Application of face centered composite central for optimization of pangasius catfish aquaculture wastewater treatment using potassium ferrate

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Abstract. This study applied ferrate in aquaculture wastewater treatment as a multi-purpose agent for pollutants' oxidation, coagulation, and disinfection. Pangasius catfish aquaculture wastewater samples were collected from three sources and their characteristics were analyzed. Face Centered Composite Central (FCCC) design was utilized for designing the experiments with two independent factors (i.e., pH and ferrate dose) and 6 responses (i.e., effluent concentrations of COD, turbidity, PO_4^{3-}, TKN, NH_4^+, and log reduction of coliform). The effects of the two factors on the responses were evaluated and the optimum conditions for each response and also for all responses were discussed. The results showed that the wastewater with low frequencies of water renewing required treatment before discharging or recirculating. pH, ferrate dose, and their interaction affected differently on the responses. The treatment was preferred at the acidic conditions for COD, turbidity, and TKN removals, but the basic environments for coliform, NH_4^+, and phosphate removals. However, the effect of pH on the treatment depended on the ferrate dose. The optimum working condition for all responses was suggested at pH 3 and 20 mg/L of ferrate dose by which the treatment efficiencies reached 99.985 % (log reduction of 3.826), 96.8 %, 93.0 %, 85.7 %, 61.7 %, and 50.0 %, for coliform, PO_4^{3-}, turbidity, COD, NH_4^+, and TKN, respectively. These pollutants' effluent concentrations met well the allowable values for discharging while the pH value required adjustment post - treatment. A further study focusing on pH and NH_4^+ treatment is suggested for the recirculation purpose of the treated water.

Keywords: Optimization, ferrate, pangasius catfish, aquaculture wastewater, face centered composite central.

Classification numbers: 3.1.2., 3.7.3.

1. INTRODUCTION

Aquaculture takes a huge account in the world's food security and ecological balance when the world aquaculture fish production provided 44.1 % of total production from capture fisheries and aquaculture [1]. As traditional aquaculture systems cause negative impacts on water quality and secondary pollution leading to serious damage to the aquatic ecosystem, improving wastewater quality, lowering the amount of wastewater discharge to the environment, and increasing the recirculating of treated wastewater are important to sustainable aquaculture systems [2].

In general, aquaculture wastewater contains organic compounds (mostly from metabolic activities and food surpluses), chemicals (fish medicine), and pathogens. The most severe impacts of aquaculture wastewater are oxygen depletion, algae bloom, and eutrophication. Furthermore, the increase in ammonia concentration is another severe side effect. A high concentration of ammonia is considered toxic to animals and humans. It is reasonable why this type of wastewater is drawing public attention. Therefore, several technologies have been developed for aquaculture wastewater treatment, including using recirculation systems in aquaculture units, constructed wetland systems, RAFT (Rafter system), and MFBS (media-filled beds system) in coupled aquaponics systems (CAPS) [2].

As a multi-purpose agent for: (i) oxidation of both organic and inorganic pollutants, (ii) coagulation of pollutants or oxidized products and their adsorption on the flocs of $Fe(OH)_3$ as well as (iii) disinfection [3 - 5], ferrate(VI) can be utilized to handle different types of wastewater. Potassium ferrate is considered an effective disinfectant and strong oxidant that is capable of removing indicator organisms [6], bacteria [7], viruses, micro-pollutants from water [8], and eliminating organic compounds, dyes and algae, and other pollutants from potable water [9, 10]. Cao *et al.* [11] also found that potassium ferrate was no longer an oxidative toxicant after 72 h of water treatment and considered this compound as a green chemical providing excellent application prospects in the aquaculture industry with extremely low probability risk. Among studies about ferrate applications, studies on aquaculture wastewater treatment using ferrate is rarely found [12]. Although response surface methodology (RSM) has been applied for the optimization of ferrate treatment for leachate wastewater [5], tannery wastewater [13], trichloroacetic acid, and turbidity removal [14], there was no research applying RSM to optimize aquaculture wastewater treatment using ferrate. Therefore, the purpose of this study is to investigate the performance and optimization of ferrate treatment using RSM on aquaculture wastewater. Firstly, the aquaculture wastewater was collected from two ponds and one tank of Pangasius catfish. RSM based on Central Composite Design (CCD) was then used to evaluate the effect of pH and ferrate doses on the treatment efficiencies of COD, turbidity, NH_4^+, PO_4^{3-}, and total coliform. Optimum working condition was then proposed, and its validation was performed.

