*)



(*c*)

Figure 1. BOD apparatus for marine pollution monitoring. (*a*) BOD apparatus, (*b*) inside configuration of the apparatus, (*c*) configuration of the detection cell.

directed onto the sensing layer at an angle of 45°. The emission fluorescence was filtered by a cut-off filter with a half bandwidth of 10 nm at 580 nm, and transferred by an optical fibre to the detection unit, which was equipped with an R928 PMT (Hamamatsu, Japan). The experimental results were then processed by the software installed in the BOD system.

An EPICS XL-4 Flow Cytometry (Beckman-Coulter) was used to control the concentration of the microorganisms.

Experimental procedures

All procedures including calibration, measurement and recovery processes for BOD determination were controlled automatically by the software installed in the apparatus. The BOD sensing film was inserted into a black, airtight detection cell, in which sample solutions were kept motionless during

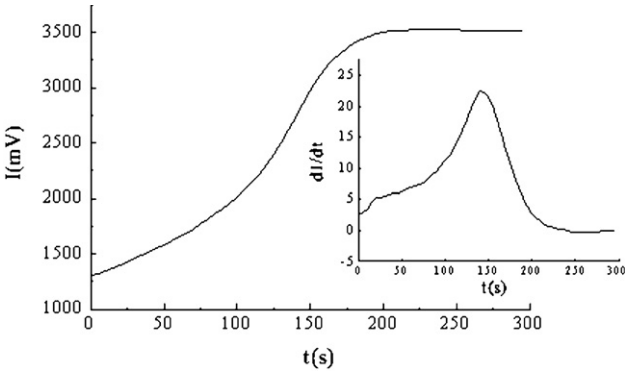


Figure 2. Typical response of the BOD sensor exposed to a standard BOD solution. Experimental conditions: constant temperature, 35 °C; pH of buffer, 7.8; salinity, 3.2%; concentration of BOD standard solution, 10 mg l^{-1}. The inset picture presents a derivative curve of the typical response; $\Delta I/\Delta t$: maximal change rate of fluorescence intensity.

all measurements. The temperature of the detection cell was maintained at 35 °C. As soon as the temperature of the sample solution reached 35 °C, the detection cell was automatically switched on, and the solution was poured into the detection cell. The output of the sensing film increased gradually and then reached a steady state after a few minutes. The typical response is presented in figure 2. In the BOD determination, a dynamic transient method (DTM) was applied. In DTM, the rate of change of the current or fluorescence intensity ($\Delta I/\Delta t$), which reflects acceleration of the microbial respiratory rate, was used for estimating the BOD value of the samples. Experimental results showed that there was a linear relationship between the maximal change rate of $\Delta I/\Delta t$ and the BOD value. After standard solutions with different concentration were used for calibration, the system was prepared for sample detection.

Results and discussion

Optimization of the biosensing system

Generally, a prepared biosensing film was immersed in a 100 mg l^{-1} GGA phosphate buffer-solution (pH 7.8) and kept at a temperature of 4 °C for longer storage time. The microorganisms immobilized in the sensing film survived in a so-called dormancy state under conditions of limited oxygen as well as the fairly low temperature. Since the microbial adaptation period was used in order to induce production of the enzymes necessary for assimilation of the desired compounds, a suitable pre-activation was used during which the BOD sensing film was alternately and repeatedly immersed into 100 mg l^{-1} GGA phosphate buffer solution and then exposed to the air for several minutes before measurement. This increased the response and stability of the BOD sensor. A number of studies [23, 24] indicate that the pre-activation process greatly enhances the biodegradation capacity of the microorganisms immobilized in the sensing film, and therefore improves agreement between measurement values and BOD_5 results. Experimental results indicated that the value of $\Delta I/\Delta t$, which represented the BOD concentration, increased in certain GGA solutions in the primary pre-activation process,

