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The oxidation reduction potential distribution along Diyala river within Baghdad city

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Abstract:

The reach of the Diyala river just before its confluence with Tigris River south of the capital city Baghdad was taken as a case-study. Its aquatic physicochemical characteristics were investigated and its pollution status was assessed in this study according to ORP (oxidation reduction potential) levels and other parameters. This segment of Diyala river was exposed to multiple points of treated and raw municipal waste water discharges, represented by the outfalls and bypass of three wastewater treatment plants of Al-Rustimiyah.

Diyala River's aquatic parameters represented by DO, BOD, COD, ORP, pH, and others were monitored and measured at nine stations along the river reach for a period of one year to assess seasonal variations. It was found that station two, which lies downstream the bypass of R3, was the most polluted station among all.

With regard to the ORP concentrations, the river was classified as anoxic conditions during winter to anaerobic conditions during summer from station two and downstream. Furthermore, it has been reached that the strong odor observed on site especially during summer, might be attributed to the formation of acid and methane production that goes with the obtained low levels of ORP.

The COD and BOD_5 levels classified the river as medium to low strength untreated wastewater during summer at station two and the downstream stations respectively.

The effect of temperature on DO and ORP was found to be reversed, while a positive nonlinear relation combined the DO concentrations with ORP levels.

The COD/BOD ratio of the river was found to be 1.2, which indicates the presence of biodegradable matter at high concentrations.

A statistical model relating DO concentration to BOD, ORP, EC and temperature was established. It was proved to be accurate.

To sum up, Diyala River at the reach of interest was found heavily polluted. The need for an urgent makeover of the water body characteristics of the river via mechanically assisted methods was found necessary to restore its original usages and ensure public health safety.

Keywords: Diyala River, ORP, DO, COD, BOD, Temperature

Introduction

Water pollution is one of the major problems facing manhood nowadays. Human activities and natural influences are the most common source that affects the quality of any water body [1]. Surface water, being the first source of water, should be protected against pollution since water is the most important resource in the world and no life is kept without it.

Wastes are most often discharged into receiving water bodies with little or no regard to their assimilative capacities [2]. Poor quality water can result in spreading disease and growth of undesirable aquatic life [3].

To protect the aquatic life of any receiving water body it is essential to determine its capacity to accommodate wastes. Quality of water can be defined in terms of the chemical physical and biological parameters of it [4]. Physico-chemical properties such as pH, dissolved oxygen, and others can be used to determine the water ecosystem integrity [5].

The dissolved oxygen (DO), for example, measures the amount of dissolved or free oxygen present in water; therefore, it represents the capacity of water to assimilate the pollution load. Dissolved oxygen in rivers results from combined impact of aeration and oxidation of organic matters [6]. The biochemical oxygen demand (BOD), defines the amount of oxygen required by bacteria to stabilize decomposable matter; therefore BOD measures the capacity of oxygen absorption of an effluent. The chemical oxygen demand (COD) represents the amount of DO required to oxidize the organic matter in a liquid. It should be greater than the BOD value for the same sample duo to the oxidation of non biodegradable matters presence in the sample along with the biodegradable matters oxidized in the BOD test [7].

The oxidation reduction potential (ORP) represents the water ability to oxidize contaminants. It is one of the essential indicators of natural and wastewater properties [8]. The ORP can be used to classify the river condition; aerobic, anoxic, or anaerobic depending on the range of ORP concentration, as depicted in **Figure 1** [9]. It also gives an indication of the present state of the river; for example, the oxidation of ammonia to nitrate is performed when the ORP concentration lies between the ranges +100 to +350 mV, while the reduction of nitrate to nitrogen occurs during the ORP ranges +10 to –50 mV [10]. **Table 1** illustrates ORP values for different biochemical reactions.

