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ABSTRACT

Water contaminated or changed their properties partially or completely as a result of household, industrial, agricultural and other uses is called as waste water. The analysis used to determine the characteristics of the waste water are those of quantitative chemical instead of those of qualitative biological or physical. These are Biochemical Oxygen Demand test (BOD_5, Chemical Oxygen Demand test (COD), Total Organic Carbon Content test (TOC) and Dissolved Oxygen (DO). In this study, BOD curves were generated for the particular reaction conditions and the effects of reaction rate constant on these curves were studied firstly. Examining of the simulation curves related with BOD it is understood that the same conversion of BOD could be reached in a shorter time by increasing the reaction-rate constant. This is to be expected in terms of the reaction kinetics. Secondly, the correlations among the results of BOD, COD, TOC and DO tests in determining the quality of water resources were searched and it was seen that finding a correlation among these tests results would be impossible directly but some correlations could be done among the results of these tests applying for the same sample diluted in different rate. However, these correlations could not show on-line changes exactly among their relationships. Therefore, instead of BOD test to realize COD and TOC tests and to get their results in shorter time is easier and it may be advised that the rates of BOD_5/COD or BOD_5/TOC for the same sample at certain time intervals are determined nearby DO measurements so that it can be said something about the qualification of the water sources.

Keywords: Waste water, chemical analysis, biological oxygen demand, total oxygen demand, dissolved oxygen

INTRODUCTION

Water contaminated or changed their properties partially or completely as a result of household, industrial, agricultural and other uses is called as waste water. The largest part of the pollution in waste water constitutes detergents, organic matters and oils. The main objective of waste water treatment is that its effects on public health and ecological balance where waste water discharged is reduced to a minimum The basic steps in wastewater treatment are to remove (1) biodegradable organic substances, (2) suspended solids, (3) harmful heavy metals and toxic compounds, (4) nitrogen and phosphorus depending on the receiving environment conditions, and to destroy (5) pathogenic organisms. The analysis used to determine the characteristics of the waste water base on quantitative chemical methods more than those of qualitative biological and physical. The quantitative methods of this analysis are gravimetric, volumetric or physicochemical. The properties of waste water are classified as physical, chemical and biological and these are summarized as below [1, 2]:

1.1. Physical Properties of Waste Water:

1. Total solids: Drainage in cities contains 720 mg/L of total solids average. A part of 500 mg/l of total solids is dissolved case and the rest is suspended. Some of dissolved and suspended solids can be volatile.

2. Smell: Gases in the waste water formed by the breakdown of organic matter causes bed smell. These matters are fats, oil and organic solvents.

3. Temperature: Typically, effluent temperature is higher than that of the air in winter. It is lower than the air temperature in the summer months.

4. Color: Water is colorless and odorless substance normally but the color of the waste water varies depending on an organic and inorganic contents.

1.2. Chemical Properties of Waste Water:

1. Organic substances in waste compose of proteins, carbohydrates, oils and fats, urea, soup, benzene derivatives like detergent and volatile components. Biochemical oxygen demand

(BOD_5) is one measure of the amount of dissolved oxygen used by microorganisms for biochemical oxidation of organic compounds and most widely used.

2. Chemical oxygen demand of the wastewater test (COD) is performed in order to measure the organic matter content. COD of the waste water is higher than that of BOD mostly.

3. Total organic carbon test (TOC) is applied for measuring total organic carbon content of waste water especially at low concentration.

4. Acidity: Inorganic content of the waste water is also important in determining its quality and pH is most widely used for this. It is the parameter of the hydrogen ion concentration in waste water and important for the biological and chemical treatment of the waste water. The pH value of drinking water is between 6-8, seawater 8, natural water 7 and sewage 7-8.

5. Chloride: Major source of chloride in the domestic wastewater is human urine. Additionally, in areas where water sources have higher hardness, chloride with large amounts is poured to waste water through the use of a water softener.

6. Alkalinity: Waste water alkalinity consists of the presence of carbonate and bicarbonate or ammonia of some elements like calcium, magnesium, sodium and potassium. The wastewater is usually alkaline.

