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Article

Correlation between BOD_5 and COD – biodegradability indicator of wastewater

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Abstract
Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) are the most commonly parameters for characterization of organic matter content of water. Correlation between BOD_5 and COD for different types of water can provide relevant information about the nature of pollution, the content of organic matter and its level of biodegradability. This correlation could also be used to assess the quality of effluent after the treatment processes, to improve the performance of wastewater treatment plants (WWTPs) and/or to monitor the quality of river water into which wastewater are discharged.
The objective of this study was to assess the degree of biodegradability of different types of water (influents and effluents of 3 important municipal WWTPs of Romania, untreated wastewater discharged by different economic units from Bucharest; effluents of 5 different hospitals and surface water - natural receptors of the effluents discharged by the municipal treatment plants), based on the ratios of BOD_5/COD. BOD_5/COD ratio (also called Biodegradability Index) varied depending on the type of water investigated and should be periodically rechecked due to variations in climatic conditions, untreated industrial wastewater discharged into natural receptors, water supply characteristics, water availability. Biodegradability Index enable the evaluation of the organic pollution of wastewater, providing the possibility of estimation regarding the biological treatability of influent of WWTP.

Keywords: *BOD_5/COD ratio, biodegradability index, wastewater*

INTRODUCTION

The organic matter content of wastewater can be measured in two common parameters: Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD), often used to indicate the degree of water pollution. The main difference between BOD and COD is that COD measures all organic material content in terms of both biodegradable and non-biodegradable compounds, whereas BOD only measures organic material which is or can be biologically degraded (the biodegradable fraction of the wastewater).

There exists a well-defined correlation between the COD and BOD_5: the ratio BOD_5/COD commonly used as an indicator of the proportion of biologically degradable organic matter to total organic matter, also called "Biodegradability index of wastewater" [1, 2]. This ratio could provide important indications on the origin of the pollution of wastewater and implicitly on the suitable treatment process that must be realized in a sewage treatment plant. It is found to be reliable and useful indicator of organic matter content in the river water [3, 4].

There is no official value for BOD_5/COD biodegradability index for different types of wastewater; reported values for biodegradability index vary from 0.4 to 0.8 for wastewater that can be considered readily biodegradable and 0.1-0.2 for wastewater that is difficult to be treated biologically or that contains toxic substances for activated sludge microorganisms. Between 0.2….0.5 values, the microorganisms responsible for the biological degradation process needs to be adapted to the influent of WWTP [5-7].

The BOD_5: COD ratio is also found to be useful indicator to evaluate the organic matter content of the river water [8, 9].
In this study, different types of water were analyzed to investigate the relationship between BOD_5 and COD and to establish the BOD_5/COD ratio (biodegradability index). Statistical analysis of the data was performed.

MATERIALS AND METHODS

In this study, over a period of 12 months in the year 2021, four different types of water (grab samples) were collected, as follows:

- influents and effluents of 3 important municipal wastewater treatment plants (WWTPs) located in Bucharest, Iasi and Cluj-Napoca;
- untreated wastewater discharged by different economic units from Bucharest;
- wastewater discharged by 5 different hospitals (chlorinated before discharge);
- surface water – 3 receiving water of WWTP effluents (rivers Dambovita, Bahlui and Somes – upstream and downstream of the WWTPs discharges).