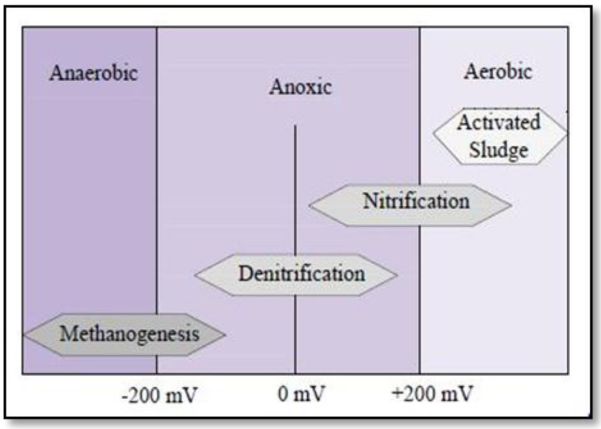

***Figure 1*: ORP ranges (mV) for typical wastewater processes [9].

***Table 1*: ORP values for different biochemical reactions [11].

Biochemical Reaction	**ORP range, mV**
Nitrification	+100 to +350
cBOD degradation	+50 to +250
Biological phosphorus removal	+25 to +250
Denitrification	+50 to -50
Sulfide (H_2S) formation	-50 to -250
Biological phosphorus release	-100 to -250
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

The present study has been concerned in making an assessment of the pollution status of Diyala river with regard to the ORP distribution along the river reach of interest among other parameters.

Materials and Methods

The study area

Diyala River is one of the tributaries of Tigris River. In the past, it contributed in about 11% of River Tigris's total water income. Unfortunately, know it is considered an effluent receiving water body.

The current study is carried out on the last part of Diyala River just before its confluence with the Tigris River in about 15 km. It is located within the capital city of Baghdad, Iraq.

This segment of Diyala River is exposed to multiple points of treated and raw municipal waste water discharges. These are represented by the outfalls and bypass of three wastewater treatment plants (WWTP) of Al-Rustimiyah. The WWTPs mentioned above are over loaded with influent that exceeds their operational capacities which in turn, affects the aquatic life of the receiving river represented by the River Diyala.

Figure 2 illustrates the zone of the study area and the locations of the WWTPs in the vicinity as well [12]. Several studies have been done to identify different types of pollution loads in Diyala River [13-19], in which none of them reported the ORP distribution in the river and its relation to pollutants.

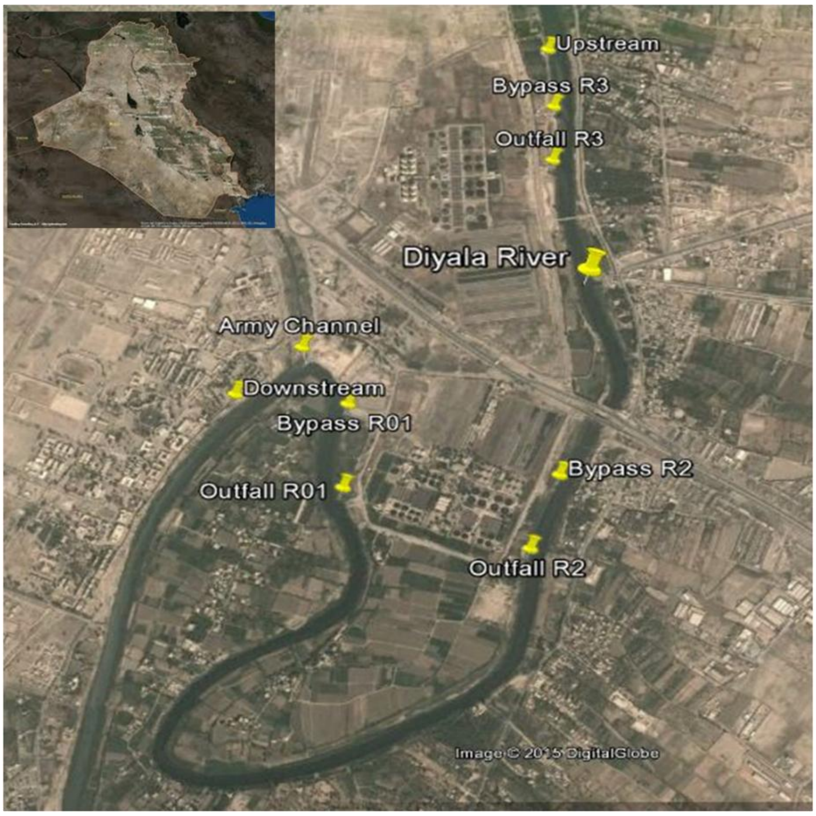

Figure 2: The study area and the locations of the WWTP's along the reach. [12]

Field Sampling

The river reach taken in this study was about 7 km long. It was divided into nine stations according to the points of pollution entering Diyala River. The first station was located upstream of all three WWTPs while further stations were located after each point of pollution submitted to the river, in an adequate distance to insure the mixing of pollutant with the river water. The final and ninth station was located downstream the last point of pollution were no other point inters the river till it pours into Tigris River. The location of each station was identified by the use of the GPS device. **Table 2** illustrates the description and coordinate of each point, while **Figure 3** shows the locations of the stations and their profile in kilometers along the river reach.

