A study on the relationship between $\text{BOD}_5$ and COD in a coastal seawater environment with a rapid BOD measurement system


ABSTRACT

The dual objectives of this study are to: (1) examine the relationship between COD and BOD in seawater environment with a rapid but reliable method for the measurement of BOD in seawater, and (2) establish the relationship model between $\text{BOD}_5$ and COD in the firth of Dongbao River to predict the values of $\text{BOD}_5$. The first objective is met by the successful development of a technique utilizing bacteria-immobilized membrane flow cell for biodegradation process, coupled with fibre optic fluorescence detection for oxygen depletion quantitation. The technique has been applied to coastal seawater samples collected in the coastal area of Shenzhen, China. The $\text{BOD}_5$ and COD values for the samples are acquired and the results show that there is no apparent linear relationship existing between $\text{BOD}_5$ and COD in relatively clean seawater samples away from the shore. However, in estuary water samples containing relatively high concentration of sewage contamination, a linear correlation does exist between $\text{BOD}_5$ and COD. The linear relationship between the two parameters allows for the calculation of $\text{BOD}_5$ values based on COD data which can be measured more readily and precisely.

Key words | $\text{BOD}_5$, coastal seawater, COD, linear correlation

INTRODUCTION

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD), which quantify the organic pollutants in aquatic environment, are important parameters in water quality (He 2001). For surface waters and wastewaters such as municipal sewage or industrial effluent, extensive researches have been conducted on this subject (Ekama et al. 1986; Orhon et al. 1997). The abundant information accumulated from different water or wastewater samples demonstrates that a systematic correlation exist between BOD and COD (Tian & Long 1988; Song 2000). Compared with fresh water systems, the measurement of COD and BOD in seawater is complicated by high salt content, variations in pH and the presence of diverse organic and inorganic contaminants. To our knowledge, there is no systematic study on the reproducibility of COD and BOD measurements and the relationship between the two parameters for seawater samples yet. In this paper, a novel method has been developed to measure the value of BOD which is denoted by $\text{BOD}_5$ in seawater samples. The method is rapid and easy to operate, taking only 30 min to complete. The method has been applied to the measurement of coastal seawater samples collected in Shenzhen sea area. A detailed analysis was carried out to examine systematically the relationship between $\text{BOD}_5$ and COD.

METHODS AND THEORY

The schematic diagram of the BOD fast measurement system is shown in Figure 1. The system is based on fluorescence detection using fibre optics. The experimental apparatus, analytical reagents used and detailed procedures...
for the measurement were described by Dai & Zhong (2003). Only a brief description of the relevant experimental setup for the fast BOD measurement is given here.

In the optical train, the light at 495 nm from LED excites the BOD sensor film, which in turn emits fluorescence at 580 nm for detection. The BOD sensor film is composed of a dissolved oxygen membrane with embedded aerobic bacteria. In the presence of organics in water, the occurrence of biodegradation reaction causes the depletion in dissolved oxygen concentration, and the signal is detected by the oxygen sensor. The extent of oxygen depletion is used to quantify the amount of organics in water samples expressed as BOD values. Using the mixed solution of glucose and glutamic acid (GGA) as the standard solution, the dynamic process can be expressed as Equation (1) (Jiang et al. 2006).

\[ \frac{dI}{dt} = 1.2401C + 194.37 \]  

(1)

in which \( d \) is the differential coefficient, \( I \) is the fluorescence intensity measured by the PMT detector, \( t \) is the time to achieve maximal steady fluorescence, and \( C \) is the BOD value of the sample (unit: mg/L).

Based on the extensive experimental data, a linear relationship exists between \( \text{BOD}_{\text{GGA}} \) and \( \text{BOD}_5 \), which can be expressed as Equation (2) (Jiang et al. 2006).

\[ \text{BOD}_{\text{GGA}} = 3.40 \text{BOD}_5 + 6.18 \]  

(2)

in which \( \text{BOD}_{\text{GGA}} \) is the BOD value from GGA standard solution detected with the BOD fast measurement system, \( \text{BOD}_5 \) is the BOD value cultivated at 20°C for 5 days (SMMPSA 1998). The correlation coefficient \( r \) for Equation (2) is 0.9856, and the equation can be used to convert the \( \text{BOD}_{\text{GGA}} \) of sample into \( \text{BOD}_5 \). With this measurement system, \( \text{BOD}_5 \) for a sample can be obtained with significantly reduced measurement time from 5 days to 30 min. The reliability of this system has been proven by the comparison of the calculated \( \text{BOD}_5 \) values from Equation (2) with those by conventional 5-day cultivation method (SMMPSA 1998).

