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Characterization of Oxidation-Reduction Potential Variations in Biological Wastewater Treatment Processes: A Study from Mechanism to Application

Xiaodong Wang [1,*], Yuxing Wu [1,2], Ning Chen [1], Heng Piao [2], Delin Sun [3], Harsha Ratnaweera [4], Zakhar Maletskyi [4] and Xuejun Bi [1]

[1] School of Environmental and Municipal Engineering, Qingdao University of Technology, Jialingjiang East 777, Huangdao, Qingdao 266520, China
[2] Jiangsu Haixia Environmental Protection Technology Development, Ltd., Nanjing 210000, China
[3] Shandong Oubeier Software Technology Co., Ltd., Jinan 250021, China
[4] Faculty of Science and Technology, Norwegian University of Life Sciences, P.O. Box 5003, 1432 Aas, Norway
* Correspondence: wangxiaodong@qut.edu.cn

Abstract: Oxidation-reduction potential (ORP) sensors would constitute a robust surveillance and control solution for aeration and external carbon dosing in wastewater biological treatment processes if a clear correlation exists between the ORP values and process variables (e.g., dissolved oxygen (DO), nitrate, and chemical oxygen demand (COD). In this study, ORP values and other water quality variables were analyzed, and principal component analysis (PCA) and analysis of variance were used to study the relationships between ORP and main reactive substances under anoxic conditions. Mathematical models were then established using multiple regression analysis. The results showed that under anoxic conditions, ORP was positively correlated with nitrate, DO, and COD and negatively correlated with ammonia nitrogen, phosphate, and pH. COD had a low correlation with the ORP value change. PCA showed that the mathematical model of ORP can be established by using DO, nitrate, and phosphate, for which the adjusted R^2 value was 0.7195. The numeric relationships among ORP, COD, and nitrate were clearly established and applied to control external carbon dosing. A precise and clear relationship between ORP and COD offers the possibility to substitute COD monitoring for process control.

Keywords: oxidation-reduction potential; process monitoring; wastewater treatment; process control; principal component analysis

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1. Introduction

Oxidation-reduction potential (ORP) is a water quality variable employed to characterize the redox capacity of the whole system, which is represented by the ORP value. Wastewater biological treatment processes have many types of oxidative substances (e.g., dissolved oxygen (DO), nitrate, and nitrite) and reductive substances (e.g., ammonium and organic matter); therefore, they lead to series of oxidation-reduction reactions. The ORP of the system is determined by the interaction of various reductive and oxidative substances in the whole system [1]. When the whole system showed oxidability, the ORP value was lower, and vice versa [2]. Initially of interest, the ORP value was supposed to indicate the DO level and control the aeration, although the function of ORP sensors was substituted with more reliable optical DO sensors [3,4]; however, ORP sensors have been used for water and wastewater treatment process monitoring [5] and chemical dosing control [6–8].

In recent years, improving effluent quality and reducing operational costs have driven the development of instrumentation, control, and automation in wastewater treatment systems [9]. Various sensors that monitor the wastewater treatment processes have been installed in wastewater treatment plants (WWTPs). Automatic control and automation have the potential to reduce labor cost and energy consumption [10], and online sensors provide real-time data to enable automatic process control [11]. However, nitrate, ammonia nitrogen (NH4-N), and other nutrient online monitoring sensors are not reliable for real-time control due to frequent sensor fault, e.g., drifting, but building the sensor network also requires a high financial cost, which results in higher initial and operational investments for WWTPs. Moreover, higher maintenance frequency is required due to the harsh environment of WWTPs, which is labor intensive. Figure 1 shows the appearance of an integrated online sensor before and after manual cleaning, which was installed to measure nitrate and ammonium of raw wastewater before biological treatment. The ion-selective membrane of the sensor would be covered by biofilm within 1 day exposure to raw wastewater. Previous studies reported that ion-selective electrodes (e.g., ammonium, nitrate, and DO) need to be maintained at least twice per week [12]. Despite the extensive cost of sensor maintenance, sensor failure is another unavoidable challenge. Ohmura et al. demonstrated two important assumptions for sensors based on the principle of ion selectivity measurement that are not valid: (i) sensor faults appear at distinct times in different sensors, and (ii) any given sensor functions near-perfectly for a significant time period following installation [13]. Sensor failure can occur at any time, and drift may happen immediately after calibration. ORP sensors have the advantages of being low cost, reliable, and robust since the mechanism of ORP measurements is based on electro-potential. The relationship between the ORP value and the other water quality variables in the process of wastewater treatment has not been well-investigated yet. Applications of ORP as an indirect water quality variable and an alternative to direct water quality variables and sensor anomaly detection are attracting increasing research interest since the initial investment and maintenance cost may be significantly reduced compared with direct measurement sensors of various wastewater quality sensors.

