An inquiry into the relationships between BOD$_5$, COD, and TOC in Tigris River, Maysan Province, Iraq

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ABSTRACT

Despite its universally wide use in water quality indices and evaluating the efficiency of wastewater treatment plants, chemical oxygen demand (COD) or biological oxygen demand (BOD$_5$) analyses have disadvantages such as being imprecise, time-consuming, insensitive, as well as the production of hazardous wastes. Total organic carbon (TOC) will introduce as an alternative analysis, the relationship between BOD$_5$, COD, and TOC has been investigated in this study. A total number of 216 samples were taken from three stations (kumait, Al Amara, and Al Majar Al Kabeer) in Tigris River, Maysan Province, Iraq. The sampling was on a monthly basis during a two-year period. The tests were performed according to ASTM D7573-18ae1, ASTM D6238-98, and ASTM D125-06 for TOC, BOD$_5$, and COD respectively at the Pollution Research Centre of the Al-Shatra Institute, the data were statistically analyzed using the SPSS program to predict a relationship between the COD or BOD$_5$ and TOC. The analysis showed a good relationship concerning to a value of correlation coefficient, i.e., $r = 0.93$ or $r = 0.94$ between TOC and BOD$_5$ or COD respectively, as well as the coefficient of determination, i.e., $R^2 = 0.91$ or $R^2 = 0.92$ between TOC and BOD$_5$ or COD respectively. The validation of the suggested formulas has been tested using data from the Pollutant Centre in Al Shatra Institute for Shat al Gharaf River. The formulas gave reasonably acceptable values. It could be used in monitoring water quality and wastewater plants as a surrogate parameter to have pre-impression of the plant efficiency.

Keywords: BOD$_5$, COD, Relationship, Tigris, TOC.

INTRODUCTION

Chemical oxygen demand (COD) and Biological oxygen demand (BOD$_5$) globally considers major water quality measurements besides modeling wastewater systems and monitoring design. It requires five days to get BOD$_5$ analyses, while it takes only a few hours to obtain COD. However, the presence of chloride at high concentrations leads to inaccurate results of organic pollutants, since BOD$_5$ is extremely sensitive to obstructing substances in water samples (Jingsheng et al. 2006; Dubber & Gray 2010; Khatun & Rashidul Alam 2020; Zidani et al. 2020; Omidi & Shariati 2021; Abdouni et al. 2021; Fallah et al. 2021). On the contrary, COD is not influenced by these substances and does not consume time. However, it is highly recommended to be aware that the resulting container sample from the COD test could contain hazardous chemical wastes such as mercury that exceeds the normal limits (Nemerow 2010). Even with the large use of COD as an alternative test for BOD$_5$, it is clear that COD cannot imitate accurately the industrial wastewater degree due to the oxidant's types impact, the catalyst, and reaction solution acidity. On the other hand, the strength of organic pollution can be reflected accurately using total organic carbon (TOC) because of the advantages that its method contains such as accurate results, not affected by the hindering substances, low production of toxic like mercury, short time procedure and
reliability (Hua et al. 2011). However, the recorded information about the possibility of employing TOC instead of COD or BOD$_5$ is little, which could be attributed to the problematically in gaining an accepted relationship between TOC and BOD$_5$ or COD (Bourgeois et al. 2001). The relationship between BOD$_5$ or COD and TOC has been evaluated recently in river and wastewater cases (Constable & McBean 1979; Aziz & Tebbutt 1980; Reynolds 2002; Waziri & Ogugbuaja 2010; Dubber & Gray 2010). Some of the studies showed a low coefficient of correlation (0.24) between TOC and BOD$_5$ for surface water (Maier & McConnel 1974), while a good coefficient of correlation has been demonstrated between TOC and COD (0.7) for the river water samples in other studies (Waziri & Ogugbuaja 2010). The same study shows the possibility to gain high correlation between BOD$_5$ and TOC up to 1.

Despite the efforts of suggesting alternative methods to minimize the time and obtain a high accuracy to estimate the amounts of organic pollutants in aquatic environments, COD or BOD is still used globally to measure organic pollutants in water samples. This study examined the relationship between BOD$_5$ or COD and TOC, the coefficient of determination ($R^2$) and the correlation coefficient ($r$) have been evaluated for Tigris River, south of Iraq using data obtained from monthly monitoring in two years since 2019.