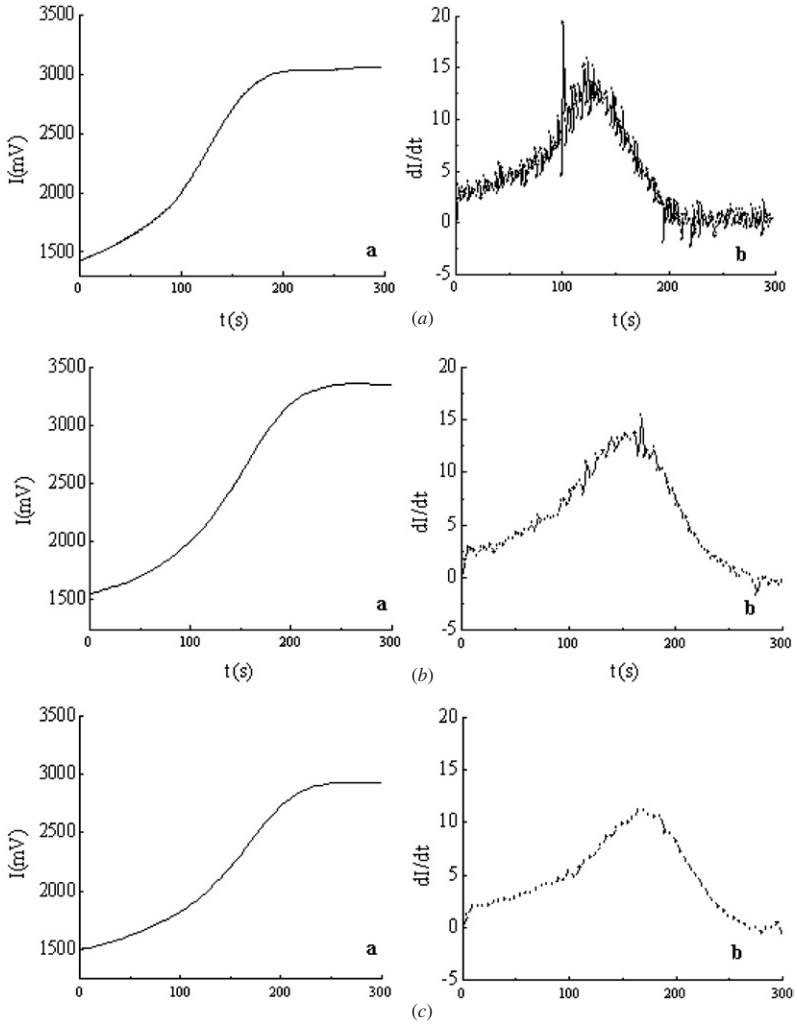


Figure 3. Response of (*a*) fluorescence intensity (I) and (*b*) $\Delta I/\Delta t$ to different frequencies of data collection: (*a*) once per second; (*b*) once per 3 s; (*c*) once per 5 s. Experimental conditions: pH, 7.8; salinity, 3.2%; temperature, 35 °C; concentration of BOD, 10 mg l^{-1}.

but the response of the sensing film became constant after four cycles of solution immersion and air exposure. In the apparatus, the four cycles for the sensing film pre-activation were automatically achieved by software control before its initial daily usage. Experimental results showed that the best times for air exposure and solution immersion were both 3 min.

In terms of the software of this BOD apparatus, the largest value of $\Delta I/\Delta t$ measured was taken as the corresponding BOD value, and the data collection frequency for BOD determination could be selected using the setting menu of the apparatus. An overly high data collection frequency can create a large data store, which would occupy more memory in the computer, resulting in a limitation to the number of data stored. In addition, any overly high data collection frequency would increase the probability of salient noise in the data recorded, which would generate an unreasonable $\Delta I/\Delta t$ value. Conversely, an incorrect low data collection frequency would result in a loss of data. In a suitable range of data collection frequency, as shown in figure 3, at a constant BOD concentration, the frequency did not greatly affect the value of $\Delta I/\Delta t$. Based on the results in figures 3(*a*) and (*b*), many salient points were obtained due to apparatus noise when the data collection frequency was selected as once per second or once per 3 s. At a data collection frequency of once per second (figure 3(*a*)), the largest value from the salient points was falsely taken as a normal $\Delta I/\Delta t$, which caused a large error in the BOD evaluation. By comparing the I–t curves in figure 3, it is clear that the system noise increased with increasing data collection frequency. At the same time, the apparatus noise was prominent with a higher frequency in the $\Delta I/\Delta t$–t curve (figure 3(*b*)). However a lower data collection frequency of once per 5 s reduced the system noise obviously (figure 3(*c*)). At this frequency, the fact that the same $\Delta I/\Delta t$ value was obtained as those at one or three times per second indicated that the data could be fully collected and, therefore, a data collection frequency of once per 5 s was selected for the experiments.