Figure 1. The integrated ammonium and nitrate sensors. (**a**) Being used for raw wastewater monitoring in influent channels for 24 h without cleaning; (**b**) after cleaning.

Previous studies have indicated that ORP may be a useful water quality indicator for wastewater treatment process control. Wang et al. studied the relationships between ORP, nitrate, and phosphate in an activated sludge system with a denitrification enhanced biological phosphorus removal process, who suggested that ORP can be used to control the process operation in the anaerobic zone for phosphorus removal [14]. Su studied the ORP variation characteristics of high concentration organic wastewater treated by the sequencing batch reactor (SBR), which demonstrated that the ORP had strong correlations with NH_4-N, chemical oxygen demand (COD), DO, temperature, and pH [15]. These studies have indicated the correlation between ORP, process operational variables, and environmental variables. For process surveillance and control purpose, further investigation is necessary.

Process control based on the ORP and other water quality variables (such as pH and DO), or with the first derivative of ORP as one of the main control parameters has been widely studied, and some progress has been made [16–21]. ORP and its first derivative play an indicator role to identify the change in nitrate concentration. Fox et al. used an online control system with ORP sensors involved for aeration control in a wastewater treatment system, which saved more than 40% of energy consumption [20]. These studies show the potential and advantages of ORP sensors in the wastewater treatment process and proved that ORP can be a reliable process control indicator. However, the pattern of ORP sensor faults and its mathematical relationship with other water quality indicators is unclear [22]. To make better use of the indicator function of the ORP sensors in the future, a more comprehensive mechanism study on the complex relationship between ORP and water quality indicators should be conducted, and the ORP variation features caused by water quality variation should be clarified. Though ORP sensors have demonstrated their ability as alternative sensors to reflect NH_4-N and nitrate concentration, the means by which to reverse reflect the changes in key water quality indicators in process control by the ORP value remains lacking in scientific basis, and no substantial research breakthroughs have been made. The application potential of carbon addition control in the anoxic zone of the wastewater treatment process remains to be explored.

The primary goal of this research was to clarify the relationship between ORP and the main reactions in the process of anoxic reactions by data analysis. After establishing the direct relationship between ORP and the denitrification degree, the secondary goal was to explore the method of using ORP to control the dosing of carbon source for denitrification in wastewater treatment processes.

2. Materials and Methods

2.1. Experimental Setup

As shown in Figure 2, an acrylic sealed reactor with a volume of 20 L volume was used to perform the mechanistic investigation of ORP and other water quality variables. A rubber pad was placed between the top cover plate and reactor to ensure a sealing effect. A hole was opened on the cover plate for passing through the sensor probes. DO and multi-parameter water quality analyzer probes were used in the experiment to measure DO, pH, and total dissolved solids (TDS) of the mixed liquid. Returned sludge from the secondary sedimentation tank and effluent from the primary setting tank of the domestic WWTP were mixed in the reactor to simulate an anoxic environmental of wastewater treatment processes. The nitrified mixed liquid was also used by sampling from the aerobic zone of the biological treatment tank to mix with the liquid in the reactor to create different oxidative or reductive levels. Moreover, biocarriers of moving bed biofilm reactors (MBBRs) from a well-operated pilot MBBR system were used to test the biochemical reaction effect caused by biofilm and the corresponding variation in ORP values.

2.2. Sensors

Temperature, pH, ORP, and TDS were measured using a multi-parameter analyzer (Lei-Ci DZS-706, Shanghai, China). DO was measured using the Hach HQ40d portable multi-parameter water quality detector with a Hach LDO 10110 fluorescence electrode (Hach, Loveland, CO, USA). Other water quality data were obtained by sampling and analyzed based on standard methods [23]. The two-point calibration method was applied for ORP sensors calibration, using the standard solution of 86 mV and 256 mV.