7. Nitrogen: It is a nutrient medium for microorganisms in waste water. It may require additional nitrogen of purification of the waste water if nitrogen in waste water is not enough. Domestic waste water has enough nitrogen necessary for biological treatment.

8. Phosphorus: It is a nutrient medium for microorganisms in waste water. If there is phosphorus in treated waste water discharged into the receiving environment it can cause to eutrophication (abnormal growth of plants in water).

9. Sulphur: Sulphur ions are naturally present in the waste water. Sulfates are reduced to sulfurs and hydrogen sulfide (H_2S) chemically under anaerobic (oxygen free) conditions. Then H_2S is oxidized to biologically sulfuric acid.

10. Heavy metals and Toxic compounds: Heavy metals such as copper, mercury, nickel, chromium, cadmium, zinc and their compounds are toxic for microorganisms. Therefore, they create problem in biological waste water treatment stage. Heavy metals and toxic elements non-exist in domestic waste water.

11. Gases: Gases present in the domestic waste water are nitrogen, oxygen, carbon dioxide, methane and ammonia. The amount of oxygen in the waste water is in very low level because of

the oxygen consumption of microorganisms. One of by-products of anaerobic decomposition of organic matters present in the wastewater is methane gas. This gas is a flammable and explosive gas with a quick. The toxic effect of H_2S is too much. Dissolved oxygen is required other aerobic life forms than microorganisms as well as the aerobic respiration of microorganisms but the O_2 has poor solubility in water. The actual amount of O_2 in solution gas solubility is related to temperature, the partial pressure of gases in the atmosphere and water purity directly.

1.4. Biological Characteristics of Waste Waters

1. Prominent group of organisms in domestic wastewater: They are plants, animals and microorganisms such as bacteria and algae, fungi, protozoa, viruses. Much of microorganisms in domestic waste water have disease-causing properties for people and animals
2. Coliform bacteria are an indicator of contamination from human waste. Algae also lead to taste and odor problems. During treatment of waste water, it decomposes organic substances by means of bacteria.

1.5. Biochemical Oxygen Demand (BOD_5)

The most widely used parameter of organic pollution applied to both waste water and surface water is the 5-day BOD (BOD_5). The general procedure for preparing the BOD bottles for incubation is illustrated in Fig. 1. When the sample contains a large population of microorganisms (untreated waste water, for example), seeding is not necessary and directly BOD test will be carried out. The incubation period is usually five days at 20 ° C and during this period would be about 70% complete incubation. Amount of BOD (mg/L) is calculated by the following equation:

$$BOD = L_{t=5day} = \frac{(D_1 - D_2) - (B_1 - B_2) * f}{P} \qquad (L > L_t \; ve \quad y_t = L - L_t)$$

where;