Effects of temperature, pH and salinity

The physiological state of microorganisms, in particular their respiratory state, strongly depends on temperature, pH and salinity. In general, the respiration and activation of

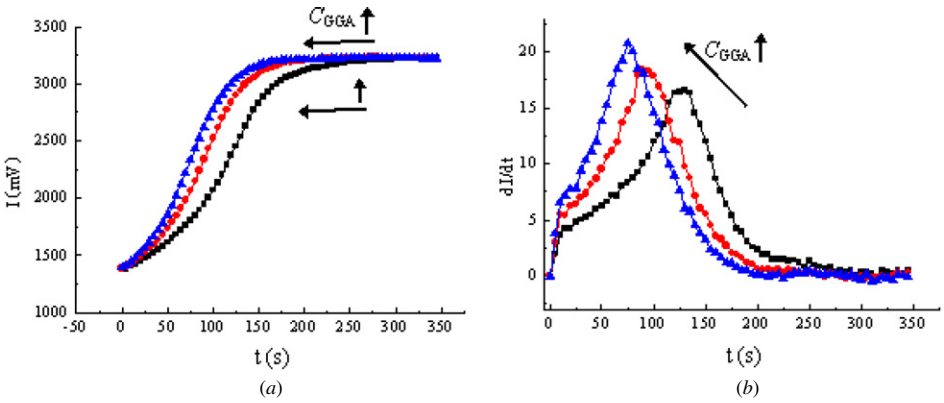


Figure 4. Response of the BOD apparatus to different GGA standard solutions. (*a*) *I*–*t* response curve, (*b*) $\Delta I/\Delta t$–*t* curve. Experimental conditions: pH, 7.8; salinity, 3.2%; temperature, 35 °C. Concentration of BOD. ♦ 0 mg l^{-1}, ● 1 mg l^{-1}, ▲ 2 mg l^{-1}.

bacteria are promoted and enhanced under an appropriate measurement temperature. An unsuitable temperature would cause the transformation of microbial conformation and metabolism and even protein solidification, resulting in the death of the microorganisms. Although the response intensity increased and the response time shortened [21] with increasing measurement temperature, the lifetime of the BOD sensing film shortened with increased temperature since the BOD sensing layer was easily dilated in water and flaked away from the oxygen-sensing layer. Furthermore, at a higher temperature, the reduction of oxygen concentration in the solution decreased the determination sensitivity. As a result, a temperature of 35 °C was selected in this study.

Taking into account the normal pH of seawater, we investigated the effect of pH on the response of the biosensing film in the pH range 5.0–8.5. Experimental results showed that the fluorescence response increased rapidly, presented a maximum at pH 7.8, and then decreased. The result indicated that a lower or higher pH value caused obvious inactivation of the microorganisms. In subsequent experiments, the pH of samples was adjusted to 7.8 using phosphate buffer.

Chloride ions are the most common component of seawater with an average concentration of 3.2%. Most biosensors involving immobilized limnetic microorganisms are not suitable for seawater application owing to inactivation of the microorganisms at this chloride concentration. However, in our sensing film, the immobilized microorganisms were cultured from seawater. In the application of this system for BOD measurement in seawater, the response intensity only decreased by 15% when the concentration of chloride ions was higher than 4%. This result indicated that the BOD sensor was able to tolerate the inhibitory effect of the high salt concentrations in seawater on the respiration of the microorganisms involved.

