Mathematical Model for BOD in Waste Water Discharges from Al Dora Refinery in Baghdad

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Abstract

This research consists of two parts, the first part concern with analyzing the collected data of BOD and COD values in discharge waste water from Al-Dora refinery during 2010 to find the relationship between these two variables The results indicates that there is a high correlation between BOD and COD when using a natural logarithm model (0.86 ln(COD)) with correlation coefficient of 0.98. This relationship is useful in predicting the BOD value using the COD value. The second part includes analyzing collected data from the same site in order to find a relationsip between BOD and other parameters COD, Phenol(phe), Temperature(T), Oil, Sulphat(SO_4),pH and Total dissolved solids(TDS) discharged from the refinery. The results indicated that the best mathematical model is

BOD= 0.786 (ln(COD))^^{2}- 3.077E83/Exp(10T) + 1.76E+48/Exp(0.1TDS)- 5.6507/Exp(100Phe)

With correlation coefficient of 0.873. The presented research demonstrates many conclusions regarding the relation between BOD and other pollutions, it is clear that the relation between BOD and COD is a direct relation, while it's a reverse relation with other pollutions and it's also clear that a linear model can be used to represent the relation between BOD and COD for a value of COD approximately less than (50 mg/L).

Key Words: BOD, COD, Al- Dora refinery, mathematical model, waste water.

الخلاصه:

تضمن هذا البحث جزئين، الجزء الاول تناول تحليل البيانات التي جمعت خلال سنه 2010 من مصفى الدوره الذي يقع الى الجنوب الغربي من مدينة بغداد، من اجل ايجاد نموذج رياضي يصف العلاقه بين المتطلب الحياتي للاوكسجين والمتطلب الكيميائي للاوكسجين في مياه المخلفات المطروحه من المصفى. تبين من النتائج ان افضل معامل ارتباط ينتج عند استخدام النموذج الرياضي اللوغارتمي الطبيعي ((0.86 ln(COD)) وبمعامل ارتباط مقداره 0.98 ، وباستخدام هذه العلاقه اصبح من الممكن التنبؤ بقيمة المتطلب الحياتي للاوكسجين بالاعتماد على قيمة المتطلب الكيميائي للاوكسجين.

اما الجزء الثاني فقد تضمن تحليل البيانات التي جمعت من نفس المكان لايجاد افضل نموذج رياضي لتمثيل العلاقة بين المتطلب الحياتي للاوكسجين و بقية العناصرمثل المتطلب الكميائي للاوكسجين ،الفينول،درجة الحراره،الزيت، الكبريتات,pH،المواد الصلبه الذائبه الكليه، حيث تبين من النتائج ان افضل معامل ارتباط هو عند استخدام النموذج الرياضي

BOD= 0.786 (ln(COD))^^{2}- 3.077E83/Exp(10T) + 1.76E+48/Exp(0.1TDS)- 5.6507/Exp(100Phe)

وبمعامل ارتباط مقداره 0.873 .

لقد اظهرت الدراسة المقدمة العديد من الاستنتاجات فيما يخص طبيعة العلاقة بين المتطلب الحياتي للاوكسجين و بقية العناصر. فيمكننا القول بان العلاقة بين المتطلب الحياتي للاوكسجين و المتطلب الكيميائي للاوكسجين هي علاقة طردية ، في حين ان العلاقة عكسية مع بقية العناصر. كما بينت الدراسة امكانية استخدام النموذج الخطي في

تمثيل العلاقة بين المتطلب الحياتي للاوكسجين و المتطلب الكيميائي للاوكسجين على ان لا تتجاوز قيم المتطلب الكيميائي للاوكسجين (50 mg/L) تقريبا .

Introduction

It is quite clear that air, water and soil are among vital elements of the life on earth (Rose, 1998). During certain period in the past, human being and other living animals enjoyed clear and clean water and air, but industrial revolution during 19^{th} century and its perfection in 20^{th} century, gradually caused air, water and soil to become polluted. Nowadays, environmental pollution has already reached to a certain scale that it threatens and endangers the health of human beings and survival of other living things. Rivers are the valuable echo- system, besides playing a crucial role in providing great portion of water demanded for agriculture, industry and drinking water, are also considered vital, social, economical problems in different societies (Jenkins, 2001). The environment around us should be exploited in such a way both to provide our reasonable daily needs and at the same time not to be confronted by damage, loss or intimidation by our side. Otherwise in long-term and sometimes short- term, the damage will not only affect us, but also will damage our future. (Sadat pour et al.2004)

The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged directly into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms.