D1 = dissolved oxygen of diluted sample immediately after preparation, mg/L

D2 = dissolved oxygen of diluted sample after 5 days incubation at 20°C, mg/L

P = decimal volumetric fraction of sample used

B1 = dissolved oxygen of seed control before incubation, mg/L

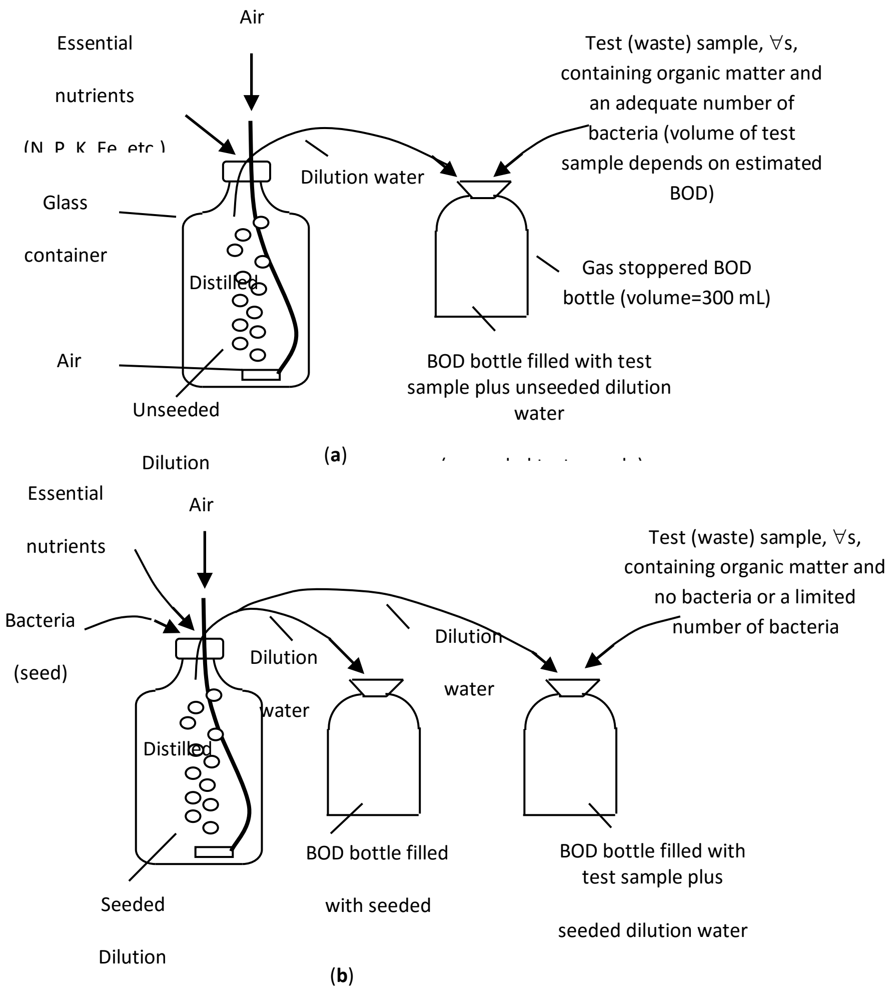

Figure 1 Procedure for setting up BOD test bottles **(a)** with unseeded dilution water and **(b)** with seeded dilution water

B2 = dissolved oxygen of seed control after incubation, mg/L

When dilution water is not seeded B1=B2=0

f = ratio of seed in sample to seed in control

The kinetics of the BOD reaction are, for practical purposes, formulated in accordance with first-order kinetics and may be expressed as

$$\frac{dL_t}{dt} = -k * L_t$$

and the solution of this equation is written as

$$\frac{L_t}{L} = e^{-k*t} = 10^{-K*t} \quad \text{or} \quad y_t = L(1 - e^{-kt})$$

and a typical value of k is was measured 23 d^{-1} at 20°C and 200 mg/L of BOD value (0.05<k<0.3). If the reaction temperature is different from 20°C k is written according to the van't Hoff-Arrhenius equation as follows (Ө value is usually given as 1047 in the literature):

$$k_T = k_{20}\theta^{(T-20)}$$

1.6. Chemical Oxygen Demand (COD)

COD is the amount of oxygen required for organic carbon to be completely oxidized to CO_2, H_2O ammonia. Oxidation reaction by using potassium dichromate in acidic medium is as follows:

$C_aH_bO_c + Cr_2O_7^{-2} + H^+$ ----- Catalyst/Temperature --- > $Cr^{3+} + CO_2 + H_2O$

How much is the difference between the COD and BOD for the sample it should be considered that it contains so big amounts of organic substance not biodegradable. But advantage of the COD test to that of BOD is that it can be only done in 3 hours and thus it may be resulted in shorter period of time (0<BOD_5/COD <1).

1.7. Total Organic Carbon (TOC)

TOC test that can be determined very quickly is more popular todays than before especially for the samples of low concentration or diluted. It bases on that carbon is oxidized to CO_2 in the presence of suitable catalysts (0<BOD_5/TOC<2). The method needs also very simple apparatus.

1.8. Dissolved Oxygen (DO)

DO levels can be measured easily with the help of a probe in the waste water samples as shown in Figure 2 [**http://www.amazon.com/Hach-8505700-Measurement-Luminescent-Dissolved**].