The relationship between COD and BOD could be better understood through an analysis of the process of biodegradation of organic matter by bacteria (Gu 1982; Gao & Zheng 1989; Weijers 1999). COD consists of \( \text{COD}_{\text{NB}} \) and \( \text{COD}_B \), which denote substance that cannot be biologically decomposed and substance that can be decomposed by microbe, respectively. In a given sea area, the environmental factors including the properties of marine sediment, the distribution and type of biological species, and the overall water quality can be treated as constants. The ratio of \( \text{COD}_{\text{NB}}/\text{COD} \) should be steady correspondingly, taking the form of Equation (3).

\[ \text{COD}_{\text{NB}} = \epsilon \text{COD} \]  

(3)

where \( \epsilon \) is a proportional constant. Based on the equation, the \( \text{COD}_B \) can be expressed by COD as Equation (4).

\[ \text{COD}_B = (1 - \epsilon) \text{COD} \]  

(4)

The COD value in Equation (4) can be measured by the classical method (SMMPSA 1998). The relationship between \( \text{COD}_B \) and BOD in municipal sewage has been reported to take the form of Equation (5) (Guo & Long 1994).

\[ \text{BOD} = (\alpha + \beta \times \gamma) \times \text{COD}_B \]  

(5)

where \( \alpha \) is the respiratory metabolism constant in oxidizing organic substances, \( \beta \) is the catabolism constant in oxidizing organic substances and \( \gamma \) is the endogenesis respiration constant in oxidizing cellulate substances. The BOD value measured by the developed method in this paper can be expressed by \( \text{BOD}_5 \). The biodegradation rates in COD and BOD process can then be expressed by Equation (6) and Equation (7), respectively.

\[ \frac{dC}{dt} = -K_C \times C \]  

(6)

\[ \frac{dL}{dt} = -K_L \times L \]  

(7)

In which the terms \( C \) and \( L \) represent the concentration of \( \text{COD}_B \) and \( \text{BOD}_5 \), respectively, and \( t \) denotes time. The relationship between \( \text{BOD}_5 \) and COD in the seawater can be expressed as Equation (8).
The experimental data for the seawater samples from Dapeng Bay are listed in Table 1. The sample collections were carried out in April, July and September of 2006. Three batches of samples from each station were collected and used to test the correlation between COD and BOD5 values.

According to Equation (8), if $y$ and $x$ denote respectively COD and BOD5 values, a unitary linear recursive equation can be set up as shown by Equation (9).

$y = b \times x + a$  

(9)

where $b$ and $a$ are the slope and intercept of the straight line, respectively. The sum of deviation squares ($Q$) can be calculated by Equation (10), using the data set shown in Table 1.

$Q = \sum_{i=1}^{n} (y_i - a - bx_i)^2, \quad n = 18$  

(10)

To calculate the least square value, $Q$ is differentiated against $a$ and $b$ respectively to yield Equation (11) and Equation (12) as follows.

$\frac{\partial Q}{\partial a} = -2 \sum_{i=1}^{n} (y_i - a - bx_i) = 0$  

(11)

$\frac{\partial Q}{\partial b} = -2 \sum_{i=1}^{n} x_i(y_i - a - bx_i) = 0$  

(12)

The values of $a$ and $b$ can then be solved by Equation (13) and Equation (14).

$b = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{x})^2}$  

(13)
In order to determine the validity of the regression curve, the linear correlative coefficient \( r \) is calculated by Equation (15) with the data listed in Table 1.

\[
r = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (y_i - \bar{y})^2}}, \quad n = 18
\]

Using \( \varepsilon \) to denote the ratio of COD to BOD\(_5\), the \( \varepsilon \) value can be written as Equation (16).

\[
\varepsilon = \frac{y_i}{x_i}
\]

In Table 1, \( n \) is 18. The values of \( a \), \( b \) and \( r \) are calculated as follows according to Equations (13)–(15).

\[
b = 0.453, \quad a = 1.32, \quad r = 0.336
\]

Table of critical value of \( r \) (Wang 1988) can be used to judge whether the regression curve has a good correlation coefficient (\( P = 95\% \)). Since \( r_{0.05,16} = 0.468 \), which is greater than the calculated \( r \) (0.336), it can be concluded that the COD and BOD\(_5\) values in relatively clean coastal seawater have certain linear correlation with a confidence level of 95%, but not remarkable.

The same procedures can be used to evaluate the correlation between COD and BOD\(_5\) in dirtier coastal seawater. One example is the firth of Dongbao River (brackish water heavily polluted by municipal wastewater), which is located in the west side of Shenzhen City, close to Zhujiangkou sea area (Pearl River estuary). In the firth of Dongbao River to sea, the salinity is in the range of 3.0 to 5.5 and dung coliform is more than \( 2.4 \times 10^4 \) cells/L. Three monitoring stations have been established in the firth along river midline from inland to the river mouth. The COD and BOD\(_5\) values are monitored to examine the existence of possible correlation (Table 2).

Each value in Table 2 represents the average of three measurements. As shown by the ratios of COD to BOD\(_5\) in Table 2, no obvious outlier exists. For data in Table 2, parameters of \( a \), \( b \), and \( r \) can be acquired via Equations (9) to (15).

\[
b = 3.54, \quad a = 2.38, \quad r = 0.983
\]

When \( P \) is 95\%, \( r_{0.05,7} \) is 0.666 which can be obtained from the critical value table for \( r \) (Wang 1988). The value, \( r_{0.05,7} \) as seen, is obviously less than \( r \) (0.983), which indicates that there is a good linear relationship between COD and BOD\(_5\) in the water samples from the firth of Dongbao River.

