Original Article

Modeling the qualitative indices of sewerage of Mashhad city with Oxidation reduction Potential

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ABSTRACT

The necessity of performing this study that is the third phase of the project "investigation of the corrosion potential of the urban sewerage by examining the concentration of hydrogen sulfide and oxidation reduction potential" is due to the need of replacing the qualitative indices of the sewerage of Mashhad city with the oxidation reduction potential to achieve rapid results after modeling. In this study, the sewerage collectors in the west of Mashhad city with the length of 26 km were qualitatively assessed. These collectors are in two different paths of collecting the urban and industrial sewerage. In the first step, by selecting six qualitative stations in the urban sewerage path, four qualitative stations in the industrial sewerage path, and three qualitative stations in the section of transferring the combination of urban and industrial sewage were assessed. The six month studies with daily and weekly sequencing indicated that a significant relationship could be predicted between ORP and qualitative indices of urban sewerage, however there was no significant relationship between the qualitative indices of the industrial sewerage and the combination of urban and industrial sewerage. In the supplementary study of the quality monitoring stations, the collectors of the urban sewage transfer section with the length of 16 km increased to 11 stations. The studies showed that there was a significant relationship with the correlation coefficient of R=0.92 and determination coefficient of R=0.85 among the qualitative parameters of sewage including pH, ORP, and temperature with the COD response variable as well as a simple relationship with correlation coefficient of 0.83 and determination coefficient of R=0.7 between ORP and COD.

Keywords: ORP, Oxidation Reduction Potential, pH, Temperature, COD, sewerage infrastructure, sewerage Collectors, Mashhad

Introduction

There are several indices to measure the pollution of sewerage. The pollution indices are measured in laboratory and the experiments performed in the site do not indicate the pollution index; hence, the necessity of replacing these indices for the possibility of online analyzing the status of sewerage and collectors is fully sensible. One of the indices easily measured in the site is oxidation reduction potential (ORP) that there are not many studies on the use of this index. The term (oxidation) was generally used for the reactions of combination of materials with oxygen and reduction has been defined as the removal of oxygen from and oxygenic compound. The meaning of these words has been gradually expanded and today, oxidation and reduction are defined based on the change in the oxidation number. Oxidation is a process in which the oxidation number of an atom increases and reduction is the process in which the oxidation number of an atom decreases. [1 ,2]

Each ion, compound, and each element in the solution presents a potential for oxidation and reduction. The sum of these

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potentials equals to the ORP value of solution (in this study, sewerage). ORP value of the sewage indicates whether the sewage environment is oxidative (positive values of millivolt) or decreasing (negative values of millivolt) and for example, the negative reduction oxidation potential shows the presence of a decreasing factor such as BOD or COD and vice versa, the positive reduction oxidation potential indicates an oxidative factor like oxygen in DO solution.

Reduction-oxidation potential is an approximate value of the balance between the oxidized and reduced materials in the sewage. The unit of this pollution index is mV (millivolt) that is related to the proportion of negative and positive ions in the solution that is significantly depended on pH changes and it can be predicated by having oxidation and reduction oxidation for the half-reactions of oxidation and reduction. [3]

The purpose of the performed study that is the third phase of the project "investigation of the corrosion potential of the urban sewerage by examining the concentration of hydrogen sulfide and oxidation reduction potential" is the need of replacing the qualitative indices of the urban sewerage of Mashhad city with ORP index in order to assess and control the sewerage infrastructure as well as presenting an experimental model that shows the relationship between the concentration of the qualitative indices in sewerage and the ORP by which, the status of each using network can be evaluated at the moment and the critical points can be identified in the least time according to the other models obtained from the mentioned project. Obviously, this significantly helps in managing the operation. According to the studies performed so far, one of the capabilities of using ORP is determining the type of oxidation-reduction reaction; for example, the sulfide reduction process occurred in the oxidation-reduction capacity of -100 to -200 and the oxidation process of CO_2 occurs at the oxidation-reduction capacity of +50 to +250. [4]