The oxygen required for the degradation of the organic matter biologically is called the Biochemical Oxygen Demand (BOD), the amount of oxygen needed to consume the organic and inorganic materials is called the Chemical Oxygen Demand (COD). There exists a definite correlation between the COD and BOD under certain conditions and by determining the COD, the information about the BOD of the water/waste water can be derived.(Walters et al,2009)

In the first part of this research some mathematical models are used to find the best relationship between BOD and COD In the waste water discharges from Al-Dora refinery in Baghdad which is an important center for fuel in Iraq, while in

the second part, computer program using the software (Matlab 09) was used to detect the constants of the mathematical model, in order to find the relationship between BOD and other pollutants like phenol, temperature,and total dissolved solid.

Al - Dora Refinery:

Al- Dora refinery is one of the biggest refineries in Iraq, it lies at the south west side of Baghdad city, this refinery initiated at 1953 and started its work at 1955, its capacity now 180000 barrel/day and it's an imported center for fuel, medical vaseline, grease, and wax (Al- Dora Refinery web site, 2012).

There is a treatment plant unit in Al Dora refinery for the industrial waste water before discharging it to the Tigris River.

The refinery wastewater generally includes oil, hydrocarbon materials and chemical additives. The following parameters, such as oil and grease, Phenol, BOD, COD, TDS, SO_4, Ph and Temperature are determined in the wastewater of the refinery.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

Biochemical oxygen demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. Biochemical oxygen demand is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the end of the test. Samples often must be diluted prior to incubation or the bacteria will deplete all of the oxygen in the bottle before the test is complete.

Chemical oxygen demand (COD) does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. COD values are always greater than BOD values, but COD measurements can be made in a few hours while BOD measurements take five days. (NGRDC,2000)

Pedro et al.2004 Made a research on Evaluation of Organic Load Measurement Techniques in a Sewage and Waste Stabilization Pond Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are the major parameters used as routine surrogate tests for measuring the load of organic carbon into the environment. In their research, evaluations of possible replacement of BOD and COD for Dissolved Organic Carbon (DOC) measurements are presented for different wastewaters. For anaerobic pond effluent, the following correlations were obtained:

COD = 1.08 DOC + 79	BOD = 0.82 DOC + 12.1
For facultative pond effluent	
COD = -0.29DOC + 109	BOD = 0.14DOC + 26. 2
For raw sewage	
COD = 4.18DOC – 2	BOD = 0.46COD + 5. 3
For aerated pond effluent	
COD = 3.57DOC + 6	BOD = 0.27COD + 3. 4
For sedimentation pond effluent	
COD = -1.34DOC + 138	BOD = 0.73DOC + 16.5

It was found that the determination of COD was not appropriate for substituting classical alternatives in tested samples in despite of the limitations of the samples.

Chemical oxygen demand fractions of municipal wastewater for modeling of wastewater treatment is a research done by I. Pasztor;etal. 2010 , They showed that when a new wastewater treatment plant is being designed by computer simulation, detailed data about organic fractions of influent wastewater (measured as chemical oxygen demand) are usually not available, but knowledge of the typical ranges of these fractions is indispensable. The influent chemical oxygen demand fractions can substantially influence the results of simulation-based design such as reactor volumes, solids residence time, effluent quality, oxygen demand, sludge production, etc. This research attempts to give an overview of wastewater organic fractions as modeling parameters and presents new chemical oxygen demand fractionation results from Hungary. According to the data from literature, the ratio of chemical oxygen demand components in raw wastewater is very different and the average composition is as follows: Inert particulate =17.1%, slowly biodegradable = 57.9 %, inert soluble =7.8 % and readily biodegradable = 17.5 %. The Hungarian wastewater samples were analyzed according to STOWA (Dutch foundation for applied water research) the obtained results were not much different from those of literature
(inert particulate = 23.7 %, slowly biodegradable = 49.8 %, inert soluble = 4.6 % and Readily biodegradable = 21.9 %), but some typical characteristics were observed.