2.3. ORP and Water Quality Correlation Investigation Method

The purpose of the water quality analysis was to study the correlations between ORP values and other water quality variables in an anoxic environment and obtain sufficient data for analysis. Batch tests were carried out in a completed mixed reactor, and the volumetric ratios of recycled sludge/settled raw wastewater were 50, 66, 100, 200, 400, and 600% to simulate the external recycling rate of the activated sludge system. DO, pH, and ORP were continuously measured by sensors during the reaction time. Mix liquid samples from this reactor were immediately filtered through 0.45 µm filter paper and analyzed according to standard methods [23].

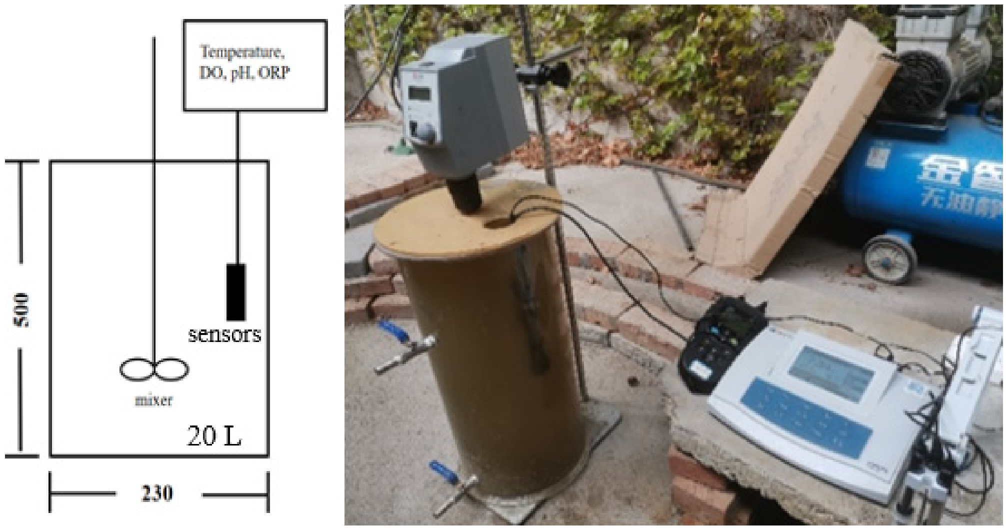

Figure 2. Schematic diagram of the experimental setup for the study of ORP correlation with water quality.

Sensor stability tests were also carried out in the same reactor to investigate the time required for the portable ORP sensor to stabilize its readings. ORP and DO sensors were applied to monitor the mixed liquid in the reactor where primary settled raw wastewater were filled. The sensor readings were recorded every 30 s.

Moreover, to investigate the potential of ORP to function as an indicating variable of the end of denitrification reaction in anoxic environment of the biological nitrogen removal process, we investigated the correlation between a low nitrate concentration 0020 (0–3 mg/L) and ORP under anoxic conditions. Biocarriers from a MBBR system were added into the reactor with a filling rate of 50% to perform the denitrification reaction. The nitrified liquid was mixed with the primary settled raw wastewater to achieve an initial nitrate concentration of approximately 3 mg/L. ORP and DO sensors were applied for data acquisition, and sodium acetate was added to provide sufficient carbon source for the denitrification. The sensor readings were recorded every 1 min, and water samples were taken into measurement of nitrate and COD with the same sampling frequency.

2.4. Statistical Methods

Two multivariate statistical methods, i.e., principal component analysis (PCA), and multiple regression, were used to analyze the experimental results in R software. The principle and implementation procedures of ANOVA were conducted according to Faraway et al. [24]. PCA was used to analyze the collinearity and correlation between different water quality variables. Previous researchers have studied how to use PCA for mathematical analysis of wastewater treatment processes [25]. The study of PCA results is mainly presented by two charts, i.e., cumulative variance and loading plot. The cumulative variance plot shows the proportion of total variance that different PCs can interpreted, while the load plot is used to observe the correlation between different variables and group them. If a small number of PCs representing the majority of variation in a large number of original variables, the original variables are considered as collinearity and can be screened to simplify the mathematical model. The relationship between ORP and multiple variables was established by applying multiple regression analysis based on the least square method. The details of the principle and applications of the least square estimation-based multiple regression was well-demonstrated in the literature [26].