2. MATERIALS AND METHODS

2.1. Wastewater sampling and analysis

Table S1 of Supplementary Data provides information on selected wastewater sources and sampling conditions. Aquaculture wastewater samples were collected randomly twice from two catfish ponds in Vinh Long province (VL) and An Giang province (AG) using 30-L plastic bottles. These sources can be representative of real commercial aquaculture ponds, which practice 30 % water renewing 1 - 2 times/day to maintain sufficient water quality. Sampling

bottles were held 10 - 30 cm below surface to prevent intrusion of floating debris [15]. The bottles were closed under water to prevent air intrusion. After sampling, the bottles were stored in ice until they reached the laboratory within 8 h after collection. The third source was wastewater from a catfish tank in the laboratory at International University (IU), Ho Chi Minh City. This source can be considered as untreated aquaculture wastewater as water exchange of 30% was done every 3 days, only enough to maintain the animals. A similar procedure was applied for sampling the IU tank on five different days (hereafter referred to as S1, S2, S3, S4, and S5 in Table S1). No preservation during transportation was required since this tank was in the laboratory.

The wastewater quality parameters comprised of pH, turbidity, coliform, phosphate, ammonia, TKN, COD, and TSS. Turbidity and pH were determined in-situ by a turbidity meter (TB400, Extech, Taiwan) and the TruLab pH 1110 pH meter (YSI, USA), respectively. The measurement of coliform and TSS was started as soon as possible after the samples arrived at the laboratory which did not exceed 24 h after sample collection [16]. Total coliform was measured based on the membrane filtration technique given by ISO 9308-1:2014, using a filter (0.45 μm, Whatman, Germany) and Chromocult coliform agar (Merck, Germany). For TSS analysis, the sample was filtered through a weighted standard glass-fiber filter and the residue retained on the filter was dried to a constant weight at 103 to 105 °C. The increase in weight of the filter represented the total suspended solids (2540 D) [16].

Other parameters (phosphate, ammonia, TKN, and COD) were also measured as soon as possible after the samples arrived. If storage was required for these parameters, the preserved samples were maintained at 4°C and pH < 2 by H_2SO_4 by which the samples may be held for up to 28 days [16]. The samples were brought to room temperature before analysis. Phosphate concentration (PO_4^{3-}) was obtained using the 930 Compact IC Flex Ion Chromatograph (Metrohm AG, Switzerland). Ammonium (NH_4^+) analysis was determined with 2 processes including distillation (4500-NH3 B) with the Pro Nitro-S machine (JPSELECTA, Spain) and titration with hydrochloric acid (4500-NH3 C) [16]. TKN was analyzed following 3 procedures including digestion (Model Bloc Digest 6, JPSELECTA, Spain), distillation (4500-NH3 B) with the Pro Nitro-S machine (JPSELECTA, Spain), and titration with hydrochloric acid (4500-NH3 C) [16]. COD was measured according to the Closed Reflux method (5220) [16]. Each measurement was performed at least in duplicate.

2.2. Potassium ferrate preparation

The wet oxidation method was applied to produce solid potassium ferrate (denoted as Fe(VI)) [17]. The molecular absorption coefficient selected to calculate the concentration of ferrate was $\varepsilon = 1150$ $M^{-1}cm^{-1}$ [18, 19]. The concentration of ferrate ([Fe(VI)], in mol/L) can be determined according to Equation (1):

$$[Fe(VI)] = \frac{\Delta A}{\varepsilon \times l} \times f \tag{1}$$

where ΔA is the average absorbance measured at 510 nm; ε (= 1150 $M^{-1}cm^{-1}$) is the molecular absorption coefficient of ferrate; l (= 5 cm) is the width of the quartz cuvette and f is the dilution factor.