Sadatipour et al. 2004 made a research on investigation on Kangan gas refinery wastewater , this research is carried out on March 2002 at Kangan refinery, which is located in Kangan city, southern part of Iran. The gas refinery wastewater generally includes oil, hydrocarbon materials and chemical additives, which are in the form of emulsion in water. The following parameters, such as oil and grease, PAHs, BOD, TH, turbidity, COD, EC, pH, TSS, SiO_2, PO_4 are determined in wastewater of the refinery in order to determine the amount of pollutants, which are affecting the area where the refinery is located. The oil and grease are analyzed by FTIR and PAHs are determined by UV-Luminance and physico-chemical parameters are determined according to the Standard Methods. The results showed that although pollution of the refinery wastewater is within world permissible limits (EPA), but since the area is affected by the wastewater and surrounding area is confined with river basin it could be concluded that pollutants, which are discharged to the echo environment, are not in the permissible limits of the similar Industries.

Determination of inert chemical oxygen demand (COD) fractions of Cumhuriyet University wastewater is a research made by F. Ciner and M. Sarioglu 2005, Some amounts of inert products are given into environment due to biological degradation of substrate in activated sludge system. The effluent of biological wastewater treatment consists of inert substrate in influent flow, soluble microbial products and non degradable or slowly degradable organic products. Soluble inert COD (SI) must be determined for discharge standards since it did not give any reaction in activated sludge system and was given with wastewater discharge. However particular inert COD (XI) accumulated in system depending on sludge retention time due to it is only wasted from system by wasted sludge.

This study focused on inert fractions of Cumhuriyet University campus wastewater which consists of domestic, hospital and laboratory wastewaters. Experimental method was used suggested by Orhon et al. and modified by Germirli et al. in order to determine directly influent particulate and soluble inert fractions. According to the experimental procedure three aerobic batch reactors, two with the wastewater and the third with glucose were run parallel. In the reactors, the change in the soluble COD profiles is observed for a period during which all degradable COD is entirely depleted, in other words, the COD profiles reach a plateau and remain unchanged. Wastewater samples were taken equalization tank in wastewater treatment plant. The conventional parameters of campus wastewater characterization were as follows:
Total COD
(CT0) = 372 mg l-1, total soluble COD
(STO) = 124 mg l-1,
total suspended solids (TSS) =177 mg l-1,
ammonia (NH3) = 31.2 mg l-1,
ortho-phosphate (PO4-P) = 11.3 mg l-1
and pH=7,4 .
In this study, in order to determine inert COD fractions in Cumhuriyet University campus wastewater, three aerobic batch reactor systems were used. At the end of approximately 381 h operation, COD composition of campus wastewater were found to be CT0=372 mg l-1,
XS0=56 mg l-1, SS0=104 mg l-1,
CS0=149 mg l-1, SI=12 mg l-1, XI=211 mg l-1, respectively
An application study in Al Dora refinery made by Abood,2004. The aim of that experimental work was for studing the Furfural removal from Al Dora refinery waste water by the adsorption process using a continuous system (fixed activated carbon bed). The equilibrium data were determined experimentally and the equilibrium isotherm was found to be of a favorable type and fit well by Langmuir and Freundlich isotherm while experimental and theoretical results were compared by estimating the deviation absolute mean error (7%, 6.8%) and root mean square (0.0119, 0.0169) respectively for the results. Regeneration process of exhausted activated carbon was carried out by three different methods(washing with dilute Alcohol, washing with boiled distilled water and the thermal process) in order to find thr regeneration efficiencies which was found to be (60-90)%

Al azzawi 2007 made a research on Evaluation of the performance of the Dora refinery waste water trearment plant, comparisons were made between the actual and the designed performance for various potential pollutants. For long term evaluation of (2004 and 2005) years the test measurements were collected and analyzed. His results indicated that the annual percentage removal of sulfide, oil, COD, BOD, and TSS, were found acceptable except for the TSS value which shows relatively low removal percent 67.58%. and the monthly percentage remonal of sulfide, oil, COD, BOD and TSS shows considerable changes among different months of the years, which may reflect considerable variation in influent water properties and treatment process.