3. Results and Discussion

3.1. Variation in ORP during Denitrification under Anoxic Conditions

Figure 3 shows the variation in the ORP profile and various water quality indicators during the denitrification under anoxic conditions. At the beginning of the experiment, the ORP value of the system was 42 mV. In the first 20 min of the experiment, the ORP value declined sharply, ranging from 42 mV to −160 mV. The ORP value decreased slightly and entered the plateau stage thereafter. At this stage, the ORP value changed from −168 mV to −191 mV and from 25 to 105 min. The ORP value decreased from −191 mV to −228 mV after 105 min. Obviously, an ORP breakpoint appeared, which has been studied by many researchers [27,28], and the breakpoint may affect the data logging for real-time process control significantly.

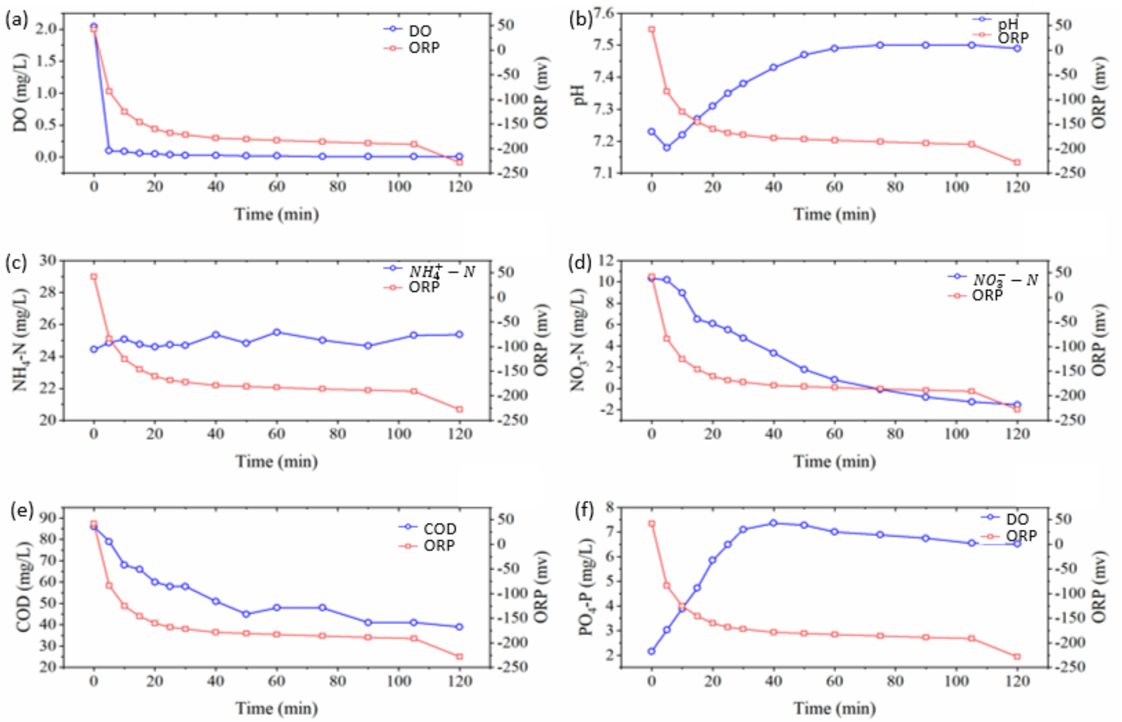

Figure 3. Variation in the ORP value together with water quality variables. (**a**) DO; (**b**) pH; (**c**) NH_4-N; (**d**) NO_3-N; (**e**) chemical oxygen demand (COD); (**f**) PO_4-P.

DO decreased to 0.1 mg/L within 5 min of the experiment and subsequently remained at a lower level of <0.1 mg/L. The mixture contained a large amount of DO at the beginning of the reaction. The initial phase of the anoxic reaction process consumed DO from the raw water, and denitrification using nitrate as the electron acceptor resulted in a sharp decline in the ORP value [29]. The ORP sensor obtained a high reading from the protective fluid and required a certain time to stabilize the reading, which also led to a deviation between the reading and the actual values. The consumption of alkalinity due to oxygen utilization led to a negligible pH decrease. Then, the system entered the hypoxic state and commenced denitrification to produce alkalinity. This led to a gradual increase in pH; the pH stabilized at 7.50 after approximately 60 min of reaction time. The NH_4-N concentration was always maintained at approximately 24 mg/L during the entire experiment and no obvious nitrification reaction occurred in the anoxic condition. Moreover, phosphorus-accumulating bacteria released phosphate, which increased the phosphate concentration of the mixed solution. The phosphate concentration increased to a peak of 7.36 mg/L at 40 min after the reaction. Then, the phosphate release basically ceased, and the phosphate concentration decreased slowly due to the simultaneous removal of phosphate along with denitrification [1].