Based on the relationship, the BOD\(_5\) values of the seawater samples could be reasonably estimated by the COD values, which can be measured more readily and

### Table 2 | Data of BOD\(_5\) and COD for samples from the firth of Dongbao River. (Unit: mg/L)

<table>
<thead>
<tr>
<th>Station</th>
<th>Mean salinity</th>
<th>April BOD(_5)</th>
<th>COD</th>
<th>Ratio</th>
<th>July BOD(_5)</th>
<th>COD</th>
<th>Ratio</th>
<th>September BOD(_5)</th>
<th>COD</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>3.0</td>
<td>16.3</td>
<td>62.3</td>
<td>3.80</td>
<td>10.3</td>
<td>39.9</td>
<td>3.88</td>
<td>9.52</td>
<td>29.6</td>
<td>3.11</td>
</tr>
<tr>
<td>D2</td>
<td>4.4</td>
<td>4.61</td>
<td>21.2</td>
<td>4.60</td>
<td>4.70</td>
<td>19.8</td>
<td>4.21</td>
<td>4.56</td>
<td>20.0</td>
<td>4.38</td>
</tr>
<tr>
<td>D3</td>
<td>5.4</td>
<td>4.14</td>
<td>18.0</td>
<td>4.34</td>
<td>4.03</td>
<td>14.2</td>
<td>3.52</td>
<td>3.21</td>
<td>13.7</td>
<td>4.27</td>
</tr>
</tbody>
</table>

### Table 3 | The comparison between the predicted BOD\(_5\) value and the measured value for samples from the firth of Dongbao River, salinity in the range of 3.0 to 5.5. (Unit: mg/L, RE: relative error between measured value and predicted value, denoted by \( |BOD_{5,P} - BOD_{5,M}| \times 100\% \))

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>8.7</td>
<td>10.0</td>
<td>11.9</td>
<td>14.0</td>
<td>16.2</td>
<td>19.1</td>
<td>20.0</td>
<td>27.3</td>
<td>29.5</td>
</tr>
<tr>
<td>BOD(_5),P</td>
<td>1.79</td>
<td>2.15</td>
<td>2.69</td>
<td>3.28</td>
<td>3.90</td>
<td>4.72</td>
<td>4.97</td>
<td>7.04</td>
<td>7.66</td>
</tr>
<tr>
<td>BOD(_5),M</td>
<td>2.21</td>
<td>2.32</td>
<td>3.29</td>
<td>3.03</td>
<td>4.23</td>
<td>4.92</td>
<td>4.70</td>
<td>7.81</td>
<td>8.88</td>
</tr>
<tr>
<td>RE (%)</td>
<td>19</td>
<td>7.0</td>
<td>18</td>
<td>8.0</td>
<td>7.7</td>
<td>4.0</td>
<td>5.7</td>
<td>9.8</td>
<td>14</td>
</tr>
</tbody>
</table>
precisely. The correlation has been established to predict the values of BOD$_5$ by detecting COD in samples from the firths of several rivers such as Dongbao River and Kuichong River in Shenzhen. In order to test the validity of the proposed relationship between the two parameters, extensive comparison experiments have been performed. BOD$_5$ values were obtained both by prediction from Equation (19) and the conventional 5-day cultivation method, respectively. Part of the results is listed in Table 3.

BOD$_{5,m}$ and BOD$_{5,p}$ are measured value and predicted value respectively. COD is measured by the standard method (SMMPSA 1998). The values listed show that the calculated values of BOD$_{5,p}$ agree reasonably well with the measured ones.

The results above show that there is not obvious linear correlation between COD and BOD$_5$ in relatively clean coastal seawater in which BOD$_5$ value is normally less than 3.0 mg/L. However, a significant linear correlation between the two does exist in heavily polluted coastal waters in which BOD$_5$ value is normally greater than 3.0 mg/L. The reasons for the different relationship between two parameters for samples from different sea areas have not yet been well understood. Considering the salinity of samples collected in Dapeng Bay is much higher than that of samples from the firth of Dongbao River, the difference in salinity may be one of the reasons accounting for the different relationship. More parameters including salinity may need to be introduced to future study for a better understanding of the relationship.

CONCLUSIONS

A rapid BOD measurement system is used to investigate the relationship between BOD$_5$ and COD in coastal seawater. The results show that there is no remarkable linear relationship ($r = 0.336$) existing between BOD$_5$ and COD in relatively clean seawater samples, but a linear correlation ($r = 0.983$) exists between them in samples from the firth of Dongbao River contaminated with municipal wastewater. The correlation has been successfully established to predict the BOD$_5$ values for samples from the river firths in Shenzhen, which provides an easier way to monitor and understand the pollution in the coastal waters.

REFERENCES


