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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: BOD5, COD, Relationship, Tigris, TOC.
Article type: Research Article.

INTRODUCTION

Chemical oxygen demand (COD) and Biological oxygen demand (BOD5) 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

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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.

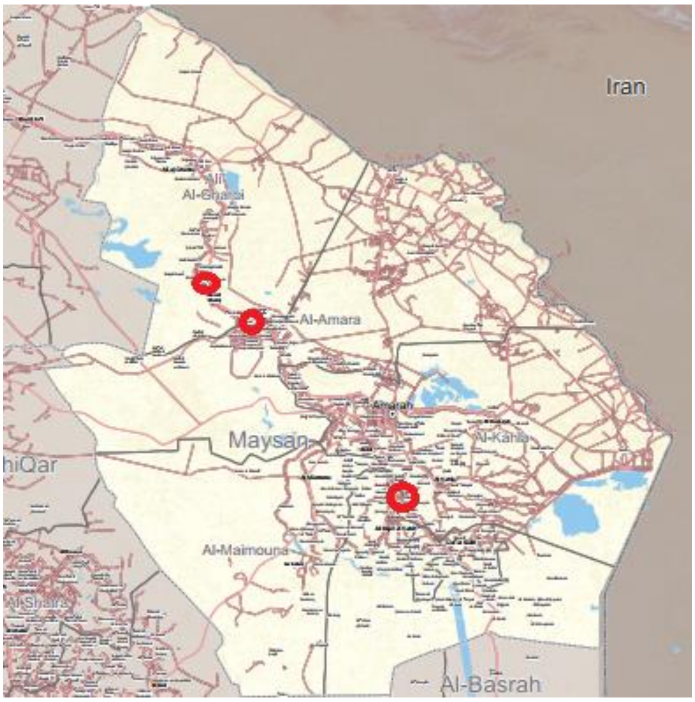

Fig. 1. The location of three stations located at the route of Tigris River in Maysan Province, Iraq.

The researcher adopted the depth integrating sampling method to ensure that the taken sample is representative of the river's water, since the concentration varies with the depth of the stream. The principle of this method is taking samples along with the depth of the river, not just from the surface. The integrating sampling method consists of descending sampler close to the stream bed, and then it is gradually raised until three-quarters of the model is filled (Ongley 1996).Depending on the fact that pollutants agglomerate and forming large masses than their original size, concentration tends to change along the river cross-section due to the new size, water discharge, water speed (Leo & Van 1993) according to this fact that the river cross-section was divided into three sections and samples were taken from (1/4, 1/2, and 3/4 width of the river) as shown in Fig. 2.

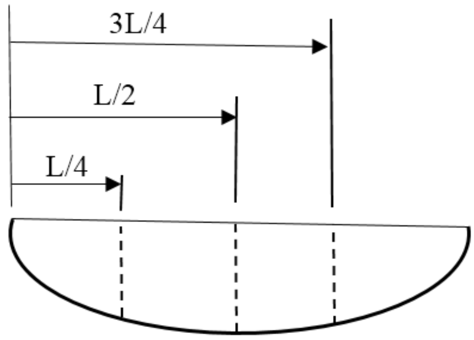

Fig. 2. Typical schematic illustration of sampling locations in the river cross-section.

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, BOD_5 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, BOD_5 and COD respectively, at the Pollution Research Centre of the Al-Shatra Institute. The results included 72 mean values for TOC, COD, and BOD_5.

RESULTS AND DISCUSSION

The collected samples were examined at the Pollutant Centre in Al Shatra Institute to obtain the BOD_5, COD and TOC at the three stations. The mean values were calculated separately for every section, resulting in 72 values for BOD_5, COD, and TOC. The average concentrations of these 72 values were 2.29 ppm, 5.01 ppm, and 2.65 ppm for BOD_5, COD, and TOC respectively. In Ali Al Sharqi Station, the minimum concentrations of BOD_5 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 BOD_5 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, BOD_5, and COD values at each station.