Nitrate and COD decreased synchronously during the whole reaction process, which proved that the system had undergone an obvious denitrification reaction. The denitrification reaction was not obvious in the first 5 min of the reaction because the DO brought by raw streams inhibited the occurrence of denitrification. Denitrification happened after oxygen depletion and the nitrate and COD started decreasing simultaneously. Theoretically, denitrifying 1 g of nitrate requires 2.86 g of COD, based on stoichiometry. However, considering microbial assimilation in the process, the theoretical carbon/nitrogen ratio is approximately 3.7. In the practice of wastewater biological treatment process operation, 4 g of COD is dosed to remove 1 g of NO_3-N as the carbon source. In the lab-scale study, 12 mg/L of NO_3-N was removed and approximately 50 mg/L of COD was consumed, which was in accordance with the theoretical value. Nitrate decreased significantly after the ORP entered its plateau (Figure 3d), and the ORP value decreased significantly when the nitrification reaction ended, indicating that the respiration reaction of nitrate or oxygen in the system had finished and entered the anaerobic state [30]. This study indicated that the progress of denitrification process can be reflected by the ORP variation, and the second sharp decrease in ORP coupled with negative ORP values may perform as an indicator of nitrate exhaustion [4,31].

3.2. Correlation Analysis between ORP and Water Quality Variables

PCA was used to analyze the collinearity and correlation between water quality variables and ORP. Principal components (PCs) were selected according to the principle that the eigenvalue of PCs should be greater than 1. Figure 4a presents the scree plot showing the eigenvalue of each PC, which indicated that the first three PCs are qualified to represent the characteristics of the original data frame (ORP and water quality variables). The eigenvalue, variance, and cumulative variance contribution rates of each PC are shown in Table 1, and the factor loads of each PC are shown in Table 2. The first PC (PC1) explained 33.27% of the total variance of the data, and the first three PCs explained 77.03% of the total cumulative variance. There was strong collinearity among different water quality indices, and three PCs could be used to replace all seven original variables.

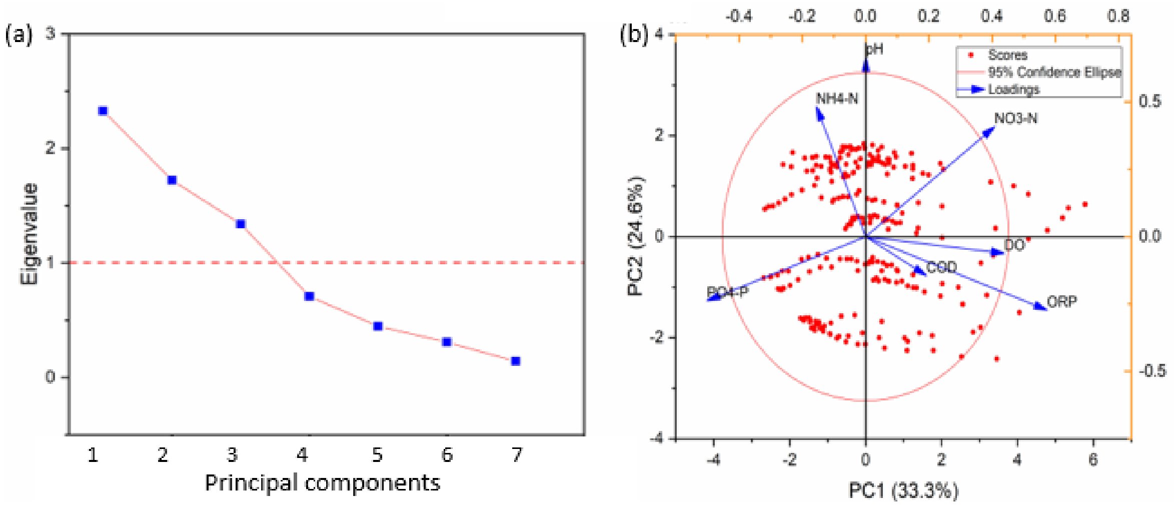

Figure 4. Principal component analysis (PCA). (**a**) Scree plot. (**b**) Biplot on the plane of principle components 1 (PC1) and 2 (PC2); the blue vector represents the loadings of each original variables and the red dots are PCA scores.