Figure 3: Stations location and sampling profile in kilometers along Diyala River in Baghdad.

***Table 2*:** The description and coordinates of the nine points taken in this study.

Station No.	Description	Coordinates
1	Upstream point	33º 17' 31.77" N 44 º 32' 16.66" E
2	Bypass R3	33º 17' 29.18" N 44 º 32' 16.42" E
3	Outfall R3	33º 17' 19.33" N 44 º 32' 15.95" E
4	Bypass R2	33º 16' 27.87" N 44 º 32' 16.21" E
5	Outfall R2	33º 16' 16.32" N 44 º 32' 2.08" E
6	Outfall R01	33º 16' 25.83" N 44 º 31' 42.68" E
7	Bypass R01	33º 16' 39.04" N 44 º 31' 43.00" E
8	Army Channel	33º 16' 47.68" N 44 º 31' 36.55" E
9	Downstream point	33º 16' 46.71" N 44 º 31' 34.23" E

The field sampling was carried out during a whole year starting from April 2014 till March 2015 in order to cover all seasonal variation that may occur in the region.

A polyethylene bottle was used to collect the samples of ORP, DO and other tests, while BOD glass bottles were used for the samples of BOD and COD. All bottles were rinsed with deionized water before usage. During sampling, the bottles were rinsed with the river water at points of collecting samples three times before taking any sample. Afterwards, all samples of BOD and COD tests were preserved at a temperature of 4˚C and transferred to laboratory.

Field analysis

The measurements were classified into two categories; Field and in lab measurements. The field measurements were represented by DO, ORP, pH, EC, Salinity and Temperature. On the other hand, the in lab measurements were BOD and COD. Field measurements were conducted on site immediately after each sample taken in order to prevent any error in the results due to their sensitivity to time and location. Devices such as DO meter, ORP meter, and pH meter were taken each trip to conduct the measurements onsite. The ORP meter, shown in **Figure 4**, adopts the standard method number 4500-H^+ of ORP measuring used in the APHA [20]. The DO, EC, and temperature measurements were done by the use of the WTW DO meter shown in **Figure 5.** This device adopts the standard method number 4500-O of DO measuring and the standard methods number 2550, 2510, and 2520 for measuring temperature, EC, and salinity respectively, used in the APHA [20]. The pH measure was done by the use of the pH meter (pH 200) Lovibond, shown in **Figure 6**. This device adopts the standard method number 4500-H^+ of pH measuring used in the APHA [20].

Figure 4: ORP 200 meter.

Figure 5: The WTW DO meter

Figure 6: The Lovibond (pH200) meter

The COD test was done by the Lovibond photometer-system device, shown in **Figure 7.** This device adopts the standard method number 5220 of COD measuring used in the APHA [20]. The BOD test was done by the Lovibond BOD-system OxiDirect device, assisted by the incubator, both shown in **Figure 8**. This device adopts the standard method number 5210 of BOD measuring used in the APHA [20].

The results obtained were evaluated by using SPSS program.

Figure 7:Lovibond photometer-system

Figure 8: Lovibond BOD-system OxiDirect and its incubator

Results and Discussion

DO

The field results of DO in mg/l for a whole year along the river reach was illustrated in **Figure 9**. As shown in this figure, the general approach of DO trend was almost similar, with a slight variation during different months of sampling. It can be seen that the DO concentration increases during cold seasons for all stations, while it decreases in certain stations during different seasons. The most critical station during the year was station number two. This in line with the site monitoring, were the bypass of R3 WWTP was continuously pouring into the river and it polluted the river tremendously. However, one can summarize this figure by **Figure 10,** in which the average value of DO concentration, for each station, was taken for the results of the whole period of study in order to simplify the display. This figure shows that the DO concentration gave its highest levels at station one, upstream from all the outfalls and bypasses of the WWTPs.