Total iron concentration was measured using test kits (HI93721-01 Iron HR reagent, Hanna instruments), which is based on an adaptation of the USEPA method 315B (phenanthroline method) and Standard Method 3500-Fe B [16]. The principle of this method is that 1,10-phenanthroline is used to react with the ferrous ions and form a reddish-orange complex, which

was measured spectrophotometrically by the Hana instrument (HI83399 Multiparameter Photometer, Romania). Each measurement was performed at least in duplicate.

2.3. Experimental design and data analysis

Central Composite Design (CCD) was employed to determine the effects of pH and ferrate concentration on the removal of various pollutants and find the optimum working condition [20]. Specifically, Face-centered Central Composite Design (FCCD) from Design Expert 11.0 software, in which its star points are located in the center of every surface of every factorial area leading to the value of alpha is ± 1 [21], was employed to design an experimental layout as well as analyze statistical data. The data analysis included two-way analysis of variance (ANOVA), fit statistics, regression equations, and generated contour plots (2D) [22] in which the regression model was statistically significant when its p-value was lower than 0.05. The independent variables, including pH and Fe(VI) dose, and their levels are given in Table 1. Responses were the effluent concentrations of COD (mg/L), NH_4^+-N (mg/L), TKN-N (mg/L), PO_4^{3-}-P (mg/L), turbidity (NTU), and log reduction of coliform.

Table 1. Independent variables and their levels in FCCD.

Variables	Coded symbols	Unit	Levels		
			-1	0	+1
pH	X_1	-	3	7	11
Fe(VI) dose	X_2	mg/L	1	10.5	20

The experimental layout included 21 experimental runs with one center point (replicates n = 5), 4 axial points (replicates n = 2), and 4 factorial points (replicates n = 2), as given in Table 3 (section 3.2.1). From the experimental data, the outcome of the response surface regression (Y) can be presented by a second-order response surface model shown in Equation (2) [22].

$$Y = \beta_0 + \beta_j X_j + \beta_{ij} X_i X_j + \beta_{jj} X_j^2 + \epsilon \qquad (2)$$

where Y is the predicted response, X_i and X_j are the coded independent variables, β_0 is the mean value of the response constant coefficient, β_j is the linear effect of the independent variable X_j, β_{jj} is the second-order effect of X_j, β_{ij} is the linear interaction between X_i and X_j, and ϵ is an error component.

The 21 experiments were randomly conducted following the conditions in Table 3. A jar test apparatus was employed to treat the aquaculture wastewater at different conditions of pH and ferrate doses. Firstly, six stirrers were placed in beakers containing 1 L of raw wastewater samples. The pH of these samples was then adjusted by adding 0.1 N NaOH or H_2SO_4 solutions. Next, various Fe(VI) doses were added to the beakers. The rotation speed of the stirrer was adjusted to 120 rpm for the first 1 min and 30 rpm for the next 30 min and left to stand still for the remaining 30 min. After that, pH, COD, turbidity, NH_4^+, TKN, PO_4^{3-}, and coliform concentration of the raw wastewater and the treated samples were determined. Log reduction of coliform and the output concentrations of the remaining parameters were entered into the software as the responses for data analysis. Log reduction of coliform was calculated by Equation (3).

$$\text{Log reduction} = -\log_{10}(N_t/N_0) \qquad (3)$$

where N_t is total coliform after treatment and N_0 is total coliform before treatment.

Additionally, the pollutants' removal efficiency was then calculated by Equation (4).

$$\%R = \frac{C_0 - C}{C_0} \times 100 \qquad (4)$$

where C_0 and C are the raw and treated concentrations of pollutants, respectively.