MATERIALS AND METHODS

This study was restricted to the south region at Iraq in Maysan Province in specific, Ali Al Sharqi kumait, and Al Amara. Tigris River are flowing in this province. The samples were taken from the stations located at the three mentioned cities in the route of Tigris (see Fig. 1). In this Fig., the entire path of Tigris through the province has been illustrated. The pollutant discharge finds its way to this river from the cities on the river, in general, the effect of human activity, industrial wastewaters, sewage discharge, and the wrong places of the industries plans appears clearly in the great degradation to the water quality in Iraq.

![Fig. 1. The location of three stations located at the route of Tigris River in Maysan Province, Iraq.](image-url)
Samples were collected monthly in two years since 2019 from three stations, located at the end of the kumait, Al Amara and Al Majar Al Kabeer cities after the river cross the cities, to ensure that the samples are represented to the cities influence on the water properties. Three samples were collected from each station (216 samples in total). The collected samples were arranged and examined to gain TOC, BOD₅ and COD values for each station. The mean value for every three samples from the river cross-section has been computed. The tests were performed according to ASTM D7573-18ae1, ASTM D6238-98 and ASTM D125-06 for TOC, BOD₅ and COD respectively, at the Pollution Research Centre of the Al-Shatra Institute. The results included 72 mean values for TOC, COD, and BOD₅.

RESULTS AND DISCUSSION
The collected samples were examined at the Pollutant Centre in Al Shatra Institute to obtain the BOD₅, COD and TOC at the three stations. The mean concentrations were calculated separately for every section, resulting in 72 values for BOD₅, COD and TOC. The average concentrations of these 72 values were 2.29 ppm, 5.01 ppm, and 2.65 ppm for BOD₅, COD, and TOC respectively. In Ali Al Sharqi Station, the minimum concentrations of BOD₅ in April, COD in April and TOC in March were 1.3, 2.99 and 1.87 ppm respectively which could be attributed to the percentage of the population in this station, because of locating it at the lower part of the river among the three stations. In Al Amara station, during August, the maximum BOD₅ concentration was 3.81 ppm, while those of COD and TOC were 7.92 and 4.31 respectively, which may be due to the large population of Al-Amara compared to the other cities. The examination of the results for the whole three stations leads to classifying the Tigris River in these cities as unpolluted river which could be explained by the absence of industrial facilities in these cities, meaning that the river does not receive industrial wastewater. Table 1 depicts the important concentration of TOC, BOD₅, and COD values at each station.

Table 1. The TOC, BOD₅ and COD concentration values in ppm at each station.

<table>
<thead>
<tr>
<th>Station</th>
<th>Concentration</th>
<th>BOD₅</th>
<th>COD</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>2.19</td>
<td>4.75</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>3.21</td>
<td>7.12</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>1.30</td>
<td>2.99</td>
<td>1.87</td>
</tr>
<tr>
<td>Kumait</td>
<td>Average</td>
<td>2.28</td>
<td>5.05</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>3.61</td>
<td>7.41</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>1.32</td>
<td>3.12</td>
<td>1.86</td>
</tr>
<tr>
<td>Al Amara</td>
<td>Average</td>
<td>2.39</td>
<td>5.24</td>
<td>3.04</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>3.81</td>
<td>7.92</td>
<td>4.31</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>1.45</td>
<td>3.33</td>
<td>2.03</td>
</tr>
</tbody>
</table>

According to the results of BOD, COD, and TOC, clearly, the BOD₅ values were lower than COD and TOC which could be explained by the fact that BOD is a good indicator for organic pollution in the water system, while TOC and COD represent both non-biodegradable and biodegradable organic pollutions (Bourgeois et al. 2001). The values of BOD₅ concentration in February, March, April, and May were the lowest among the other months which could be related to the fact that these months have the most rain during the year and also the BOD level can be
affected by the discharge of low-BOD water from snowmelt or rain. The correlation between BOD$_5$, COD and TOC are illustrated in Figs. 3 and 4.