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

Station	Concentration	BOD5	COD	TOC
Ali Al Sharqi	Average	2.19	4.75	2.72
	Maximum	3.21	7.12	3.98
	Minimum	1.30	2.99	1.87
Kumait	Average	2.28	5.05	2.88
	Maximum	3.61	7.41	4.11
	Minimum	1.32	3.12	1.86
Al Amara	Average	2.39	5.24	3.04
	Maximum	3.81	7.92	4.31
	Minimum	1.45	3.33	2.03

According to the results of BOD, COD, and TOC, clearly, the BOD_5 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 BOD_5 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.

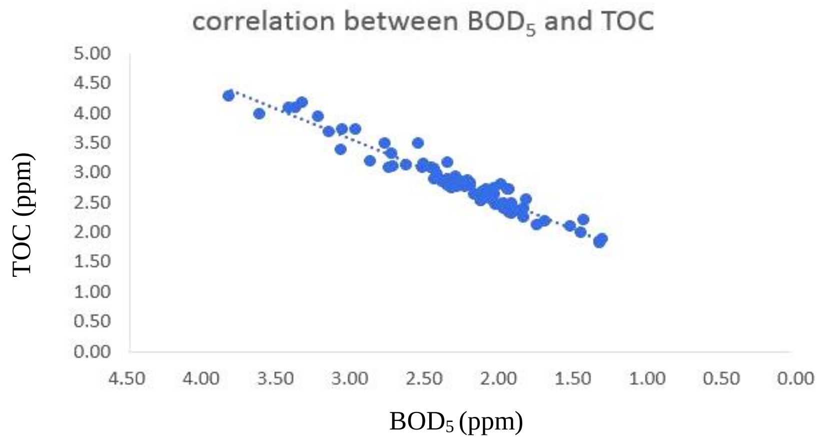

Fig. 3. Correlation between BOD_5 and TOC in Tigris River.

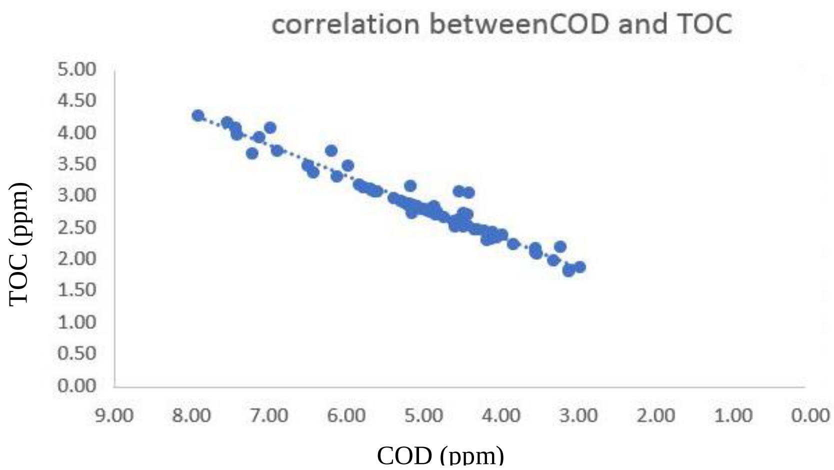

Fig. 4. Correlation between COD and TOC in Tigris River.

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 (R^2) for the new suggested formulas.

	r	R^2	Fitting formula
BOD5/TOC	0.93	0.91	$BOD_5 = 0.65 \times TOC^{1.18}$
COD/TOC	0.94	0.92	$COD=1.5\times TOC^{1.132}$

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

Formula	Percentage of Error									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
BOD formula	94%	100%	100%	100%	100%	100%	100%	100%	100%	100%
COD formula	96%	99%	100%	100%	100%	100%	100%	100%	100%	100%

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 BOD_5 is close to that of expected BOD_5 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 BOD_5 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 BOD_5 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 BOD_5 of influent wastewater and treated effluent which confirms the results of the present study (Christian *et al.* 2017).