Building Of the Mathematical Models:

In order to find a suitable relationship between BOD and COD concentration, and BOD with other pollutants, the following points must be achieved:

1- Removing all the data that can be consider as irregular.

2- Separating the data in to two parts. The first part which represent 60% of the total data are used to find the optimum model for the relationship between BOD and COD, and the second part of ratio 40% of the total data that used to evaluate the estimated relationship.

3- Using of correlation coefficient and T-test in order to select the suitable relationship.

4-Calculating the constants corresponding to each term in the selected model so that the error between the real values and the calculated values minimized. A computer program using the software (Matlab 09) was used to detect the constants of the mathematical model.

5- Evaluating the resulting model by using the second part of data, which is 40% of the total data?

Results:

Step one: The mathematical models that used in describing the relationship between BOD and COD are shown in table 1, where Y=BOD and X=COD Figur 1 and figure 2 indicated that the relationship between BOD and COD is liner for the values below 50mg/lit, this relationship is

$$BOD=0.901X+5.214 \qquad 6$$

with correlation factor 0.965.

Step two: The mathematical models that were used in describing the relationship between BOD and other pollutants are shown in table 2, where:

Y=BOD, x = T, TDS or Phe

z = 10x for T , 0.01x for TDS, 100x for Phe, x for SO4 & PH, 0.01x for Oil

f = 10x for T , 0.1x for TDS, 100x for Phe, , x for SO4 & PH, 0.01x for Oil

Step three: Selected the best mathematical models that used to describe the relationship between BOD and other pollutants are shown in table 3

Figure 3 and figure 4 indicated that the modeled data and the origin data has the same trend.

Discussion and Conclusions

The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms.

The two parts considered in the presented research demonstrated the major conclusions given hereafter:

-The best correlation coeficient between BOD and COD is 0.980, based on natural logarithm model, Table 1. Hence, the best relationship between BOD and COD is:

$$BOD = A \ln(COD)^2 \qquad 7$$

Where A is a constant of the model.

- The relation between BOD and COD is a direct relation and can be relatively represented using a linear model (0.901X + 5.214) with correlation factor 0.965, for a value of COD approximately less than (50mg/L) , as shown in figures 1and 2.
- The estimated natural logarithm relationship can use in predicting the value of BOD according to the value of COD, COD values are always greater than BOD values, but COD measurements can be made in a few hours while BOD measurements take five days.
- In part two of the research there were many pollutants were examined in order to find the suitable mathematical model, these pollutants are COD, phe ,T,Oil,SO4 and TDS.
- The correlation coefficient show that there is weak correlation between BOD and Oil and between BOD and SO4 and BOD and pH, therefore, these values were neglegted, table 2, and the mathematical model was build according to the values of TDS,T,Phe.
- The relation between BOD and Phe, TDS, and T is a reverse relation, table 3
- The magnitude of BOD is more sensitive to the change in the COD contains rather than to the change in the Phe, TDS, and T contains.
- the modeled data and the origin data has the same trend as shown in figures 3,4.

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Table 1: The mathematical models for BOD-COD relationship

Mathematical Model	Correlation Coefficient
Y= x^2	0.846
Y= x^3	0.807
Y= 1/x	-0.682
Y= exp (0.12x)	0.804
Y= (ln (x)) ^{2}	0.980
Y=log (x)	0.953
Y= $x^{1.8}$	0.857
Y= exp($x^{0.5}$)	0.804
Y= exp(1/x)	-0.675
Y= 1/exp(x)	0.439
Y= x^6	0.804
Y= $(\exp(x))^{0.5}$	0.804
Y= $(\exp(x))^{0.75}$	0.804