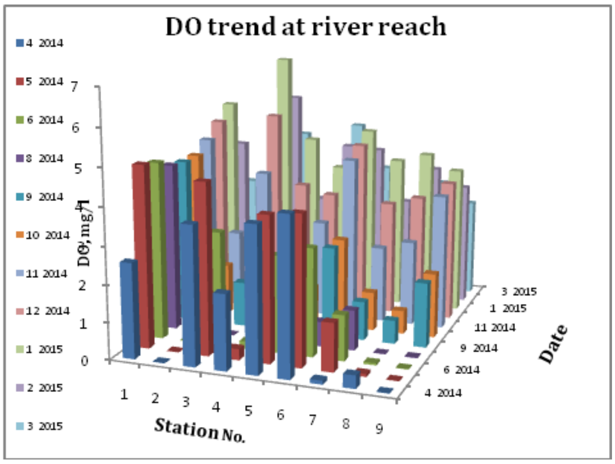

Figure 9**:** Dissolved Oxygen (DO) trend for a whole year along the river reach in mg/l.

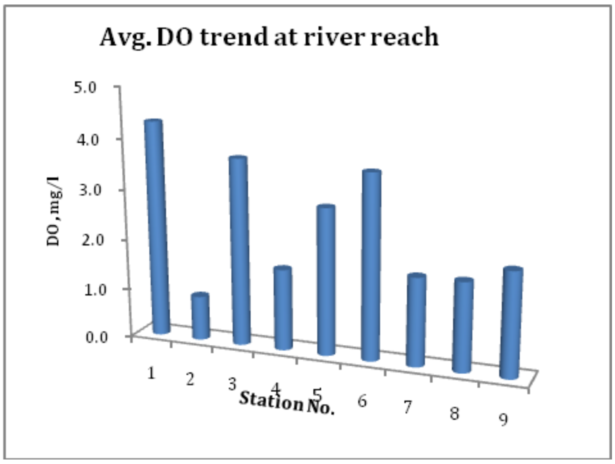

Figure 10**:** Average DO values for a year along the river reach in mg/l.

ORP

The ORP levels at the river reach were very low during the year and along stations. The lowest ORP concentration occurred at station two during summer season with a value of -352 mV. While the highest ORP value occurred during the spring at station one with a value of 75mV. All stations, except for number one, recorded negative ORP values during the year, as illustrated in **Figure 11**. As for the average ORP of the whole year, depicted in **Figure 12**, it was clear that station two and four gave the lowest average ORP values. This could be attributed to the presence of bypasses from the WWTPs at both points.

When comparing the ORP results with **Figure 1**, the river reach from station two and downstream can be classified as anoxic conditions during winter to anaerobic conditions during summer.

It was concluded, when compared to **Table 1**, that acid formation and methane production might occur at the river reach during the summer. This can be the reason of the strong odor observed on site especially during summer.

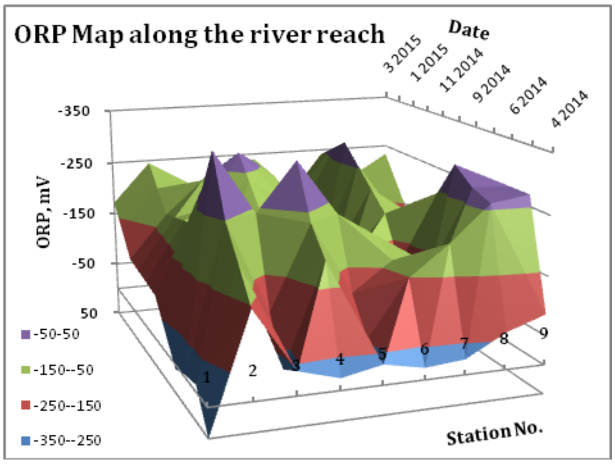

Figure 11: ORP contour map along the river reach.

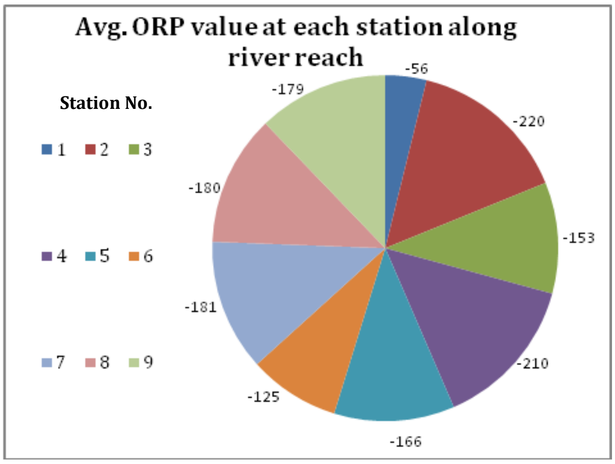

Figure 12: Average ORP levels at each station along the river reach.