Sampling of WWTP influents and effluents, as well as the receiving surface water of WWTP effluents, was carried out in March and September 2021. The samples of chlorinated wastewater discharged by five infectious diseases hospitals (three located in Bucharest and one each in Iasi and Cluj-Napoca) were taken in the months of March, June and September 2021 from the final channels that discharge into the city sewerage network. Untreated wastewater samples (industrial effluents) were collected during the year 2021 from economic units with different fields of activity, located in Bucharest.
Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) are the most commonly used parameters for the characterization of water samples. Chemical Oxygen Demand (COD) was determined according to the ISO standard method [10]: the organic matter and inorganic chemicals such as ammonia and nitrite is chemically oxidized (digested) using potassium dichromate in acid solution. After 2 h of digestion, the residue dichromate is measured by titration with iron (II) ammonium sulfate.
Biochemical Oxygen Demand (BOD_5) was determined according to the European method standard [11]: a specific sample volume diluted with seeded dilution water (dilution water with nutrients, saturated in oxygen and containing bacterial inoculum) is stored in the dark at a temperature of 20 °C for 5 days. The oxygen concentration, before and after five days of incubation, is measured in all sample dilutions, using the membrane electrode method [12]. The BOD_5 is computed for each sample dilution from the difference between initial and final DO, includes correction factor for oxygen depletion resulting from presence of seed. The relationship of oxygen that was consumed during the five days and the volume of the sample increment is also used to calculate the BOD_5. The final BOD_5 value represent an average of the individual BOD_5 results for the sample dilutions.
COD and BOD_5 analysis were used to determine the correlation between these main parameters that characterize the degree of pollution of the aquatic environment [13]. The BOD_5/COD ratio (biodegradability index), generally considered the „cut-off point" between biodegradable and non-biodegradable wastewater, was determined for all water samples.

RESULTS AND DISCUSSION

To evaluate the biodegradability index, different types of water were collected, the global indicators – COD and BOD_5 were performed and the average and standard deviation (SD) values were calculated. In order to analyze correlation of BOD_5 and COD the results obtained for each type of water are presented in Table 1 in term of minimum value (X_{min}), maximum value (X_{max}) and average value ($X_{average}$). The variability parameters - standard deviation (SD) and coefficient of variation (CV) were calculated for each set of analyzed water samples.

The biodegradability index was also calculated for all types of water and the results of average biodegradability index (BOD_5/COD) were plotted as it is presented in Figure 1.

For wastewater – influents of WWTPs, BOD_5 mean value of 132 mg/L was observed, whereas COD mean value of 321 mg/L was registered. The average BOD_5/COD ratio was 0.41±0.02.

For effluents of WWTPs, BOD_5 mean value was 16.6 mg/L, whereas COD mean value was 47.6 mg/L. The average BOD_5/COD ratio was 0.35±0.04. The results obtained for COD and BOD_5 of effluents (untreated wastewater) discharged by economic units into city sewers varied over a wide range of values, with the mean value of COD about 1300 mg/L and the mean value of BOD_5 of 289 mg/L. The average BOD_5/COD ratio was 0.23±0.06.

The results obtained for effluents of hospitals (chlorinated wastewater discharged into city sewers) highlighted COD mean value of 354 mg/L and respectively a mean value of 92 mg/L for BOD_5. The average BOD_5/COD ratio was 0.27±0.04.

The results obtained for the water samples collected from the 3 studied rivers highlighted a relatively high organic load, the average values obtained for COD and BOD_5 being in the range of 17-32 mg O_2/L and 4-7 mg O_2/L, respectively. For the river samples the BOD_5/COD value was 0.22±0.04.

Table 1. Characteristic parameters of the wastewater and river water

Wastewater	COD (mg O_2/L)			SD	CV	BOD_5 (mg O_2/L)			SD	CV
	X_{min}	X_{max}	$X_{average}$	(mgO_2/L)	(%)	X_{min}	X_{max}	$X_{average}$	(mgO_2/L)	(%)
Influent WWTP	170	500	321	100	31	70	220	132	43	33
Effluent WWTP	18	90	47.6	25	52	6.0	30	16.6	8.7	52
Effluent Economic Unit	350	3000	1297	828	64	85	750	289	172	59
Effluent Hospital	80	750	354	227	64	26	202	92	60	65
River water										
Dambovita	10	65	32	16.5	51	3.0	14	7.0	4.5	63
Bahlui	15	45	28	10	36	2.5	12	6.5	2.6	41
Somes	10	30	17	7.0	42	2.0	5.0	3.6	1.4	39

The results of the statistical analysis (Table 1) showed that there were differences between the values of COD and BOD_5 obtained for municipal samples collected from WWTPs and industrial water samples.