Y=BOD , x=COD

Table 2: The mathematical models for BOD - other pollutants relationship

Mathematical Model		Correlation Coefficient				
	T	TDS	Phe	SO4	PH	Oil
Y= x^2	0.105	0.022	0.529	-0.195	-0.054	0.052
Y= x^3	0.128	0.054	0.500	-0.225	-0.058	-0.001
Y= 1/x	0.003	0.111	-0.552	0.078	0.043	----
Y= $x^{0.5}$	0.057	0.043	0.561	-0.139	-0.049	0.259
Y= $(1/x)^{0.5}$	-0.018	0.009	-0.555	0.099	0.045	-0.093
Y=log (x)	0.038	-0.061	-----	-0.119	-0.047	----
Y= exp (z)	0.007	0.149	-0.058	-0.055	-0.076	0.180
Y= 1/exp(f)	0.800	0.811	0.877	-0.130	0.019	-0.155
Y= $(\exp(x^{0.5}))^2$	0.156	0.029	----	-0.235	-0.059	-0.021
Y= exp(1/x)	0.005	0.038	-0.353	0.078	0.043	-0.124
Y= ln (x)	0.038	-0.061	----	-0.119	-0.047	----
Y= 1/ln (x)	-0.012	-0.002	----	0.103	0.043	----

Table 3: The selected mathematical models for BOD - other pollutants relationships

Mathematical Model	$(\ln(COD))^2$	1/exp(10T)	1/exp(0.1TDS)	1/exp(100Phe)
Correlation Coefficient	0.980	0.800	0.811	0.877

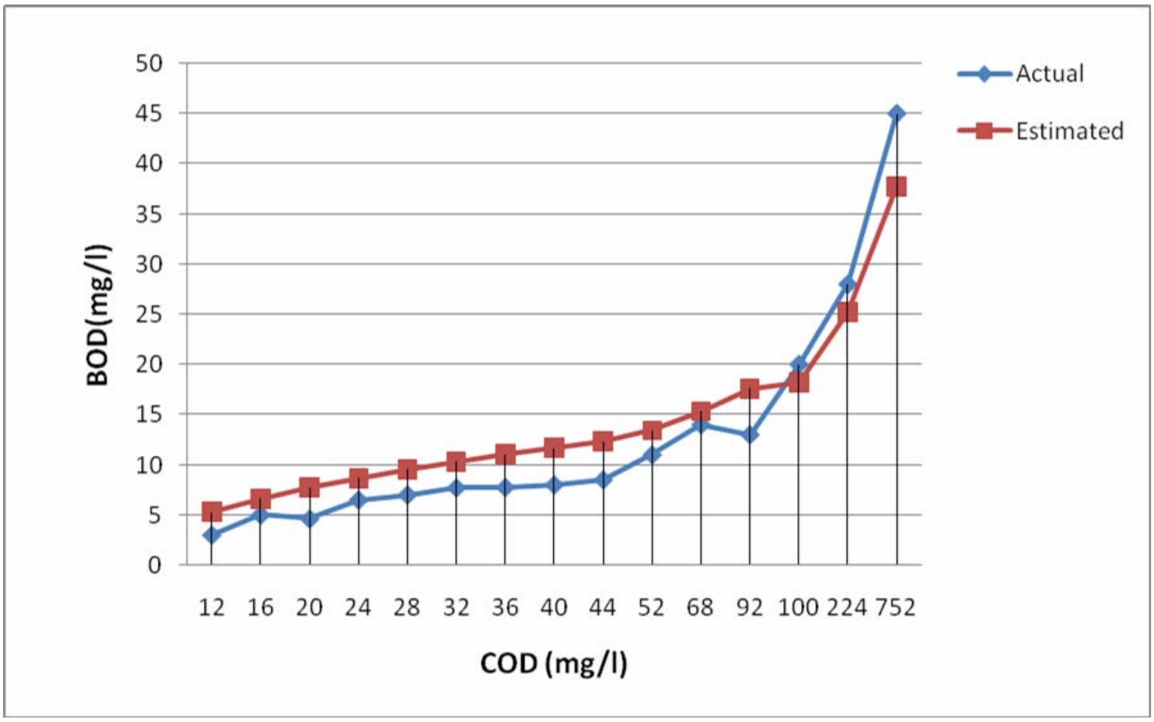

Figure 1: BOD versus COD during the period under study
(First set of data - Modeling)