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BOD

The BOD_5 values varied during the year and among different stations between 2 and 253 mg/l, having the lowest concentration at station one upstream of the WWTPs during winter, while the highest concentration occurred at station two during all seasons. This was clearly attributed to the fact that station two lies downstream the bypass of R3 which was the most active one among all three WWTPs. The average BOD_5 of the whole year among the river reach was demonstrated in **Figure 13**.

COD

The COD concentrations, as like the BOD_5, gave its least values at station one during the whole year. On the other hand, station two occupies the maximum COD concentrations for most of the year. This was illustrated in **Figure 13.** When comparing the BOD_5 and COD values with the typical compositions of untreated wastewater given in literature [21], then the river water at the reach of interest could be classified as medium strength untreated wastewater during summer at station two and low strength untreated wastewater at other stations except for number one.

pH

The pH levels were almost constant during different seasons and among all stations, as shown in **Figure 14**. Its range lies within 6.9 to 8.6.

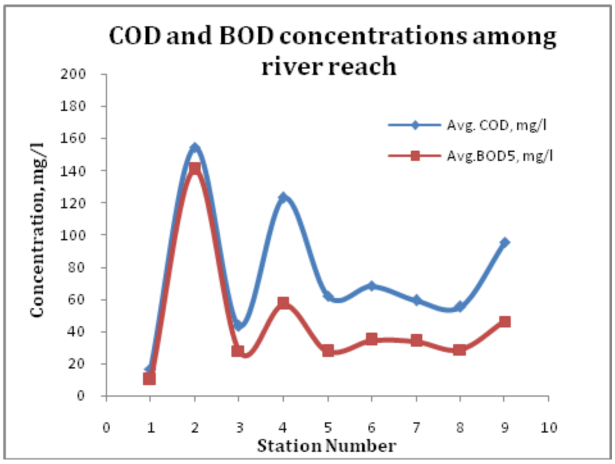

Figure 13: Average COD and BOD levels along the river reach.

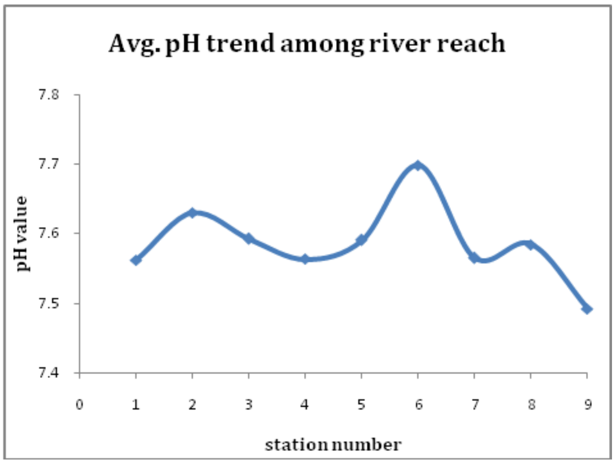

Figure 14: Average pH values throughout the river reach.

Temperature, Salinity, and Electric Conductivity (EC)

Temperature was almost constant along the river reach during the same site visit. It differed around the year of course. Temperature had indirect effect on most of the parameters, as will be illustrated later.

EC ranged between 2.14 and 3.12 mS/cm, having the highest value at station one which is normal duo to the existence of several drains upstream the river such as Al- khalis north and south outfall drains, Al-Nahrawan outfall drain and others, which contributes with high concentrations of dissolved solids.

Salinity was recorded almost constant during the year along the river reach; it ranged from 1.1 to 1.8 PSU.

Temperature Relations

DO

The obtained relation between temperature and DO was found to be reversed, as illustrated in **Figure 15,** which commensurate with the literature in this regard, that is higher temperatures revels lower DO concentrations [21].

ORP

The ORP relation with temperature was found to be reversed as well. Higher temperatures revealed lower values of ORP concentrations which adequate with the fact that summer season had the lowest ORP value, as mentioned before. This is clearly depicted in **Figure 15**.

