Original Article

Modeling of the amount of sulfide production in sewage collectors in Mashhad

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ABSTRACT

This study is the fourth phase of the project "Investigation of the potential of corrosion of urban sewage networks through investigation of the concentration of hydrogen sulfide and reduction oxidation potential". The purpose of this study was to model and predict the production of sulfide in sewage in Mashhad. Sulfide production is the main cause of the phenomenon of corrosion and instability in operating conditions of sewage installations and, if possible, prediction of it can improve and stable the conditions of exploitation. The annual damage caused by sulfide production in sewage infrastructure installations around the world is over millions of dollars spent on rebuilding the installations. In this study, sewage collectors in west of Mashhad, with a length of 16 km, were selected and evaluated for quantitative and qualitative parameters by selecting 11 monitoring stations during a year. According to the results of the evaluations, there was a significant relationship between sulfide production and quality indices of ORP, COD, pH and temperature, as well as quantitative parameters such as hydraulic radius, retention time and the ratio of surface to volume of sewage collectors. The results of the multivariate regression model allow achieving the sulfide production prediction model based on the quality indices with a correlation coefficient R = 0.77 and the coefficient of determination R^2 = 0.61, also using quantitative and qualitative indices together, a model with a correlation coefficient R = 0.88 and coefficient of determination R^2 = 0.77 were obtained. Considering the necessity of the model's applicability and the possibility of measuring the indices online, an appropriate model was presented for the operators with a correlation coefficient R = 0.77 and coefficient of determination R^2 = 0.59 to predict the amount of sulfide.

Keywords: S^{2-} sulfide, ORP, oxidation and reduction potential, pH, temperature, COD, sewage installations, sewage collectors, Mashhad

Introduction

Sewage collection and transportation networks are one of the most important infrastructure installations around the world, and millions of dollars are spent annually on maintenance and repair of them. These installations play a significant role in providing human health, and in the present century they are one of the most basic sources of water reuse, and the collected sewage from wastewater plays a key role in the sustainability of human society. The reuse of water due to the 21st century droughts and the climate change that has taken place in the current century has increased the importance of sustainable utilization of sewage collection and transportation installations. One of the key factors that causes the sustainability of utilization of sewage installations to face a serious problem, and which results in a significant reduction (up to 50%) in the useful life of the installations, is the biological corrosion event caused by the production of sulfide S^{2-} in the installations. S^{2-} sulfide formation is one of the major problems occurred in sewage installations. The production and release of sulfide is the main

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cause of corrosion and dangerous odors in these installations [1, 2]. Studies conducted so far suggest that the destruction of sewage installations can be attributed primarily to corrosion caused by sulfuric acid attack due to biological activity, which results in the severe destruction of the structure and eventually the failure and structural destruction of the installations [3, 4]. There are many examples of sewage installations that have been designed and implemented over the past 50 to 100 years and have undergone substantial degradation due to corrosion of hydrogen sulfide (H_2S) after only 10 to 20 years. These events are rarely seen by installation operators in the absence of scientific models, and when a catastrophic collapse occurs, the installations renovation approach begins. The prediction of sulfide production in sewage installations is greatly evaluated useful in developing appropriate strategies for controlling sulfide formation or H_2S release. Obviously, the prediction of sulfide production in both phases of design - the implementation, operation and maintenance of sewage installations is critical to considering engineering measures to reduce sulfide production and increase the useful life of installation.

Since 1959, several empirical equations have been developed to predict the formation of sulfide [5-7]. These models have been used as the basis for many studies in recent decades. There have been, however, discussions about the accuracy of the models [8, 9]. Studies conducted so far [8] have shown that none of the Pomeroy [5] and Thistlethwayte [6] equations can be an appropriate equation for predicting sulfide formation. These studies prove that the different quantitative and qualitative conditions of human sewage as well as the operating conditions of sewage installations cause major changes in these equations. For example, the proposed Boon & Lister [7] model does not consider the flow velocity according to the specific conditions of its research, which is one of the important parameters of hydraulic conditions [10]. This suggests that for sewage collection and transfer installations, models should be evaluated case by case and a proportional model should be provided to predict sulfide production in each installation.

S^{2-} sulfide production in sewage installations

S^{2-} sulfide is one of the substances produced by bacteria (SRB) in anaerobic conditions in sewage installations. In recent years, various studies have been carried out on sulfide production in sewage installations, and various empirical equations have been presented [6, 10, 11].