As shown in Table 2, DO, ORP, and PO_4-P had large weights on PC1, which indicated their strong correlations to PC1. PC2 explained 24.61% of the variance and mainly represented pH. NH_4-N and COD were mainly represented by PC3, which explained 19.15% of the variance.

Table 1. Eigenvalues, variances, and cumulative variances.

Principal Component	Eigenvalue	Variance Contribution Rate (%)	Cumulative Variance (%)
1	2.33	33.27	33.27
2	1.72	24.61	57.88
3	1.34	19.15	77.03

Table 2. Principal component (PC) of each variable.

Indicator	PC1	PC2	PC3
DO	0.4383	−0.06182	0.28301
ORP	0.57371	−0.27286	−0.07986
pH	8.84462×10^{-4}	0.66654	−0.20011
NH_4-N	−0.15559	0.48268	0.54411
PO_4-P	−0.50098	−0.23805	0.33222
NO_3-N	0.40813	0.40849	0.10586
COD	0.19231	−0.14471	0.67516

Figure 4b shows the loadings of at the PC1 and PC2 panels. The load vector of COD was obviously smaller than that of other original variables, which indicated that its influence on the PCA results was obviously smaller than that of other variables; therefore, the influence of COD could be ignored. At the PC1 level, PO_4-P, and NH_4-N had negative weights, whereas DO, ORP, and NO_3-N had positive weights. The weight of pH was almost zero, indicating that pH contributes merely to PC1 and the pH variation could not be explained by PC1. Regarding PC2, pH, NH_4-N, and NO_3-N had positive weights; whereas, other original variables had negative weights. DO and ORP, which were close to each other in the biplot (Figure 4b), indicating a similarity of variation and collinearity. The preliminary results of PCA showed that DO, NO_3-N, and PO_4-P are the most significant variables correlated with ORP variation.

3.3. Quantitative Correlation Analysis of ORP and Water Quality Variation

The anoxic zones of bioreactors at WWTPs are adopted to perform denitrification for nitrogen removal from wastewater. Therefore, it is of great practical significance to establish the relationship between the ORP value and nitrate for process surveillance purpose. Hence, nitrate should be included as one of the explanatory variables for the ORP quantitative model. Considering the difficulty of real-time phosphate monitoring in practice, phosphate was screened out from the list of explanatory variables. COD was neither an easy-to-measure variables nor a significant essential variable to ORP variation, COD was also excluded for ORP quantification. Thus, three original variables were selected to establish the quantitative model for ORP quantitative analysis (Equation (1)). The adjected R^2 of this fitted model was 0.7195. The overfitted model with all the water quality variables are also constructed (Equation (2)), which was slightly better in terms of or adjusted R^2 (0.7592). The fitting results showed a close relationship between the change in the ORP value and nitrate removal during denitrification. The ORP value was positively correlated with DO, nitrate, and COD, and negatively correlated with pH, phosphate, and NH_4-N. The coefficient before DO in the model implied that a small fluctuation in the DO concentration may result in a large variation in the ORP value under anoxic conditions. Although NH_4-N cannot be removed under anoxic conditions, the NH_4-N concentration had a significant effect on the ORP value fluctuation.

Equation (1) is the simplified model with easy-to-measure variables and overfitting was avoided, which make the model to be valid in most practical cases for the interpretation of ORP and water quality variation in anoxic denitrification process.

$$ORP = -63.92 + 65.57 \cdot DO + 8.93 \cdot NO_3\text{–}N - 6.20 \cdot NH_4\text{–}N \quad (1)$$

$$ORP = 297.32 + 0.22 \cdot COD + 57.89 \cdot DO + 6.07 \cdot NO_3\text{–}N - 4.70 \cdot NH_4\text{–}N - 47.71 \cdot pH - 7.53 \cdot PO_4\text{–}P \quad (2)$$

ORP online monitoring sensors are reliable in terms of accuracy, drifting, and anomality. However, the most commonly used nitrate/ammonium sensors in wastewater biological treatment system are online monitoring.

But the reliability of a nitrate online monitoring instrument can be verified theoretically according to the model; alternatively, the ORP value obtained by the ORP online monitoring instrument can be used to substitute the measurement of the nitrate concentration in the anoxic zone.