Figure 2 Hach 8505700 HQ40d BOD Measurement Package with LBOD101 Luminescent/Optical Dissolved Oxygen Probe with Bottles

RESULT & DISCUSSION

Water contaminated or changed their properties partially or completely as a result of household, industrial, agricultural and other uses is called as waste water. The largest part of the pollution in waste water constitutes detergents, organic matters and oils. The main objective of waste water treatment is that its effects on public health and ecological balance where waste water discharged is reduced to a minimum The basic steps in wastewater treatment are to remove (1) biodegradable organic substances, (2) suspended solids, (3) harmful heavy metals and toxic compounds, (4) nitrogen and phosphorus depending on the receiving environment conditions, and to destroy (5) pathogenic organisms. The analysis used to determine the characteristics of the waste water base on quantitative chemical methods more than those of qualitative biological and physical. Biochemical oxygen demand (BOD_5) is one measure of the amount of dissolved oxygen used by microorganisms for biochemical oxidation of organic compounds and most widely used.. COD is the amount of oxygen required for organic carbon to be completely oxidized to CO_2, H_2O ammonia. How much is the difference between the COD and BOD for the sample it should be considered that it contains so big amounts of organic substance not biodegradable. But advantage of the COD test to that of BOD is that it can be only done in 3 hours and thus it may be resulted in shorter period of time ($0<BOD_5/COD<1$). TOC test that can be determined very quickly is more popular todays than before especially for the samples of low concentration or diluted. It bases on that carbon is oxidized to CO_2 in the presence of suitable catalysts ($0<BOD_5/TOC<2$). The method needs also very simple apparatus. DO levels can be measured easily with the help of a probe in the waste water samples. In this study, BOD curves were generated for the particular reaction conditions and the effects of reaction rate constant on these curves were studied firstly. Examining of simulation curves related with BOD it is understood that the same conversion of BOD could be reached in a shorter time by increasing the reaction-rate constant. This is to be expected in terms of the reaction kinetics. Secondly, the correlations among the results of BOD, COD, TOC and DO tests in determining the quality of water resources were searched and it was seen that finding a correlation among these tests results would be impossible directly but some correlations could be done among the results of these tests applying for the same sample diluted in different rate. However, these correlations could not show on-line changes exactly among their relationships. Therefore, instead of BOD test to realize COD and TOC tests and to get their results in shorter time is easier and it may be advised that the rates of BOD_5/COD or BOD_5/TOC for the same sample at certain time intervals are determined nearby DO measurements so that it can be said something about the qualification of the water sources.

EXPERIMENTAL

On this section BOD curves was created for specific reaction conditions and the effects of the reaction constant on these curves were analyzed. Kinetic calculations were modeled and simulated in MATLAB. The following program was written for the modeling and simulation results were plotted on Figure 3 and Figure 4 [4].

```
 % BOD_Formation_and_k_Effect_on_BOD_01.m*
 % BOD_Formation
clc, clear, clf
Llow=0;Lup=300;Lmean=(Llow+Lup)/2;
   L=Lup
tlow=0; n=20; tup=n; tt=tlow:1:tup;
```

```
   t=tt;
klow=0.05;kup=0.35;kmean=(klow+kup)/2;
   k=kmean
yt=L*(1-exp(-k*t)); Lt=L-yt;
figure(1), plot(t,yt,'+b',t,Lt,'.r')
xlabel('time, day'),ylabel('y (+),  Lt(.) -  mg/L')
title('BOD  exeerted (+) and remaining (.) k=0.200')
% k_Effect_on_BOD
m=5; Dk=(kup-klow)/m;
   k=klow:Dk:kup
   i=1
   for ki=1:m+1
     for j=1:n
      ytk(i,j)=L*(1-exp(-k(ki)*t(j)));
     end
     i=i+1;
   end
   ytk
figure(2), plot(t(1:20),ytk(1,1:20),'+b',   ...
            t(1:20),ytk(2,1:20),'.r',   ...
            t(1:20),ytk(3,1:20),'-.g',  ...
            t(1:20),ytk(4,1:20),'+r',   ...
            t(1:20),ytk(5,1:20),'-g',   ...
            t(1:20),ytk(6,1:20),'.b')
xlabel('time, day'),ylabel('BOD -  mg/L')
title('k-> 0.0500 +b, 0.1100 .r, 0.1700 -.g, 0.2300 +r, 0.2900 -g, 0.3500 .b')
```

As seen from Figure 3 and Figure 4 with increasing reaction rate or reaction rate constant k for a given L value it could be reached to maximum BOD value in more shorter reaction time and this is to be expected in terms of the reaction kinetics.