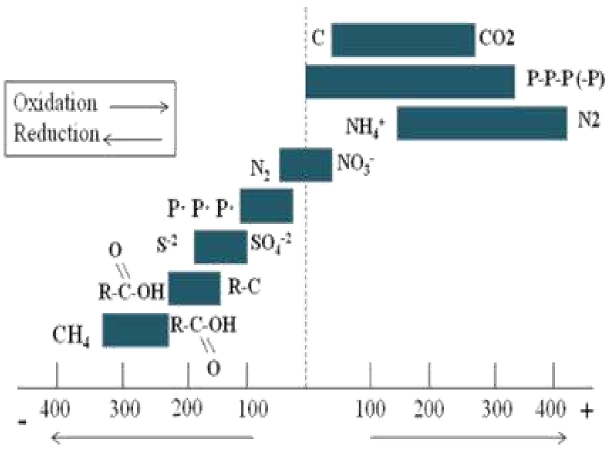


Figure 1: approximate limits of ORP in common sewage processes [5]

As a scale of the oxidation status in the solution systems, the oxidation reduction capacity can be used as a helpful instrument to show the biologic status of systems. The application of ORP measurement in the urban sewage refineries has been previously studied as an effective method in measuring DO. Charpenter et al. used ORP as a control parameter for optimizing the aeration of a wastewater treatment plant in a bench scale that desirable results were obtained from the correlation between ORP and the total hydrogen and nitrate of the wastewater [6]. Moreover, in many cases, ORP can be compared with pH and the reaction and possible responses of ORP in various systems are experimentally compatible with the reaction of pH in that system. [5] Another one of the uses of ORP addressed by the researchers is the diagnosis of production of Hydrogen Sulfide gas in the sewerage system. In fact, the oxidation reduction capacity in places where S^{2-} is about -250 to -100 millivolt . It should be noted that the oxidation reduction capacity is measured in the solution. [2] Not in biofilm layer where the sulphate reduction occurs. Thus, according to the experimental equations proposed by Nernst, the laboratory (experimental) levels of the measured oxidation reduction capacity are not compatible with the theoretic levels required for sulphate production. In an oxidation-reduction potential less than -100 millivolt, the anaerobic conditions rules in the sewage, while in the oxidation-reduction potential between -100 and 0 millivolt, anoxic conditions rule the sewage. [1, 7]

As it was previously said, limited researches have been conducted in the field of using ORP index as well as using this index in determining the qualitative indices of the sewage.

Materials and Methods

The present study consists of two main parts, including data preparation and homogenization of the study area, and estimating the regression coefficients of the independent variables that affect the response variable. In order to replace the quality indicators of the sewerage system in Mashhad city with the oxidation-reduction potential and to analyze the statistical relationship between the COD and ORP variables, it is necessary to evaluate the collectors and determine the sampling stations. To this end, sewage collectors in the west of Mashhad with the length of 26 km were selected as the site, which are the oldest sewage collecting infrastructure in Mashhad city and an independent sewage collector with special characteristics of sewerage transfer of different urban and industrial qualities. In terms of the quality and type of the sewage, the studied area is divided into three parts of urban, industrial, and combined (urban-industrial) sewage. The change range of COD qualitative index in the urban sewage section is 600 – 900 mg/lit, in the industrial sewage section, it is in the range of 750 – 1500 mg/lit, and in the combination of urban and industrial sewage, it is in the range of 650 – 1070 mg/lit. Different sections of the studied area can be observed in Figure 2. In the first phase of this study, six qualitative monitoring stations in the urban sewage transfer section, four qualitative monitoring stations in the industrial sewage transfer section, and three qualitative monitoring stations in the section of transferring the combination of urban and industrial sewage were chosen. In the primary study on the mentioned stations, for six month, daily and weekly, the qualitative variables listed in the table below were measured by sampling.

Table 1: The frequency of tests in monitoring stations in the studies of the first phase (six month) and supplementary phase (one-year)

Daily tests					
Evening			Morning		
Specialized sewage	Public sewage		Specialized sewage	Public sewage	
ORP	PH	TEMP	ORP	PH	TEMP
Weekly tests					
PH	SCOD		TCOD	TEMP	