The organic sulfate in the sewage installations is decomposed by bacteria (SRB) and produces (H_2S, HS^-, S^{2-}). Effective factors in the sewage that play a major role in the production of sulfide, according to studies conducted so far, include pH, temperature, concentration of organic substances COD, oxidation and reduction potential ORP, flow velocity and length of the network routes (retention time of installations), hydraulic radius, surface, and the volume of the pipes [5, 6, 12, 13].

In an ORP aqueous environment, there is an approximation criterion of the balance between the reduction and oxidation of materials in the fluid. Previous studies have shown that the proper range of ORP (Table 1) is for the optimal SRB bacterial activity in the range of -50 mV to -300 mV [14].

Table 1 - The appropriate range of ORP for producing S2- sulfide by SRB bacteria in sewage installations

Range of ORP	References
The favorite range of ORP for sulfide built-up by SRB	
-200 mV to -300 mV	Eliassen et al,1949 [15], Richard,1972 [16]
-100 mV to -250 mV	Boon, 1995 [10]
-50 mV to -300 mV	Edwards et al. 2001 [17]
-50 mV to -250 mV	Michael, 2007 [18]
The range of ORP for circumvent of sulfide built-up by SRB	
>50mv	Deek. 1995 [19]
≥50mv	Faridah et al. 2011 [20]
The favorite range of ORP for methane production by methane producing bacteria	
-175 mV to -400 mV	Michael. 2007 [18]

In most empirical relations for prediction of sulfide production in sewage installations BOD5 or COD have been used as indicators of organic matters, while SRB bacteria use only organic matter of the soluble [12, 13, 21].

Table 2: Relations of prediction of sulfide production in past studies

No	Equations	Sources
1	$\Delta S = 0.0265 * COD^{0.5} * 1.07^{(T-20)} * t_h * (A/V)$	Harlina, 2011 [11]
2	$\Delta S = 1.5 * 10^{-3}(COD - 50)^{0.5} * 1.07^{(T-20)} * t_h * (A/V)$	Hivitved-Jacobsen,1998(T) [12]
3	$\Delta S = 1.52 * 10^{-3} * BOD_5 * t_h * \{(1 + 0.004 * D)/D\}$	Boon,1995(TT) [10]
4	$\Delta S = 0.0026 * 10^{-5} * E_{BOD} * t_h * \{(1 + 0.01 * D)/D\}$	Pomeroy, 1959(TTT) [5]
5	$\Delta S = 0.228 * 10^{-3} COD 1.07^{(T-20)} t_h (A/V)$	Hivitved-Jacobsen,2002 [22]
6	$\Delta S = 1.5 * 10^{-3}(COD_S - 50)^{0.5} 1.07^{(T-20)} t_h (A/V)$	Moussavi, 2007(TTTT) [23]

(T) cited by Tanaka,2001

(TT) t_h in min and D (diameter) in cm

(TTT) E_{BOD} stands for effective BOD_5: $E_{BOD} = BOD_5 * 1.07^{(T-20)}$

(TTTT) COD_S, represents soluble COD, i.e., coefficient for typical domestic wastewater with $COD_s < 500$ mg/L.

These relations have been studied and developed with the aim of predicting the production of sulfide in various sewage installations. In these relations, quantitative and qualitative indices such as organic matter content of COD or BOD5, temperature, retention time of pipes and surface to volume ratio of pipes have been used [24]. Although pH and ORP indices have a significant effect on the amount of sulfide production, but assuming that these indices are in their optimal range in sewage installations, they has not been considered in the modeling that are usually used for short-length and without entry sewage installations in the range of case study. In summary, the modeling performed in the past uses the schema presented in relation 1 [5, 10, 12].

$$\Delta S = a * C^b * 1.07^{(T-20)} * t_h * (A/V) \qquad (1)$$

ΔS = Changes S^{2-} (mg / lit)
C = amount of soluble organic matter or total in COD or BOD_5 (mg / lit)
T = degrees Celsius
A = inner tube surface (m^2)
V = tube volume (m^3)
T_h = Retention time in the tube (hours)

The coefficients a and b= coefficient b is equal to one in most relations and a is different depending on the organic matter used, BOD5 or COD.
The models presented in previous studies have been evaluated to predict the production of sulfide in installations that there is no sub-connection to them and the flow velocity at the beginning of the study area is equivalent to the output flow velocity. This causes the ORP and pH indices range to remain constant. Therefore, the indices used in all proposed models are limited and the key indicator is the only amount of organic matter COD and / or BOD_5.