3.4. Analysis of Stability Time of ORP Sensor Reading

The ORP sensor readings locate within the range of −220 mV to 300 mV when placed the sensor in wastewater treatment processes. The correct reading of the measured data by the sensor is critical for data application. As shown in Figure 5, DO and the ORP value were recorded every 30 s by submerging the sensors in raw wastewater. The ORP sensor reading was 93 mV initially and dropped dramatically at the first 100 s, and it stabilized to a negative value after 400 s. The continuous decline in the ORP value was related to the gradual decline in the DO concentration in the reactor. The slope of the declining ORP curve changed continuously before 360 s. The purple line in Figure 5 started to collinear with ORP from the 360th second to 600th second, which indicates a first-order linear changing of ORP versus DO changing after ORP values reached minus.

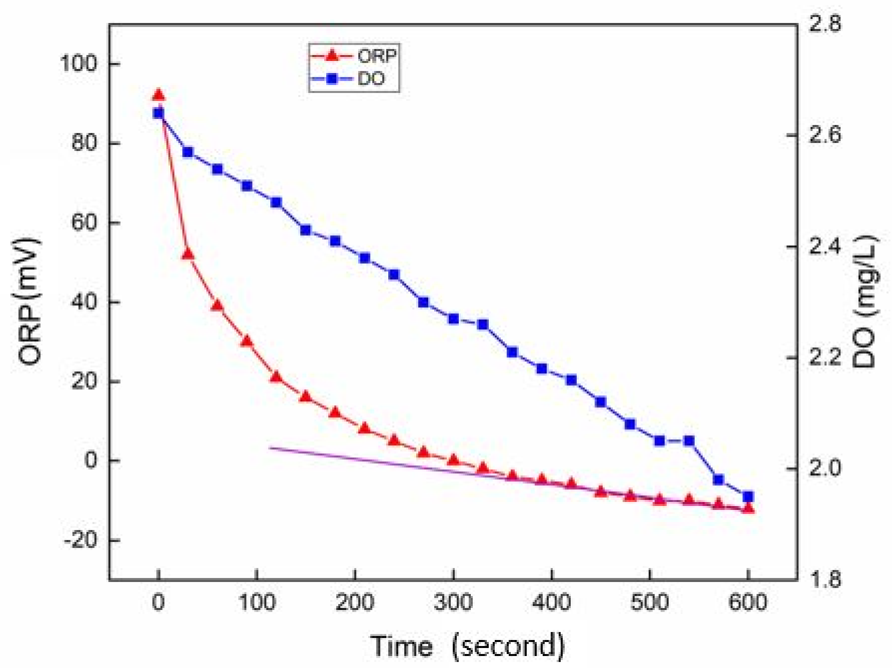

Figure 5. The DO and ORP profiles of during a test submerging the sensors into raw wastewater. The blue curve is the DO profile, and the red curve represents the ORP variation during denitrification. The purple line is the tangent to the ORP curve at 600th second.

3.5. Correlation Analysis of Low Nitrate Concentration and ORP

Figure 6 shows the variation trends of nitrate and ORP values during the denitrification process initialized with low nitrate concentration. By mixing the effluent from the primary settling tank with the recycled nitrified solution, the nitrate concentration was 2.2 mg/L at the beginning of the reaction when the corresponding ORP value was −59 mV. The nitrate concentration decreased by approximately 0.2 mg/L after 1 min of reaction. Nitrate was exhausted when the reaction continued for 13 min. In this test, the ORP breakpoint appeared and the corresponding ORP value was −138 mV. It was consistent with the ORP of previous experiments in which the ORP value decreased significantly when the nitrate concentration was depleted, proving that the ORP value can play an indicator role in the nitrate concentration depletion.