Figure 2: The location of sewerage collectors in the west of Mashhad

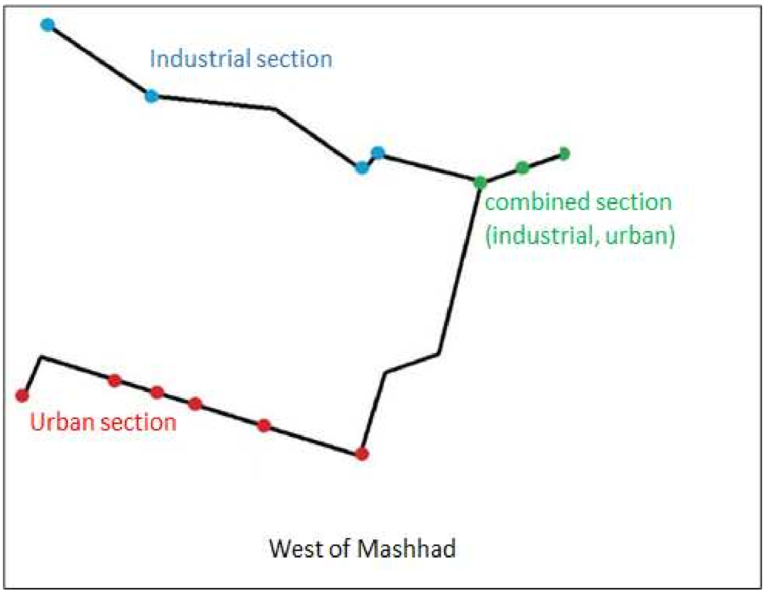


Figure 3: Location of the sampling stations of the first phase of studies

Table 2: the location of the qualitative monitoring stations in the first phase studies (six-months)

Station	Status	Location	Genus	Next diameter	Previous diameter	Line slope		UTM	
						After	Before	X	Y
1	Urban	Corner of Vakil Abad 52	RFC	900 × 1350	900 × 1350	0.001	0.001	722533	4023843
2	Urban	The beginning of Imamat Blvd.	RFC	2000	2000	0.007	0.014	727347	4022318

3	Urban	Imamat 52	RFC	900×1350	900×1350	0.012	0.012	727672	4024185
4	Urban	Azadi 50	RFC	1580×2400	1580×2400	0.002	0.002	728594	4024854
5	Urban	Toward Fayaz Bakhsh	RFC	1800	1800	0.0015	0.0015	728526	4025483
6	Urban	Fayaz Bakhsh	RFC	1500×2000	1500×2000	0.004	0.004	728727	4025341
1	Industrial	Tous Industrial Town	RFC	600×900	600	0.0068	0.021	718874	4035376
2	Industrial	Milad	RFC	700	700	0.007	0.007	720148	4036009
3	Industrial	Imam Doust 56	RFC	2000	2000	0.0016	0.0016	726441	4028731
4	Industrial	Corner of Tous 64	RFC	1400	1400	0.0012	0.0012	728103	4028456
1	Combined	The old road of Quchan	RFC	2000	2000	0.008	0.006	728157	4028322
2	Combined	Parkand Abad Neighborhood	RFC	2000	2000	0.00438	0.00291	728289	4028317
3	Combined	Parkand Abad	RFC	2000	2000	0.0043	0.0044	730081	4030954

The methodology of the present study is applicable in terms of the purpose, and it is from the kind of descriptive-analytical researches in term of nature and method. The data collection tool for investigating and analyzing the relationship between COD and ORP variables is sampling from the determined stations in filed method (figures 2 and 3, and table 2). In the previous studies, the statistical methods used for analyzing the relationships among the qualitative variables of sewerage include the spatial analysis, advanced evolutionary regression, linear interpolation, multivariate regression, etc., however, by the initial investigation of the samples data and examining and studying the resources as well as the researches done, it was determined that the multivariate regression is more strong to express the analysis among the variables and it is the most appropriate method to analyze the relationship among the variables; hence, the linear multivariate regression was used to perform the statistical analysis of this study. The multivariate regression provides the possibility of simultaneous analysis of the effect of many independent variables on a dependent variable; since the effect of the qualitative sewage variables on its pollution level includes the effect of several different indices, using multivariate regression method is appropriate. In this method, the relationships of a dependent variable and a set of independent variables are simultaneously analyzed. In this study, COD is the dependent variable and ORP, pH, and TEMP are the independent variables collected daily and weekly for six months. The steps of multivariate regression and preparation of the multivariate statistical model are as follows:

a) Data entry to SPSS software for performing the systematic model of the linear multivariate regression
b) Extracting the coefficients related to the factors with a significant relationship with the dependent variable
c) Obtaining the regression equation

The R^2 determination coefficient criteria of root mean square error (RMSE) were used in validating the models.