To find the correlation between TOC and COD or BOD$_5$ the data were analyzed using the SPSS program. Table 2 depicts the correlation coefficients ($r$) and the coefficient of determination ($R^2$) between TOC and BOD$_5$, COD in Tigris River. A strong linear relationship between TOC and BOD$_5$ represented by the values of the correlation coefficient ($r = 0.93$) and the coefficient of determination ($R^2 = 0.92$). The analyses show that BOD$_5$ could be estimated depending on the value of TOC using the following formula:

$$BOD_5 = 0.65 \times TOC^{1.18}$$

Furthermore, the correlation coefficient ($r$) between COD and TOC has the value of 0.94 and coefficient of determination ($R^2$) of 0.91. The value of COD could be estimated depending on the value of TOC using the fitting equation:

$$COD = 1.5 \times TOC^{1.132}$$

The validity of the new fitting formulas has been tested by two types, statistical analysis and graphical method using data from the Pollutant Centre in Al Shatra Institute for Shat al Gharaf River.

The statistical analysis

Using the percentage of error, the two new suggested formulas have been tested statistically by comparing the observed BOD$_5$, and COD with the predicted BOD$_5$, and COD. Table 3 presented the result for the percentage of error for the two suggested formulas. The two suggested formula shows matches in 90% of the tested data, while the deviation was slight in 10% only.
Table 2. The correlation coefficients (r) and the coefficient of determination (R²) for the new suggested formulas.

<table>
<thead>
<tr>
<th>Fitting formula</th>
<th>r</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD5/TOC</td>
<td>0.93</td>
<td>0.91</td>
</tr>
<tr>
<td>COD/TOC</td>
<td>0.94</td>
<td>0.92</td>
</tr>
</tbody>
</table>

COD = 1.5 × [TOC]^1.132

Table 3. Evaluation using Percentage of Error for the new formulas.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Percentage of Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>BOD formula</td>
<td>94%</td>
</tr>
<tr>
<td>COD formula</td>
<td>96%</td>
</tr>
</tbody>
</table>

The graphical comparison

The results of the two new formulas are compared graphically with the observed values. The comparison showed that how the observed concentration of BOD₅ is close to that of expected BOD₅ using the BOD formula. In addition to the observed COD close to the expected COD, the good distribution of points along the diagonal line in the graphical comparison indicates the convergence of the results obtained from the proposed equation with the true target values. Figs. 5-6 show the graphical comparison for the two new formulas. Although BOD₅ is a standard method approved by most Environmental Protection Agency and is generally the only approved analytical method as a water quality measurement and regulatory compliance of wastewater plants, it is necessary to adopt a fast-alternate test procedure. The replacement of BOD₅ by TOC, provides a good indicator for water quality as presented in the statistical analysis and the graphical comparison. Treatment facilities in California and Nevada started adopting total organic carbon (TOC) to estimate the BOD₅ of influent wastewater and treated effluent which confirms the results of the present study (Christian et al. 2017).

![Graphical comparison for the observed and predicted BODs](image1.png)

![Graphical comparison for the observed and predicted COD](image2.png)
CONCLUSION
The relationships between TOC and BOD, or COD has been provided based on the results of a two-year study of water quality data for the experimental sample tests for Tigris River, south of Iraq from three monitoring stations. Two formulas were suggested to predict the concentration of BOD or COD depending on TOC value. A higher value of correlation coefficient (r = 0.93) or (r = 0.94) was detected between TOC and BOD or between TOC and COD. In the meanwhile, the coefficient of determination (R²) was 0.91 or 0.92 between TOC and BOD or between TOC and COD. Due to the result of good relationships between TOC, and COD or BOD, our results suggest the possibility of using the predicted formulas to estimate BOD and COD depending on TOC in Tigris River, south of Iraq. However further studies are to be conducted for the correlation of BOD and TOC in other rivers in Iraq.

REFERENCES
Dubber, D & Gray, NF 2010, Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste. Journal of Environmental Science and Health Part A, 45: 1595-1600.
Leo, C & Van, R 1993, Principle of Sediment transport in River Estuaries and coastal Seas. The Netherlands, Aqua publication.