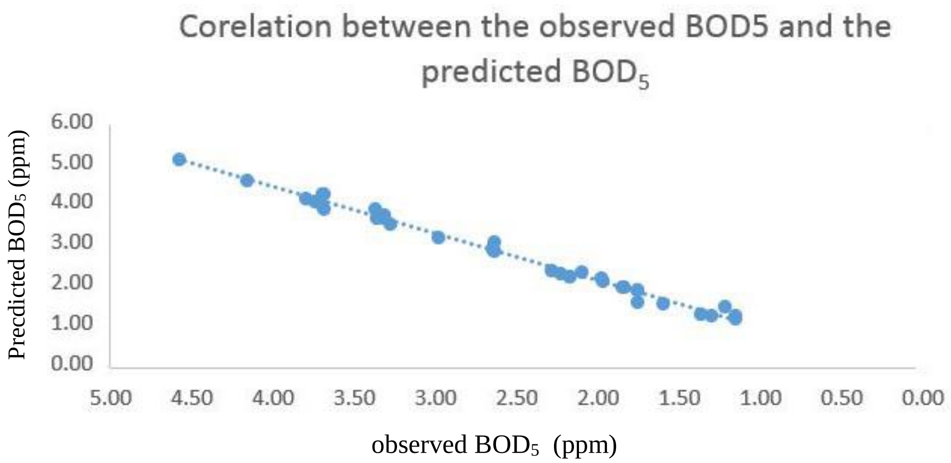

Fig. 5. The Graphical comparison for the observed and predicted BOD_5.

CONCLUSION

The relationships between TOC and BOD_5, 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_5, and COD depending on TOC value. A higher value of correlation coefficient ($r = 0.93$) or ($r = 0.94$) was detected between TOC and BOD_5 or between TOC and COD. In the meanwhile, the coefficient of determination (R^2) 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_5, our results suggest the possibility of using the predicted formulas to estimate BOD_5 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.

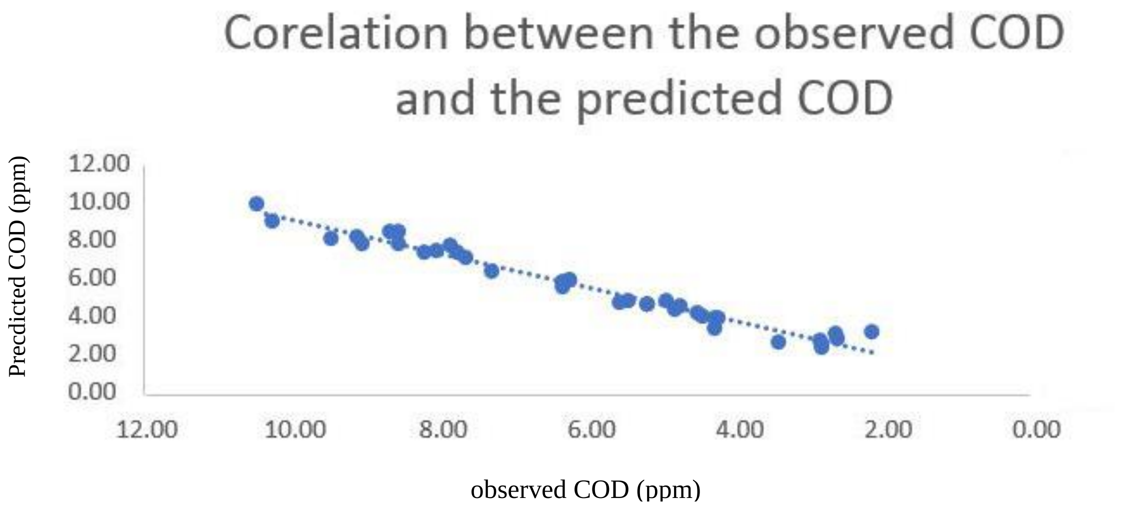

Fig. 6. The Graphical comparison for the observed and predicted COD.

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