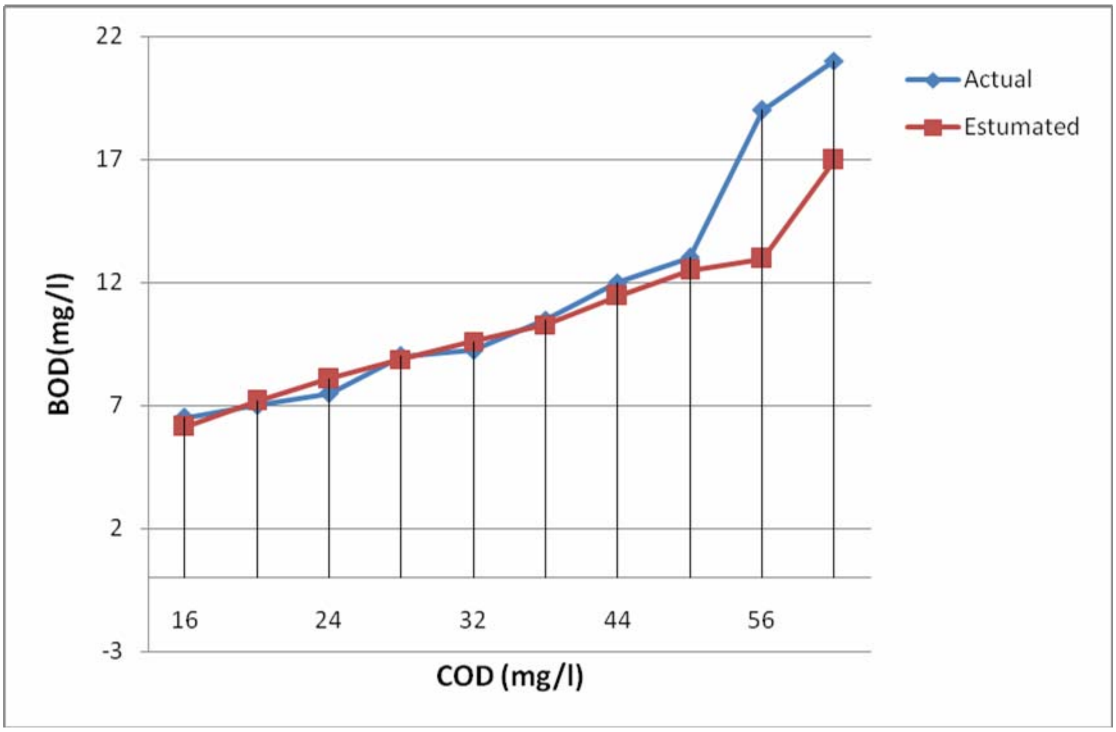

Figure 2: BOD versus COD during the period under study
(Second set of data - Evaluation)