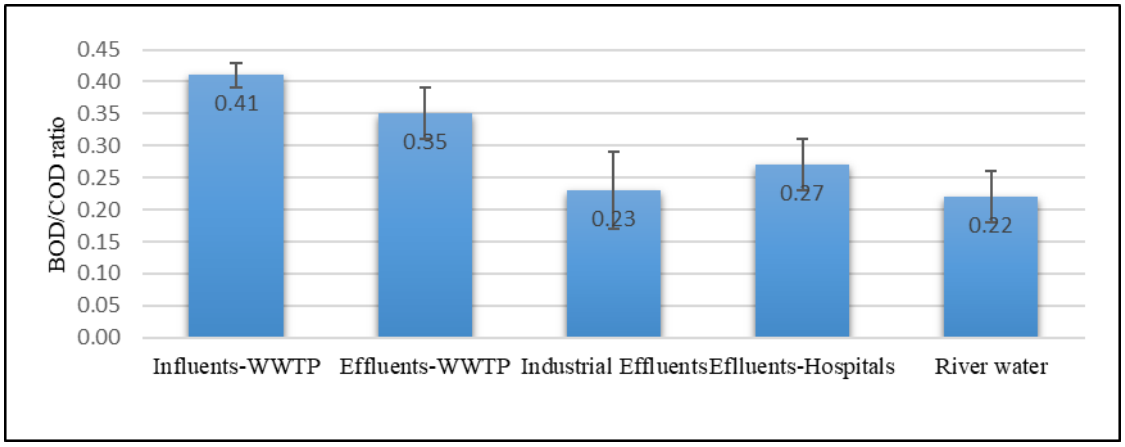


Fig. 1. Average Biodegradability Index of tested water

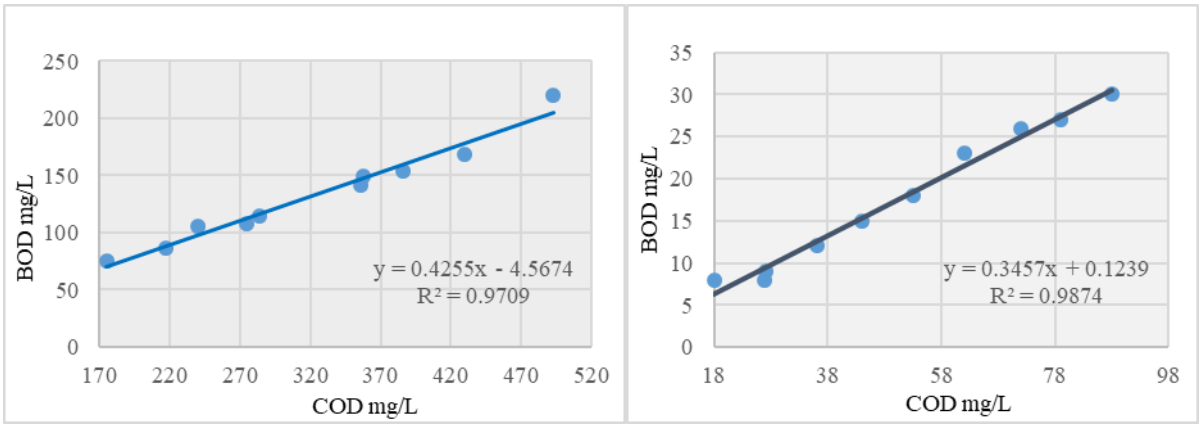
As shown in figure 1, biodegradability index of wastewater collected from municipal WWTPs (that apply the classic treatment with activated sludge in the biological treatment process) registered

values ≥ 0.35 and consequently, these are of domestic predominance with considerable portion of organic matter that is biodegradable in nature.

BOD_5/COD ratio of the tested industrial effluents, as well as effluents discharged from hospitals was lower than 0.3 and these raw sewages could be considered not susceptible to biodegradation, since microorganisms of activated sludge have limited potential to easily decompose their organic matter content. The water samples collected from rivers Dambovita, Bahlui and Somes (which are receiving water of WWTP effluents) recorded index values of approximately 0.2, specific to surface water samples.