1) $$R^2 = 1 - \sum_{i=1}^{n} \frac{(Z^* - Z)^2}{\sum_{i=1}^{n} (Z - \bar{Z})^2}$$

2) $$MAE = \frac{\sum_{i=1}^{n} |Z(x_i) - Z^*(x_i)|}{n}$$

3) $$RMSE = \sqrt{\frac{1}{n} \left(\sum_{i=1}^{n} (Z^*(x_i) - Z(x_i)\right)^2}$$

In these equations:

$Z^*(x_i)$: The estimated COD value

$Z(x_i)$: The observed COD value

As RMSE is closer to zero, the higher the estimation will be. Moreover, as R^2 is closer to one, the more precise the regression model will be.

The results obtained from the first phase studies performed during six months of sampling indicated that there was a significant relationship among the independent variables pH, TEMP, ORP, and the COD response variable in the collector lines of urban sewage transfer; nevertheless, it is not possible to achieve the reliable model based on the initially selected monitoring stations; moreover, it is determined that there is not any significant relationship among the independent variables pH, TEMP, ORP, and the COD response variable in the collector lines of the industrial sewage transfer or the combined (industrial and urban) sewage transfer. The reason of lack of any significant relationship for the industrial and combined sewages can be the variety of industrial activities of the studied area. The majority of industrial units of the studies area are the converting industries and each of these industries has different productions in different months of the year.

According to the results obtained from the first phase of the studies, the necessity of revising the qualitative monitoring was inevitable; hence, by a comprehensive survey of the urban sewage transfer collectors with the length of 16 km, 11 new qualitative monitoring stations were located as described in table 3, and in order to ensure data adequacy, the tests were performed again for a one-year interval according to the Table 1.

Table 3: the location of qualitative monitoring stations in the supplementary stage studies (one-year)

Station	Number of manhole	Location	Genus	Next diameter	Previous diameter	Line slope		UTM	
						After	Before	X	Y

1	416155	Ladan Square	RFC	800 × 1200	300	0.00729	0.006	722062	4023319
2	416817	Hafte Tir-Vakil Abad Blvd.	RFC	900×1350	900×1350	0.001	0.001	724517	4023134
3	416843	Honarestan-Vakil Abad Blvd.	RFC	900×1350	900×1350	0.013	0.013	725218	4022887
4	416850	Under Hashemieh Bridge	RFC	1200	1200	0.0108	0.012	725774	4022691
5	416863	Before Farabi Hospital	RFC	1200	1200	0.0094	0.0108	726511	4022428
6	416873	In front of Imamt-Vakil Abad	RFC	1200×1800	1200×1800	0.0074	0.0091	727234	4022184
7	410629	Imamt Blvd.-Imamt 50	RFC	2000	2000	0.015	0.015	727703	4024113
8	410628	Imamt Blvd.- Imamt 52	RFC	2000	2000	0.015	0.015	727715	4024179
9	419290	Qaem Square	RFC	2000	1580×2400	0.003	0.004	728618	4025126
10	419287	Fayaz Bakhsh	RFC	1500×2000	1500×2000	0.004	0.004	728727	4025341
11	419526	In front of Tous 56	RFC	1800	2000	0.005	0.005	728294	4028078

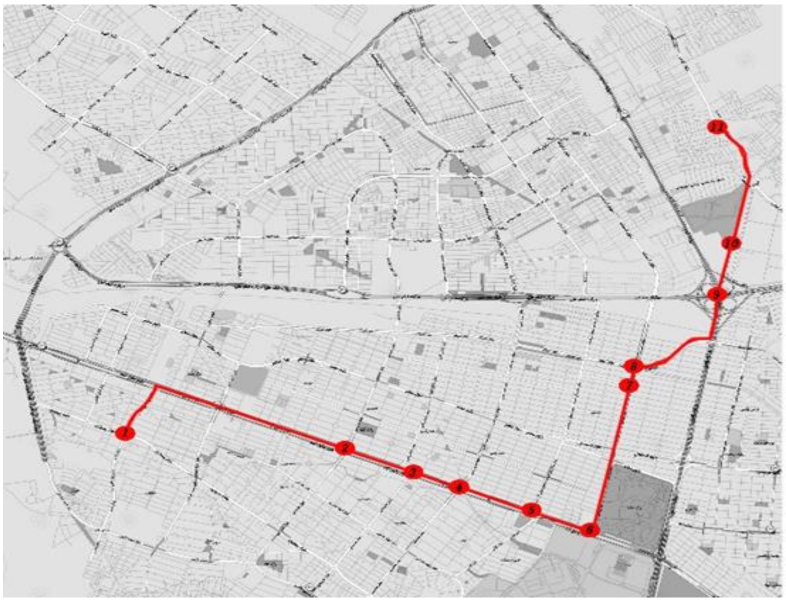


Figure 4: the location of urban sewage transfer collectors of west of Mashhad city and the supplementary phase monitoring stations