Both DO and ORP relations with temperature gave R^2 values of 0.802 and 0.791 respectively. This illustrates the presence of other factors that affects the DO and ORP rather than temperature, represented by the polluted loads of AL-Rustimiyah WWTPs.

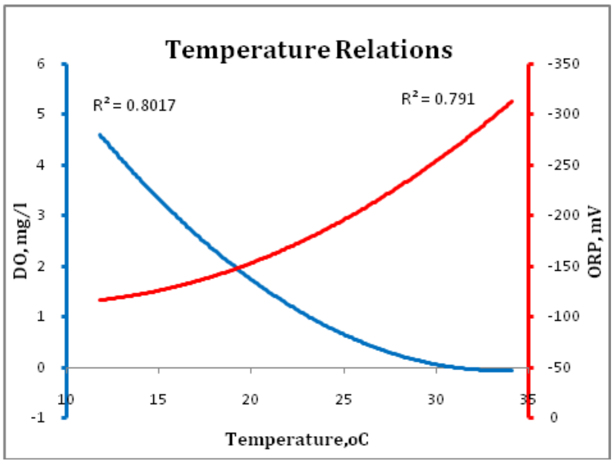

Figure 15: Temperature relations with DO and ORP

ORP-DO Relation

The relation of ORP with DO was found to be nonlinearly positive as shown in **Figure 16**. Higher DO concentrations gave higher ORP concentrations to a certain extent then the relation becomes mild were the effect of DO on ORP decreases. This can be attributed to the presence of other factors that may affect the ORP values such as the presence of pollutants mentioned above.

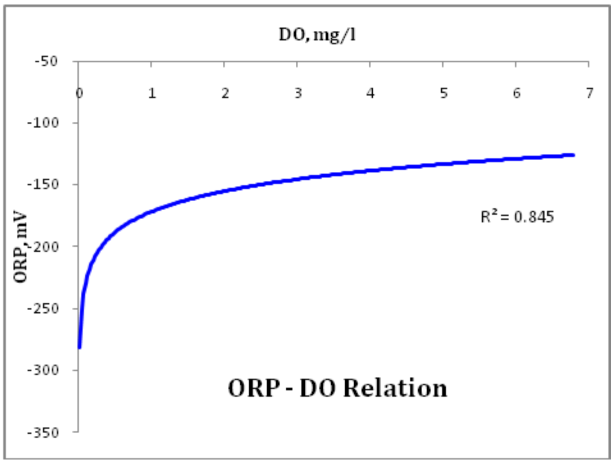

Figure 16: ORP-DO relation.

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COD/BOD Ratio

The COD/BOD ratio, illustrated in **Figure 17**, depicts a linear relation between them. The R^2 value of this relation was 0.91. The overall COD/BOD ratio was found to be 1.2 which indicates the presence of biodegradable matter at high concentrations at the river reach.

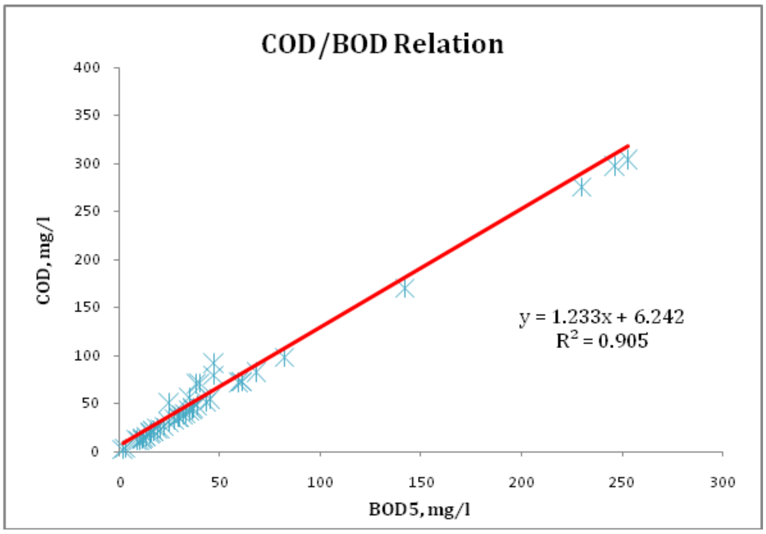

Figure 17: COD/BOD relation inside the reactor

Statistical Analysis of Results

A statistical model was obtained for the measured data using the SPSS version 20 program. In the model, the dissolved oxygen concentration (DO) in mg/l was adopted as the dependent variable (DV) and all other parameters as the independent variable (IV).