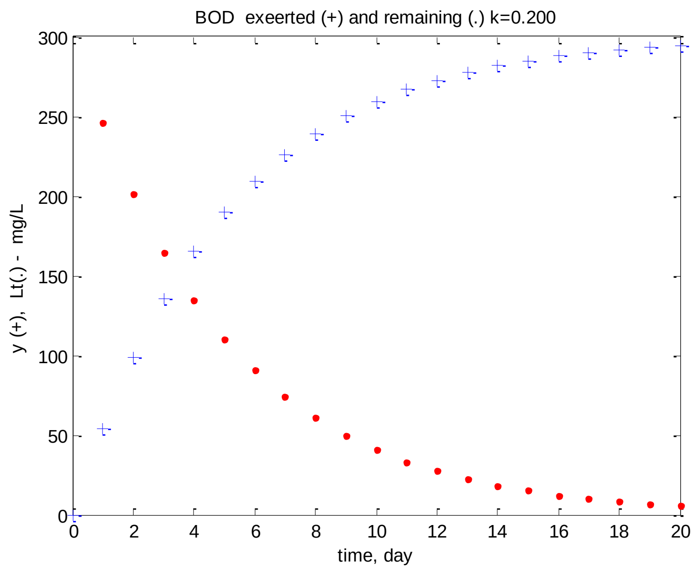

Figure 3 Formation of the first stage BOD curve

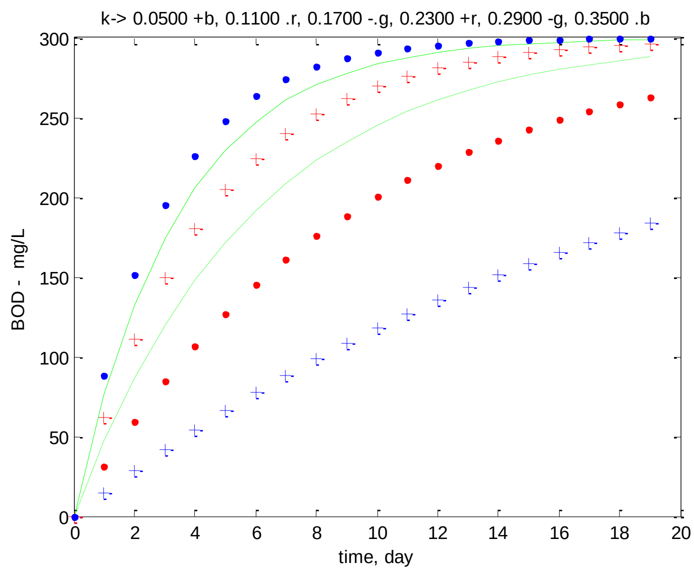

Figure 4 Effect of the rate constant k on BOD (for a given L value)

REFERENCES

[1] Tchobanogluos, G., Burton, F. L., (1991), *Wastewater Engineering Treatment, Disposal, and Reuse*, McGraw-Hill Book Co

[2] Eltem, R., (2001), *Atık Sular ve Arıtım*, Ege Uni. Fen Fak. Yay., 172

[3] http://www.amazon.com/Hach-8505700-Measurement-Luminescent-Dissolved /dp/ B00R 3EGHJ4 , (2016)

[4] https://en.wikipedia.org/wiki/Biochemical_oxygen_demand, (2016)

[5] Meyers, D.N., Wilde, F. D., (2012), USGS TWRI Book 9–A7 (Third Edition), http://water.usgs.gov/owq/FieldManual/Chapter7/NFMChap7.pdf

[6] Arifoğlu, U., (2005), MATLAB 7.04 SIMULINK ve MÜHENDİSLİK UYGULAMALARI, Alfa Ltd..