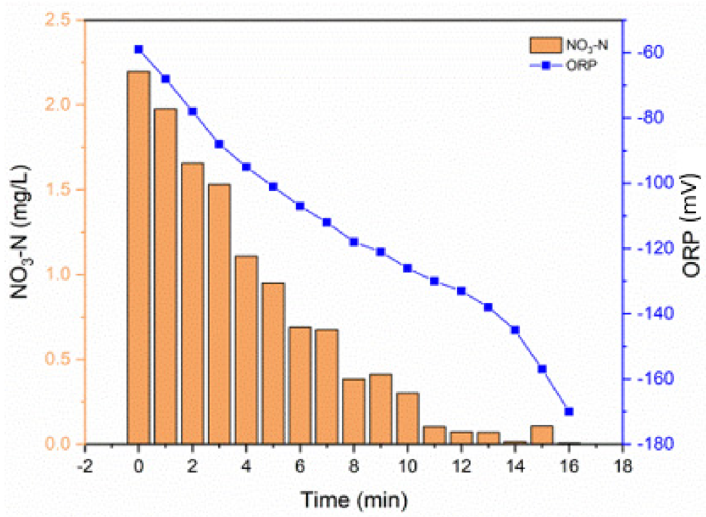

Figure 6. Variation trends of the nitrate concentration and ORP value. The histogram represents the nitrate concentration, and the blue curve represents the ORP value change.

Generally, a carbon source is dosed to the anoxic zones of the biological wastewater treatment processes to ensure the denitrification effect. If the relationship between a low nitrate concentration, COD, and the ORP value can be established, then the amount of carbon source dosage can be determined. A regression model fitted based on the denitrification with low nitrate loading was presented as Equation (3).

$$ORP = -83.3944 - 1.0221 \cdot COD + 41.4904 \cdot NO_3\text{–}N \quad (3)$$

The adjusted R^2 was 0.5737 for the model in Equation (3). The established model can be rewritten according to Equation (4):

$$NO_3\text{–}N + 5e^- + 6H^+ = \frac{1}{2}N_2 + 3H_2O \quad (4)$$

5 mol e^- is needed for denitrification to remove of 1 mol nitrate nitrogen, i.e., 2.5 mol of COD is needed to provide electrons. Therefore, the amount of carbon source required is 2.5 × 16/14 = 2.86 g COD/g nitrogen, based on COD. According to the activated sludge model, the sludge yield coefficient Y_H = 0.67, i.e., the proportion of COD assimilated by microorganisms to the total COD intake, was 67%. Therefore, the total COD demand of microorganisms with denitrification of 1 mol nitrate was 2.86/(1 − 0.67) = 8.67 g COD/g nitrogen. The nitrogen consumed by assimilation was 0.07 g nitrogen/g COD, and the nitrogen removed by microbial assimilation was 8.67 × 0.67 × 0.07 = 0.41 g nitrogen. Therefore, (1 + 0.41) g nitrogen was removed, when a total of 8.37 g COD was removed. The COD required to remove 1 g nitrogen was 8.67/(1 + 0.41) = 6.15 g COD/g nitrogen, or 1.39 g COD/g NO_3-N. The model formula was rewritten according to the above derivation as Equation (5):

$$COD = 1.4721 + 0.0177ORP. \quad (5)$$

The unit for COD is mg/L and that for ORP is mV. The relationship between COD and ORP was established, which can be applied to carbon source dosing control systems. The ORP online monitoring sensors can be used to determine the COD requirement as well as the carbon dosage.

4. Conclusions

The relationships between ORP values and various water quality variables in wastewater under different reaction environments were studied, and correlations between low nitrate concentrations and ORP under anoxic conditions were investigated. The conclusions are as follows:

(1) Under anoxic conditions, the ORP value exhibited a plateau period (during which the denitrification rate decreased significantly) and then decreased significantly at the end of the denitrification reaction. Under anoxic conditions, ORP was positively correlated with DO, nitrate, and COD, and negatively correlated with phosphate, NH_4-N, and pH;
(2) PCA showed strong collinearity among different water quality variables under anoxic conditions and that three PCs can be used to replace all the original variables. The change in the ORP value was the result of the combined influences of multiple factors. However, changes in the COD and ORP values were not significant;
(3) The ORP value correlated with NH_4-N, nitrate, and DO, and the R^2 value was 0.7195. In theory, the ORP online sensors can assist in verifying the accuracy of the nitrate online sensors or serve as its substitute;
(4) ORP sensors used for water sample measurements require a period of stability to approach the true value;
(5) Under the conditions of a low nitrate concentration (3 mg/L), a direct relationship between COD and ORP was obtained according to a series of transformations. The results can be used for process control in carbon source dosing for nitrogen removal at WWTPs.

Overall, the mechanism of ORP response to water quality variation was investigated which may provide insights for online monitoring of anoxic process using ORP sensors. The correlation models can serve as tools for COD prediction at anoxic environment and carbon dosing control for denitrification in future applications.

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