Materials and Methods

The research area of this study is the sewage collectors in west of Mashhad, which are the oldest sewage installations in the city. These collectors, the urban sewage transports of the west of Mashhad, have a length of 16 km and are from an ovoid cross section with a diameter of 800 * 1200 mm to a final circular cross section of 2000 mm in diameter. Along the route, all of the sewage collection networks in the west of Mashhad are entered to these collectors. These conditions cause changes in the quality and quantity of sewage along the route. Due to the specific circumstances of the project, selection of monitoring and sampling stations is of particular importance. Also, the quantitative and qualitative indices affecting the modeling are different from previous studies and should be redefined for this research. Accordingly, studies were divided into two parts. The first part involves determining the modeling method and determining the quantitative and qualitative indices affecting the model and the second part involves data development and presents a model to predict sulfide production.

A) Part One: Determining the modeling method and determining the quantitative and qualitative indices affecting the model

In the first step of this section, statistical studies conducted on the areas where the variables are, in addition to internal quality changes (chemical and biological responses), influence by external changes such as increasing or decreasing quantitative and qualitative variables were evaluated. Based on the studies, the multivariate regression method was identified as the most suitable method for evaluating and modeling the hydraulic and qualitative variable conditions of sewage collectors in west of Mashhad city to predict the amount of sulfide.
The multivariate regression method can lead to an appropriate prediction model by providing the possibility of simultaneous analysis of the effect of some quantitative and qualitative independent variables on a dependent variable. The steps of implementing multivariate regression method and providing multivariate statistical model are as follows:

A) Data entry to SPSS software to implement step by step the multivariate linear regression modeling
B) Extracting coefficients related to factors that have a significant relationship with the dependent variable
C) Obtaining the regression equation

In performing validation of the models, the criteria of determination coefficient (R^2), correlation coefficient (R) and root mean square error (RMSE) were used.

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

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

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

In these equations:
$Z^*(x_i)$:: Estimated amount of sulfide
$Z(x_i)$: The observed amount of sulfide

The closer RMSE to zero, the higher the precision will be. Also, the closer R^2 to one, the greater the accuracy of the regression model will be.
- In the second step of this section, quantitative and qualitative indices that have significant relationship with the amount of sulfide production were evaluated. Accordingly, six monitoring and sampling stations in the 16 km range of sewage collectors west of Mashhad that are urban sewage transfers are determined according to Fig. 1 and Table 3 and quantitative and qualitative indices were monitored in a six-month interval with daily and weekly frequencies, as described in Table 4.

Figure 1- Location of sampling stations in the first step of studies

Table 3 - Location of qualitative monitoring stations in the first step of studies (six months)

UTM		Line slope		Previous diameter	Next diameter	Genus	Location	State	Station
X	Y	After	Before						
722533	4023843	0.001	0.001	900 × 1350	900 × 1350	RFC	Corner of Vakil Abad 52	Urban	1
727347	4022318	0.007	0.014	2000	2000	RFC	**Beginning of the** Imamate Blvd.	Urban	2
727672	4024185	0.012	0.012	900×1350	900×1350	RFC	Imamate 52	Urban	3
728594	4024854	0.002	0.002	1580×2400	1580×2400	RFC	**Azadi 50**	Urban	4
728526	4025483	0.0015	0.0015	1800	1800	RFC	Toward Fayyaz Bakhsh	Urban	5
728727	4025341	0.004	0.004	1500×2000	1500×2000	RFC	Fayyaz Bakhsh	Urban	6

Table 4 - Frequencies of the tests at monitoring stations in the first step of studies (six months)

Daily Tests										
Evening					Morning					
Specialized to Sewage		General of sewage			Specialized to Sewage		General of sewage			
H_2S	ORP	Q	pH	TEMP	H_2S	ORP	Q	pH	TEMP	
Weekly tests										
S^{2-}	HS^-	SO_4^{2-}	TDS	TSS	BOD_5	SCOD	TCOD	DO	pH	TEMP

The results of the first step of the studies that took place during the six months of sampling revealed that, despite previous studies, there was no significant relationship between the amount of sulfide changes ΔS and quantitative and qualitative sewage indices and this is due to the addition of sewage flows along the rout of collectors, which eliminates sulfide changes from complete dependence on internal (chemical and biological) reactions. However, there was a significant relationship between sulfide concentration and quality indices of TEMP, pH, COD and ORP, also, a significant relationship was found between the combination of the above mentioned quality indices with the network characteristics, including path length, pipe surface and volume, and hydraulic indices of velocity and hydraulic radius.