Characteristics of the BOD sensing system

The response of biosensors using enzymes is highly selective, but BOD sensors respond to a wide range of substrates. A BOD system (unlike the biosensors composed of specific test compounds which require singularity in the selection of the immobilized microorganism) should be designed with a microbial film possessing low selectivity and high assimilability for a wide range of organic compounds, or containing several different microorganisms for conventional analysis. Three microbial species, *Bacillus licheniformis, Dietzia maris* and *Marinobacter marinus,* were isolated from the seawater and were employed for BOD sensing film preparation. The response characteristics of the BOD apparatus equipped with this BOD sensing film were tested. A linear relationship between standard GGA concentration and change of velocity of the $\Delta I/\Delta t$ in this apparatus was observed in the range of 0.2–40 mg l^{-1} GGA solution, and the linear fluctuant coefficient (R^2) was 0.985. The detection limit of the method was 0.18 mg l^{-1} with a standard deviation less than 2.5% in a series of 12 blank solutions. In the routine BOD detection, three concentrations of GGA with 0, 1 and 2 mg l^{-1} were selected for the standard curve calibration. A typical $\Delta I/\Delta t$ response, which changed with GGA concentration, is presented in figure 4. Good linearity is shown, with a coefficient of 0.9945, between $\Delta I/\Delta t$ value and GGA concentration. The full measurement process (except for curve calibration) for analysis of a seawater sample took only 20 min.

The sensing film-to-film reproducibility greatly depended on the number of microorganisms immobilized, the thickness of the oxygen sensing layer, the characteristics of the ORMOSIL-PVA material and the experience of the film producer. The number of immobilized microorganisms could be accurately counted using a flow cytometer. The characteristics of oxygen and the ORMOSIL-PVA layer could be controlled well based on the description in a previous study [21]. For the preparation of sensing films in our laboratory, a student generally achieved reproducibility within a mean value of ±10% using different pieces of sensing film in 2.0 mg l^{-1} GGA standard solution after only one month of training.

The stability and reproducibility of the BOD system using a 2.0 mg l^{-1} GGA standard solution and a seawater sample during 10 h of continuous detection was investigated. The standard deviations were ±2.8% ($n = 20$) and ±3.6% ($n = 18$) for GGA solution and seawater from Dalian, China, respectively. A slight decrease in the BOD system response could be observed when the system was repeatedly used to measure the same seawater. This response decrease might have been caused by incomplete sensing film recovery, or a slight increase in the endogenous respiration rate of the microorganisms after frequent measurements.

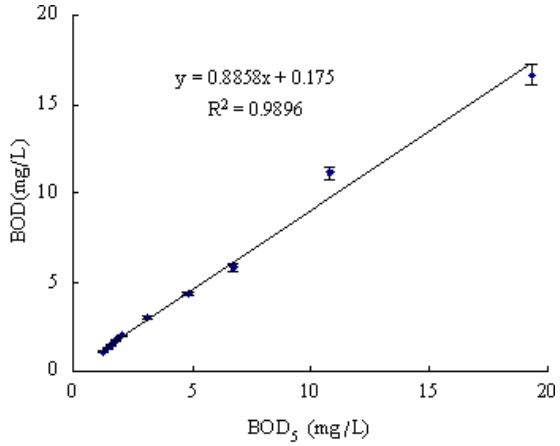


Figure 5. Correlative curve between the BOD apparatus and BOD_5 results (E121°44′ N39°01′, $n = 10$).