There are many studies that have highlighted values of biodegradability index similar to those obtained in this paper, respectively: values between 0.3-0.9 is typical for domestic and municipal wastewater that can be treated / purified by the biological processes with activated sludge [4, 14]; BOD_5/COD ratio < 0.30 is specific value for industrial effluents, which are generally more difficult to be degraded and require an acclimatization of the microorganisms involved in the biodegradation and consequently a longer retention time in biological treatment processes [4]. Usually, the biodegradability index values recorded for surface water (rivers) are ≤ 0.2, as they are rich in nutrients, mineral salts and other inorganic substances and, most of the time, with a low content of biodegradable organic matter [8].

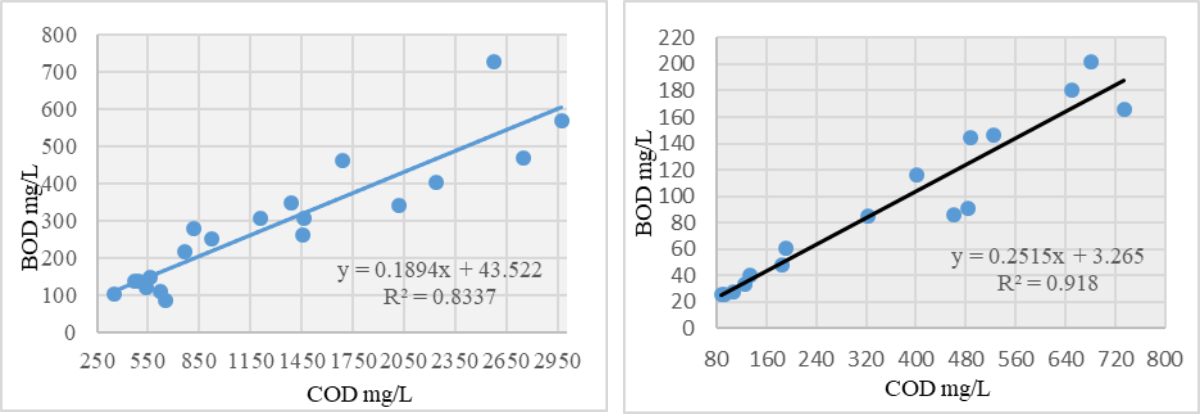
For each of the studied type of wastewater, the linear equation (95% confidence limits), the coefficient of determination (R^2) and the analysis of variance were used to examine the correlation between the two parameters – COD and BOD_5. All values of BOD_5 obtained for each type of wastewater (mg O_2/L) were plotted against the COD values for regression analysis and graphics were represented in Figures 2 and 3.



(a) (b)

Fig. 2. Scatter plot and linear regression lines of COD-BOD_5 values registered for wastewater collected from WWTPs (a-influents; b-effluents)

All values of BOD_5 obtained for each type of wastewater (mg O_2/L) were plotted against the COD values for regression analysis and graphics were represented in Figures 2 and 3. To determine the relationship strength between the plotted parameters, the correlation of determination R-squared (R^2) and Correlation Coefficient (r value) were calculated using the Pearson's formula. The equation of the linear regression line fitted to the plotted data may be used to express the correlation between BOD and COD as shown by regression equation presented in table 2.



(a) (b)

Fig. 3. Scatter plot and linear regression lines of COD-BOD_5 values registered for effluents discharged into municipal sewage (a-industrial effluents; b-hospital effluents)

The coefficient of determination R^2 recorded values higher than 0.9 for wastewater collected from WWTPs and hospitals, while for industrial effluents R^2 was 0.83, indicated there is a linear positive correlation for all types of wastewater.

Strong correlation coefficients (r) of 0.99 were observed between BOD_5 and COD values obtained for influents and effluents of WWTPS and large positive correlation (r of 0.91-0.95) was found between the BOD_5-COD values of wastewater discharged into the city sewer. The positive value of empirical parameters (a and b) indicates that with the increase in variable x (that is COD), the value of y (that is BOD) also increases.