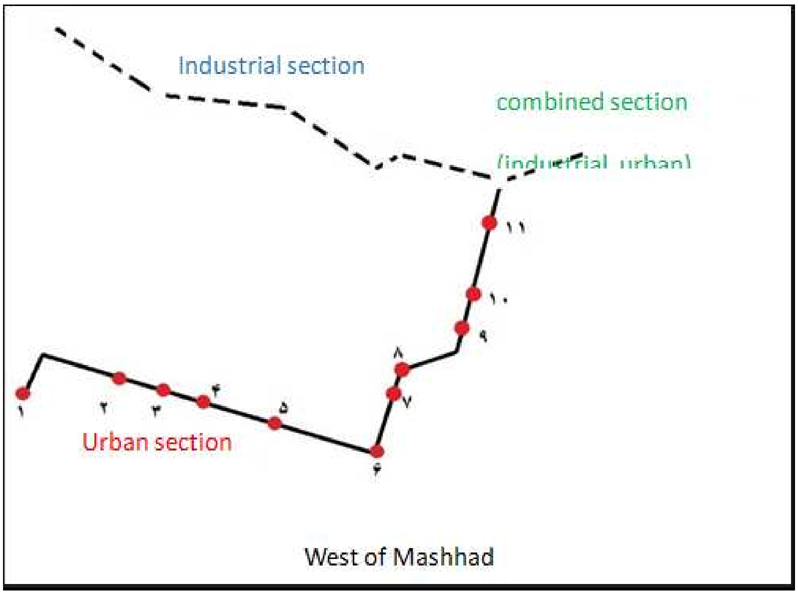
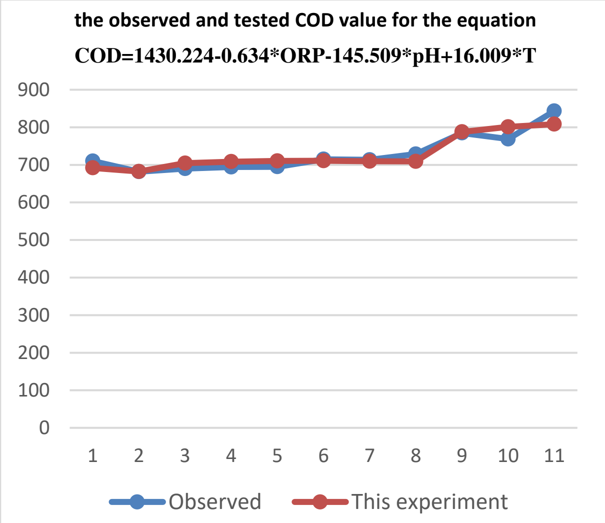


Figure 5: the location of monitoring stations of supplementary phase

After performing the systematic multivariate regression in the supplementary phase of the studies, two significant relationships between the independent variables TEMP, pH, ORP and COD response variable were obtained. The first relationship is linear with the correlation coefficient of R=0.92 and determination coefficient of $R^2 = 0.85$ and RMSE = 18.30:

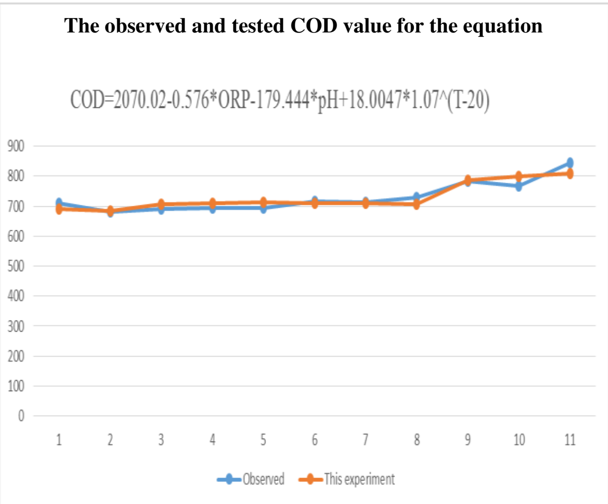
Regression equation 1: COD=1430.224-0.634*ORP-145.509*pH+16.009*T