Application of the BOD system to natural seawater

The BOD biosensor approach will over-represent the most easily biodegradable organics present in a sample, which means that only a small portion of the available carbon will be degraded in the limited reaction time; typically, less than 1% of the available carbon is degraded in a BOD biosensor assay, compared with >60% for the standard BOD_5 assay [25]. In addition, the relative proportion of the readily biodegradable fraction will vary between samples, thus, the BOD value obtained from the biosensor method would show up as an alternative to the BOD_5 value. The BOD and BOD_5 values obtained by adding different GGA concentrations into a seawater sample from Dalian, China, were measured and are compared in figure 5. The difference between the BOD and BOD_5 values ranged from −0.5% at a concentration of 1.8 mg l^{-1} BOD to −12% at a concentration of 17 mg l^{-1}. These observations were to be expected for the above-mentioned reason. Fortunately, at lower concentrations of BOD (between 1.2 and 3.0 mg l^{-1}), which covered the BOD value of most seawater samples, the BOD values corresponded well with those of BOD_5, as shown in figure 5.

The system equipped with the BOD sensing film was used to determine BOD in the seawater around Dalian (E121°44′ N39°01′), China. Seawater samples were pumped and filtered through a membrane filter with a pore size of 200 μm. Before testing, about 20 ml seawater was pre-warmed at 35 °C in a cell, and then poured into the detection cell for BOD measurement. The BOD detection results are listed in table 1.

There are obvious differences in BOD concentration between the samples from clean seawater and those from around a sinkhole. Obviously, the higher concentration of BOD around the sinkhole was caused by the direct introduction of human wastewater. In addition, in table 1, comparing the BOD and BOD_5 values obtained, we noticed a maximum 16% subtractive error for seawater samples from the sinkhole area, but only 6.8% for the sample from the clean site. In our view, the bio-degradation process was insufficient in the limited measurement time, especially in the case of higher BOD concentrations, which led to a larger subtractive error between BOD and BOD_5 values. Furthermore, insoluble organic components in the seawater can be partially degraded by microorganisms during incubation in the conventional 5 day BOD method, and thus can contribute to the BOD_5 values but not to those measured using BOD sensors. The different composition of the samples also might increase the subtractive error.

Table 1. BOD and BOD_5 of the seawater around Dalian ($n = 5$).

Sampling pot	No	pH	Salinity (‰)	BOD_5 (mg l^{-1})	BOD (mg l^{-1})
Seawater (E121°44′ N39°01′)	1	8.01	34	1.2 ± 0.1	1.2 ± 0.2
	2	7.98	34	1.4 ± 0.2	1.3 ± 0.3
	3	7.68	29	1.5 ± 0.2	1.5 ± 0.3
	4	8.05	33	1.8 ± 0.1	1.7 ± 0.2
	5	7.82	32	2.0 ± 0.2	2.0 ± 0.2
	6	7.79	32	3.1 ± 0.2	3.0 ± 0.3
Seawater around the sinkhole	7	7.80	32	4.8 ± 0.3	4.4 ± 0.2
	8	7.81	33	6.7 ± 0.3	5.9 ± 0.3
	9	7.85	33	11.2 ± 0.4	11.1 ± 0.3
	10	7.92	32	19.3 ± 0.6	16.6 ± 0.5

Conclusions

We have constructed and improved a robotic BOD sensing apparatus using a sensing film immobilizing three species of microorganisms, *Bacillus licheniformis, Dietzia maris* and *Marinobacter marinus*, from seawater. An ORMOSIL-PVA material was synthesized for immobilization of the microorganisms. The sensing film could be employed successfully for BOD measurement of seawater samples, and presented satisfactory characteristics in its practical application. The optimum response of the BOD sensing film was obtained at pH 7.8 and 35 °C. The minimum measurable BOD was 0.18 mg l^{-1}. The results obtained from actual seawater demonstrated a good correlation with those obtained from conventional BOD_5 analysis.

When using this type of BOD sensor for seawater samples, the effect of salinity is of major concern. The selection and incubation of microorganisms from seawater, which have a high assimilation efficiency, is an effective route to improve the response characteristics and the application life of sensing films for seawater samples. Additionally, the approach by which various microorganisms are immobilized in a sensing film would reduce the subtractive error between BOD and BOD_5 values.

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