Table 2. Regression analysis for BOD_5 and COD of studied wastewater

Wastewater	Regression Equation	R^2	r	BOD_5/COD ratio (from equation)	BOD_5/COD ratio (recorded)
Influent WWTP	y = 0.4255x - 4.5674	0.97	0.99	0.42	0.41
Effluent WWTP	y = 0.3457x + 0.1239	0.98	0.99	0.35	0.35
Effluent Economic Unit	y = 0.1894x + 43.522	0.83	0.91	0.19	0.23
Effluent Hospital	y = 0.2515x + 3.265	0.92	0.95	0.25	0.26

COD results are typically higher than BOD values, and the ratio between them will vary depending on the characteristics of the wastewater.

All investigated influent and effluent wastewater for WWTPs indicated the average biodegradability index was higher than 0.3 and a very good correlation between the two parameters BOD_5 and COD. Industrial effluents and wastewater discharged from hospitals recorded biodegradability index below 0.3, which indicates that these water may have potentially toxic constituents or acclimated microorganisms may be required for degradation.

The results showed that BOD_5: COD ratio can be used as a good indicator for measuring water pollution, and it can also be used as an indicator to predict the relationship between BOD and COD, as well as knowing the organic matter content in wastewater and industrial water.

The present work focused on the correlation between COD and BOD_5 of different water samples collected from WWTPs, economic units that discharge into the municipal sewer and surface water (rivers). Results obtained in this study showed that there exists a mutual linear relationship between BOD_5 and COD that have been confirmed by other researchers, too [15, 16]. BOD_5/ COD ratios depends on source of water and inform us about the nature of pollution and the level of biodegradability of the organic matter.

Before any wastewater can be treated, it must first be characterized in terms of organic matter, because knowing the biodegradability index of the raw influent wastewater is essential for successful design and operation of wastewater treatment plants [14]. If BOD/COD higher than 0.5 the wastewater is fairly biodegradable, and can effectively be treated biologically. If BOD/COD ratio is between 0.3-0.6, seeding is necessary to treat the wastewater biologically and the acclimation of the microorganisms will help in the degradation process, while BOD/COD lower than 0.3, biodegradation will not proceed, the wastewater generated from these activities inhibits the metabolic activity of bacterial seed due to toxicity or refractory properties and it is not possible to treat biologically [17-20].

CONCLUSIONS

For the investigated wastewater collected from WWTPs, the Biodegradability Index varied from 0.33 up to 0.46, which indicate the insignificant variability in the value of BOD_5/COD ratio. The average value of index of all investigated wastewater from WWTPs was higher than 0.35 that indicates that generally wastewater are biodegradable. BOD_5 and COD parameters are obviously correlated, and the correlation is a linear positive.

For industrial effluents and wastewater discharged from hospitals, the highest mean Biodegradability Index was 0.26, while the lowest mean was 0.23, this type of wastewater may contain a significant fraction of non-biodegradable compound or some toxic / refractory compounds and should be periodically monitoring in terms of COD and BOD parameters and their correlation should be rechecked. A good correlation between the two parameters BOD_5 and COD was also highlighted for the tested industrial water, which means that it is possible to estimate, with sufficient accuracy, the values of BOD_5, knowing the regression equation (between BOD_5 and COD) for a given type of wastewater.

The COD analysis determines the amount of organic matter in a water in no more than 3-4 hours, rather than the BOD_5 test, which requires five days of analysis. Considering the positive linear correlation obtained between the 2 studied parameters, the BOD_5/COD ratio (with a specific value that can be assigned depending on the type of water analysed) can be used as an alternative for estimating the BOD_5 value, when the COD value was determined experimentally.

The BOD_5/COD ratio is found to be reliable and useful indicator to relate organic matter content both in waste water and in surface water, as well as regarding the capacity of biodegradation of organic matter.

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