B) Part two: Data development and presentation of the model for predicting sulfide production

Based on the results of the first step of the studies, the necessity of revising the evaluated quantitative and qualitative indices and the position of the quantitative and qualitative monitoring stations was inevitable. Therefore, with a comprehensive field survey of 16-kilometer urban sewage transferring collectors, 11 new quality monitoring stations were located in accordance with Fig. 2 and Table 5. In order to ensure the adequacy of data, experiments were carried out in a one-year interval based on indices that had a significant relationship with the sulfide production, according to Table 6.

Figure 2 - Location of urban sewage transferring collectors in west of Mashhad and monitoring stations of the supplementary stage

Table 5 - Location of quality monitoring stations in the supplementary stage of the studies (one year)

UTM		Line slope		Previous diameter	Next diameter	Genus	Location	Manhole number	station
X	Y	after	Before						
722062	4023319	0.00729	0.006	300	800 × 1200	RFC	Ladan Square	416155	1
724517	4023134	0.001	0.001	900×1350	900×1350	RFC	Haft Tir - Vakil Abad Boulevard	416817	2
725218	4022887	0.013	0.013	900×1350	900×1350	RFC	Honarestan-Vakil Abad Boulevard	416843	3
725774	4022691	0.0108	0.012	1200	1200	RFC	Under Hashemie Bridge	416850	4
726511	4022428	0.0094	0.0108	1200	1200	RFC	Before Farabi Hospital	416863	5
727234	4022184	0.0074	0.0091	1200×1800	1200×1800	RFC	Opposite Imamate-Vakil Abad	416873	6
727703	4024113	0.015	0.015	2000	2000	RFC	Imamate Blvd.-Imamate 50	410629	7
727715	4024179	0.015	0.015	2000	2000	RFC	Imamate Blvd.-Imamate 52	410628	8
728618	4025126	0.003	0.004	1580×2400	2000	RFC	Ghaem Square	419290	9
728727	4025341	0.004	0.004	1500×2000	1500×2000	RFC	Fayyaz Bakhsh	419287	10
728294	4028078	0.005	0.005	2000	1800	RFC	Opposite Tous 56	419526	11

Table 6: Frequency of the tests at monitoring stations in supplementary stage of studies (one year)

Daily Tests				
R	ORP	V (m/hr)	pH	TEMP
Weekly tests				
S^{2-}	TCOD	ORP	pH	TEMP

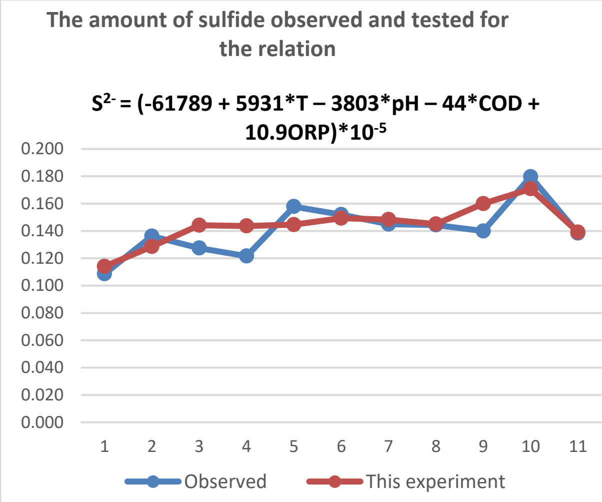
It is worth noting that in the supplementary studies it was determined that the characteristics of the sewage network, considering the ratio of the surface to volume A / V and the combination of the hydraulic characteristics of the flow velocity V (m / hr) and network characteristics, the path length as the hydraulic retention time T_h = L / V, as well as the hydraulic radius R, have a significant relationship with the amount of sulfide production that was used in determining the quantitative and qualitative integration model.

After analyzing stepwise multivariate regression in the complementary stage of the studies, a significant relationship was found between the independent qualitative variables of TEMP, pH, COD and ORP with the S^{2-} response variable and a significant relationship was also found between the mentioned independent qualitative variables and their integration with the quantitative independent variables include A / V, T_h and R with S^{2-} response variable.