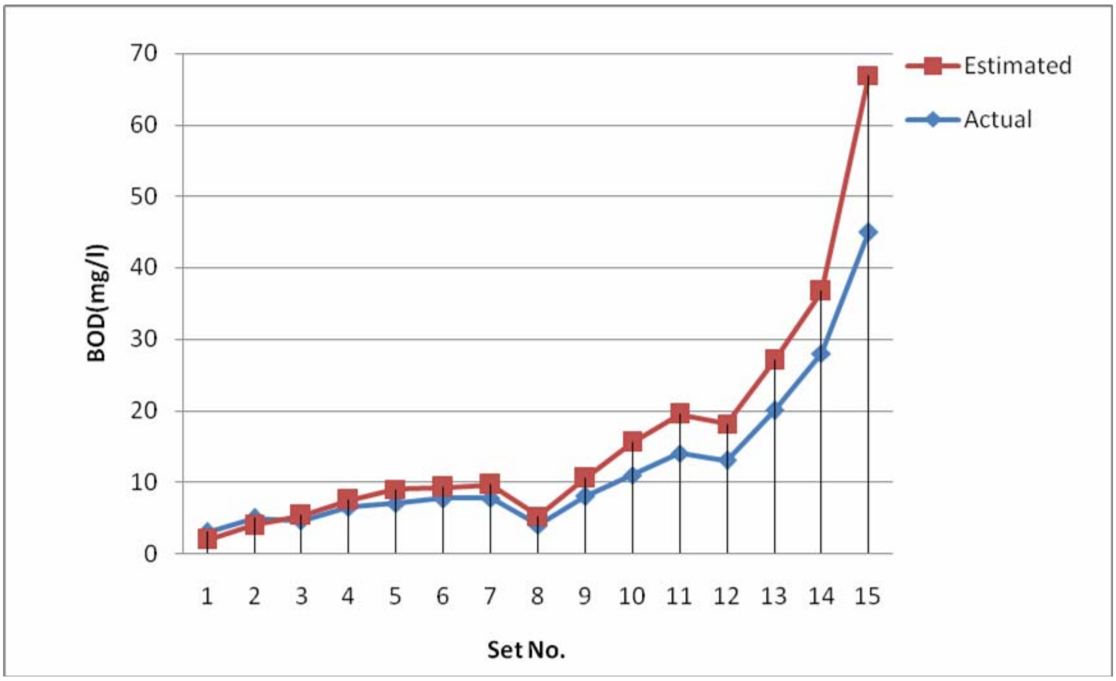

Figure 3: BOD evaluation during the period under study
(First set of data - Modeling)

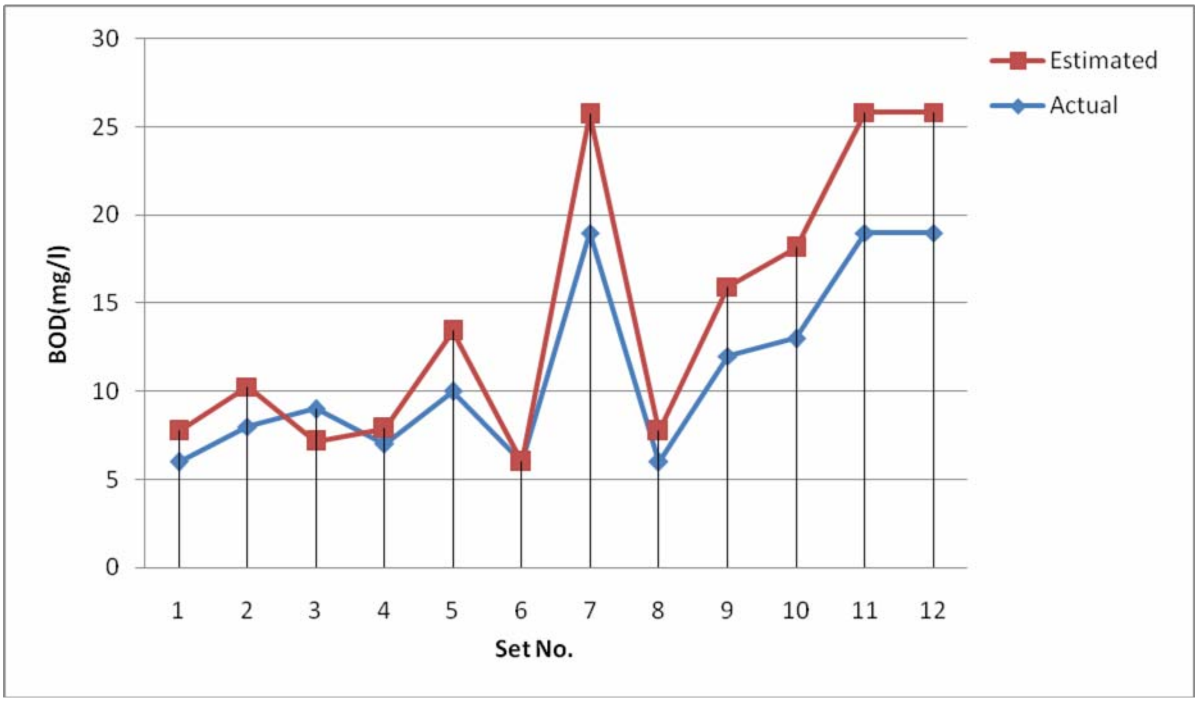

Figure 4: BOD evaluation during the period under study
(Second set of data - Evaluation)