Graph 1: Comparison of the results obtained from the linear regression equation with the real results for the COD response variable

The second equation is exponential; however, its important point is the similar correlation coefficients of R=0.92 and the determination coefficient $R^2 = 0.85$ with the linear equation, and only its complete square error is slightly greater that the linear equation RMSE 18.41. The exponential equation is:

Regression equation 2: COD=2070.02-0.576*ORP-179.444*pH+18.0047*$1.07^{(T-20)}$

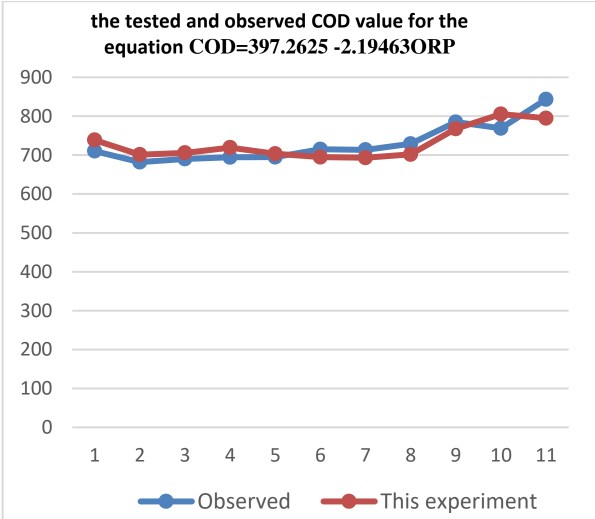


Graph 2: Comparing the results obtained from the exponential regression equation with the real results for COD response variable

Regarding the equations obtained from the systemic multivariate regression, it is determined that due to the lack of significant difference in the correlation and determination coefficients as well as RMSE, it is not recommended to use the exponential equation due to the computational complexity; and as the best result of regression, the linear equation will be the criterion of performing the future studies.

In the same regard, in order to achieve the acceptable results with minimum information, the regression was again performed only by considering the oxidation reduction potential ORP as the independent variable and COD as the response variable and the most appropriate equation with the correlation coefficient of R=0.83 and determination coefficient of $R^2 = 0.70$ and the RMSE=26.43 in linear form was obtained as follows:

Regression equation 3: COD=397.2625 -2.19463*ORP



Graph 3: Comparing the results obtained from the simplified linear regression equation with the independent variable ORP and the real results for COD response variable

The obtained simplified equation shows that by accepting the acceptable error, ORP index can be used alone for estimating the qualitative conditions of sewage. The most important application of the simplified equation is to detect the unauthorized discharges into the sewerage.

Conclusion

The approach of this study is to achieve the alternative indices of the conventional qualitative indices with the indices that can be calculated at the moment in order for the benefactors to be able to timely make the required decisions and monitor the sewerage infrastructure. This study was performed with the purpose of modeling the qualitative indices of the sewerage of Mashhad city with the oxidation reduction potential. The studied area that included the sewerage collectors of the west region of Mashhad city that is the oldest sewerage infrastructure of the city and collects the industrial and urban sewage that was assessed during two phases of six-months and one-year. The results obtained from the first phase studies indicated that there was a significant relationship between the independent variables of pH, TEMP, and ORP with the COD response relationship in the collector lines of the urban sewage transfer. However, it is not possible to achieve the reliable model based on the initially selected monitoring stations; as well, it was determined that there was no significant relationship between the independent variables pH, TEMP, ORP, and the DOD response variable in the collector lines of industrial sewage transfer or the combined industrial and urban sewage transfer lines. The additional studies performed on the sewage collectors transferring the urban sewage by considering 11 qualitative monitoring stations and over one year of sampling indicated that the exponential relationships do not have any advantage over the linear equations. With the equation COD=1430.224-0.634*ORP-145.509*pH+16.009*T with the correlation coefficient of R=0.92 and determination coefficient of $R^2 = 0.85$ and RMSE=18.30, in is possible to accurately model the most important qualitative index of the urban sewage COD with a variation range of 600 – 900 mg/lit. Moreover, in the specific conditions, by accepting the correlation coefficient of R=0.83 and determination coefficient of $R^2 = 0.70$ and RMSE = 26.43, we can use the equation COD=397.2625 - 2.19463*ORP with an acceptable error level to model COD.

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