The significant relationship between qualitative variables and S^{2-} response variable having correlation coefficient R = 0.77 and coefficient of determination R^2 = 0.61 with the error RMSE = 0.01 is:

$$S^{2-} = (-61789 + 5931*T - 3803*pH - 44*COD + 10.9ORP)*10^{-5}$$

Relation (2)

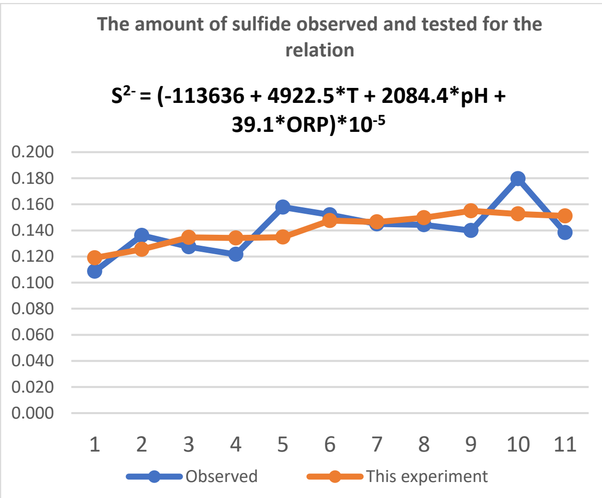


Considering the proper fitting of the model on real data, it is possible to predict the production of sulfide based on quality indices with a proper accuracy. Among indices having significance relationship, however, it is not possible to measure index COD in place so that operators can not instantly get proper information about the status of systems management. However, with the advancement of technology, it is possible to use the advanced analyzers to measure the COD index instantaneously, but this will be possible at a great expense and only at constant monitoring stations.

Accordingly, the results of the third phase of these studies aimed at replacing the qualitative indices with the oxidation reduction potential, COD index replacement with the ORP was performed and the resulted relationship between qualitative variables with S^{2-} response variable having a correlation coefficient R = 0.63 and the coefficient of determination R^2 = 0.40 with the error RMSE = 0.01 is:

$$S^{2-} = (-113636 + 4922.5*T + 2084.4*pH + 39.1*ORP)*10^{-5}$$

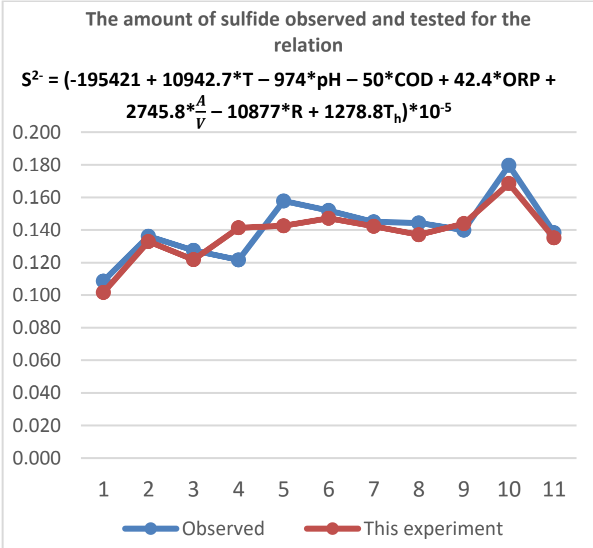
Relation (3)



Despite the error rate of RMSE = 0.01 in this relation and the correlation coefficient R = 0.63 due to the low coefficient of determination that is equal to R^2 = 0.40, this relationship was not recognized as suitable for modeling. At this stage, the modeling was performed again by combining the qualitative indices with the quantitative hydraulic indices and network specifications and the significant relationship between the combination of qualitative and quantitative variables with S^{2-} response variable having correlation coefficient R = 0.88 and coefficient of determination R^2 = 0.77 with the error RMSE error = 0.008 is:

$$S^{2-} = (-195421 + 10942.7*T - 974*pH - 50*COD + 42.4*ORP + 2745.8*\frac{A}{V} - 10877*R + 1278.8T_h)*10^{-5}$$