The individual relations between the DV and IV's were found to be linear. For that a multiple linear regression analysis was conducted using the stepwise method.

The final relation was illustrated by equation (1):

$$DO = 13.753 - 0.167\,Temp. - 0.012\,BOD_5 - 2.29\,EC + 0.01\,ORP \quad (1)$$

Where:

DO: The Dissolved Oxygen concentration at any point in mg/l.

Temp.: The water temperature at the point of interest in °C.

BOD_5: The biological oxygen demand at the point of interest in mg/l.

EC: The electric conductivity at the point of interest in mS/cm.

ORP: The oxidation reduction potential concentration at the point of interest in mV.

Equation (1) has a value of R^2 =94%, and a p-value of zero, which categorizes the model as significant.

The measured DO concentrations, which represent the actual values, were plotted verse the predicted DO concentrations, from equation (1), as shown in **Figure 18**. The relation gave a valuable regression among the actual and predicted concentrations. Furthermore, the accuracy of the obtained statistical model was established.

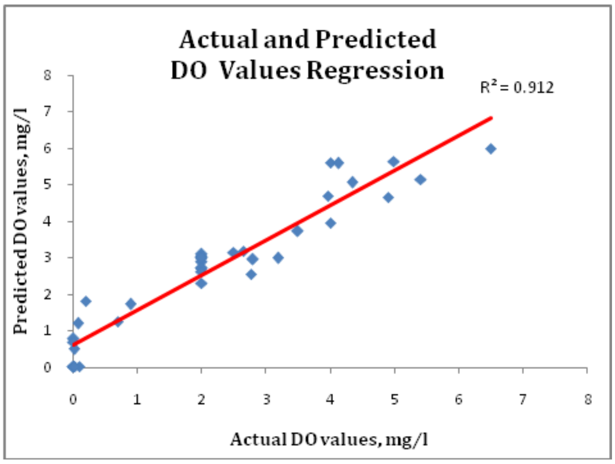

Figure 18: Actual and predicted DO concentrations' regression.

The statistical analyses of the measured parameters were summarized in **Table 3**.

Table 3: Statistical analysis of the parameters studied in this paper.

Parameter	Unit	Min	Max	Mean	Standard Deviation	Variance	Range	Standard Error
pH	—	6.9	8.6	7.6	0.34	0.11	1.7	0.034
EC	mS/cm	2.14	3.12	2.48	0.17	0.03	0.98	0.02
Salinity	—	1.1	1.8	1.25	0.12	0.014	0.7	0.02
Temp.	˚C	11.8	34.1	22.2	6.06	36.77	22.3	0.61
DO	mg/l	0.01	6.78	2.51	1.76	3.1	6.77	0.18
ORP	mV	-352	75	-175.55	86.08	7409.7	427	8.65
COD	mg/l	7.2	305	75.67	71.97	5180	298	7.23
BOD5	mg/l	2	253	45.47	50.6	2560	251	5.09

Conclusion

Diyala River at its last reach opposite Al-Rustimiyah WWTP's was monitored. Several tests such as DO, ORP, BOD, COD, pH, and others were measured. The river reach of interest was found heavily polluted. It can be concluded that the pollutants were at their highest levels at station 2, which lies downstream the bypass of R3, afterwards the concentrations varied along the river reach depending on the location of stations taken. The converse can be said on DO levels were its highest concentrations occurred at station1 before any pollution from the WWTP's fall into the river, while the lowest concentration of DO was monitored at station 2 which has the highest concentration of pollutants.

As for the ORP concentrations, the river reach from station two and downstream could be classified as anoxic conditions during winter to anaerobic conditions during summer. Moreover, it was concluded that the strong odor observed on site especially during summer, might be attributed to the formation of acid and methane production that goes with the low levels of ORP obtained.

From the COD and BOD_5 point of view, the river was classified into medium strength untreated wastewater during the summer at station two and low strength for downstream points.

A statistical model relating DO concentration to other parameters was established. It was proved to be accurate.

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