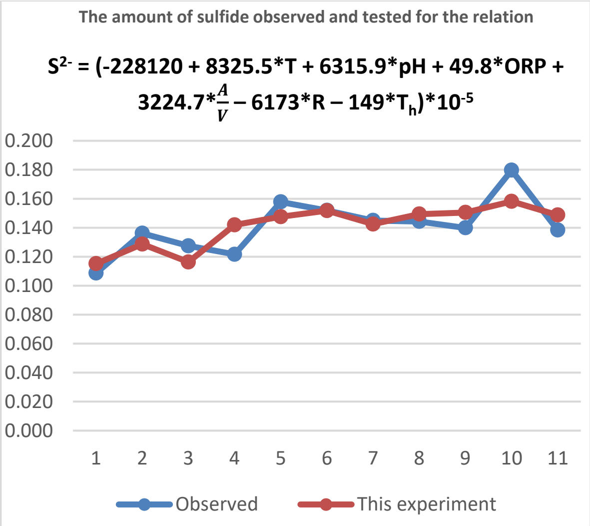
Relation (4)



Due to the most proper fitting of the model on real data, it is possible to predict the production of sulfide based on the combination of qualitative and quantitative indices with a high accuracy as online in the fixed stations equipped with COD analyzers. According to the article "Modeling the qualitative indices of sewage systems in Mashhad with the oxidation reduction potential", from the same authors, to achieve a suitable and applicable model that can be used to predict online the amount of sulfide production with high precision with standard quality assays, the COD qualitative index in the new model was replaced by oxidation and reduction potential. On this basis, there is a significant relationship between the combination of common qualitative and quantitative variables with the S^{2-} response variable having the correlation coefficient R = 0.77 and the coefficient of determination R^2 = 0.59 with the error RMSE = 0.01 is:

$$S^{2-} = (-228120 + 8325.5*T + 6315.9*pH + 49.8*ORP + 3224.7*\frac{A}{V} - 6173*R - 149*T_h)*10^{-5}$$

Relation (5)



This model can be a guide for operators to control the conditions of management of the sewage installations online, due to its proper coefficients and desired fitting as well as insignificant error.

Conclusion:

The approach of this research is to achieve a model for predicting the amount of sulfide production in sewage installations online, so that operators can take actions to monitor instantly the sewage installations and take decisions. This research was conducted with the aim of modeling based on qualitative indices of sewage in Mashhad and its integration with quantitative indices for prediction of the amount of sulfide production. The study area was the sewage collectors in the west of Mashhad with a length of 16 km. This installation is the oldest sewage installation in the city with an ovoid section and diameter of 800 x 1200 mm to a final circular section of 2000 mm. The research was conducted in two stages of six months and one year on quantitative and qualitative indices. The results of the first stage studies indicated that there is a significant relationship between the independent variables TEMP, pH, COD and ORP with the response variable S^{2-} in the urban sewage transferring collector lines, but achieving a reliable model based on initially selected monitoring stations is not possible. It was also found that, despite previous studies, there is no significant relationship between the independent variables TEMP, pH, COD and ORP with the response variable ΔS in the collector lines. Supplementary studies were carried out on sewage collectors transferring urban sewage taking into account 11 quality monitoring stations during one year of sampling. It was determined that the characteristics of the sewage network, considering the ratio of the surface to volume A / V, and the combination of the hydraulic characteristics of flow velocity V (m / hr) and the network characteristics, the length of the path as the hydraulic retention time T_h = L / V, as well as the hydraulic radius R has a significant relationship with the amount of sulfide production and providing a quantitative and qualitative integration model will allow accurate prediction of sulfide. Based on the obtained results the best qualitative model was presented according to the relation S^{2-} = (-61789 + 5931 * T-3803 * pH-44 * COD + 10.9ORP) * 10^{-5} which has a correlation coefficient R = 0.77 and the coefficient of determination R^2 = 0.61 with the error RMSE=0.01. Also, the best model including the combination of qualitative and quantitative indices and the characteristics of the installations to predict the amount of sulfide production by the relation **$S^{2-} = (-195421 + 10942.7*T - 974*pH - 50*COD + 42.4*ORP + 2745.8*\frac{A}{V} - 10877*R + 1278.8T_h)*10^{-5}$**, which has a correlation coefficient R = 0.88 and a coefficient of determination R^2 = 0.77 with an error of RMSE = 0.008 was presented. Considering that the focus of the research is on providing an applicable model for operators with the ability to predict online sulfide production amount based on measurable information in place, by replacing the qualitative index COD with oxidation reduction potential, the applied model of sulfide production prediction based on the relation **$S^{2-} = (-228120 + 8325.5*T + 6315.9*pH + 49.8*ORP + 3224.7*\frac{A}{V} - 6173*R - 149*T_h)*10^{-5}$** , which has a coefficient of correlation R = 0.77 and coefficient of determination R^2 = 0.59 with error RMSE = 0.01 was presented.

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