3. RESULTS AND DISCUSSION

3.1. Aquaculture wastewater characteristics

In general, aquaculture wastewater characteristics vary depending on various factors such as the type of species, their density, fish ages, feeding regime, and wastewater renewing regime. Figure 1 shows characteristics of aquaculture wastewater from Vinh Long (VL) and An Giang (AG) ponds and the IU catfish tank. The characteristics of Vinh Long and An Giang samples were combined due to their similarity conditions for commercial farming, including feeding regime and water exchange rate of 30 % volume once or twice per day. The catfishes in the IU tank were cultivated in a laboratory condition in which water exchange was limited (once every 3 days) during the experimental period to simulate aquaculture wastewater samples without treatment and find the demand for its wastewater treatment.
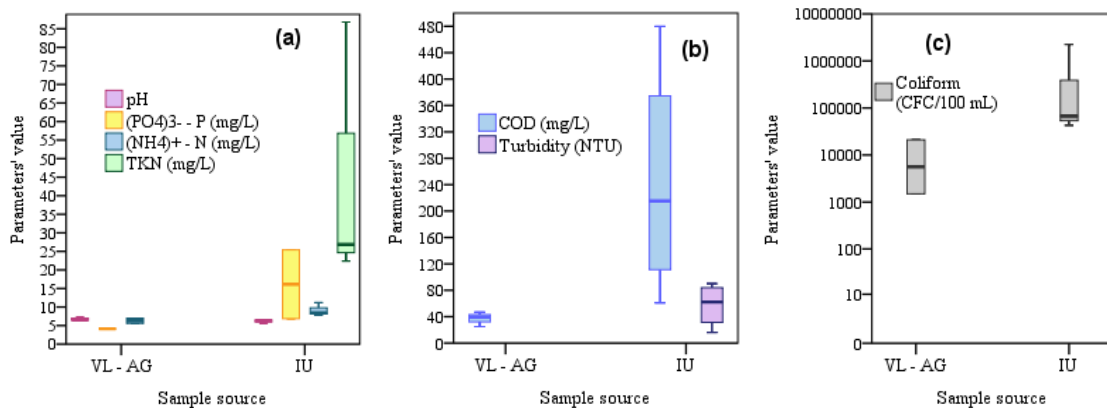

Figure 1. Characteristics of aquaculture wastewater from Vinh Long – An Giang ponds (n = 2 - 4) and IU tanks (n = 3 - 5): (a) pH, PO_4^{3-}, NH_4^+, and TKN, (b) COD and turbidity, and (c) coliform.

As can be seen from Figure 1, the ranges of pH and NH_4^+-N concentrations between VL-AG samples and IU samples were quite close while the PO_4^{3-}-P, COD, and coliform concentrations in IU samples were significantly higher than those in VL-AG samples. It is reasonable due to the difference in the water exchange regime between VL-AG and IU samples. In addition, the pH values of VL-AG and the IU samples (5.7 - 7.0) were also close to the pH from the previous studies (e.g. pH 6.3 - 7.3, [23-26]) (Table 2). Similarly, the range of ammonium concentrations from IU and VL-AG samples (i.e., 7.8 - 11.2 and 5.6 - 7.0 mg/L, respectively) were quite consistent with the ranges found by the previous studies of 0.08 - 7 mg NH_4^+-N/L [12, 23 - 25, 27]. Regarding PO_4^{3-}-P concentration, VL-AG and IU samples contained 4.15 and 25.39 mg/L, respectively, which were within the range found from other studies (i.e. 2.5 - 62 mg PO_4^{3-}-P/L, [23, 24, 26]). Similarly, COD concentrations in IU and VL-AG samples were 60.8 - 480 and 25.0 - 46.9 mg/L, respectively, which were within the range of 4 - 700 mg/L found in previous reports [23 - 27]. In contrast, the IU sample contained turbidity from 16.1 to

90.0 NTU which was lower than those found in other works (i.e., 328 and 920 mg/L, respectively [12, 26]).

With the exception of pH values meeting well the standards and turbidity not being regulated, other parameters such as PO_4^{3-}, NH_4^+, COD, and coliform concentrations in some samples from VL-AG ponds and all samples from the IU tank exceeded the allowed values given in QCVN 40:2011/BTNMT, QCVN 02-20:2014/BNNPTNT, and QCVN 08-MT:2015. This suggests the requirement of wastewater treatment before discharging or recirculating. In addition, the wastewater from the IU tank was more polluted and required thorough treatment while those from the VL and AG were at lower levels. Hence, this study focused on the treatment of wastewater from IU tanks.

Table 2. Aquaculture wastewater characteristics from various sources.

Parameter	Wastewater sources							Regulation 1*		Regulation 2**		Regulation 3***
	Fishpond farm [23]	Fish farming ponds [24]	Aquaculture wastewater [25]	Catfish pond [27]	Fish pond [26]	Fish pond [12]	IU tank (This study)	A	B	Supply	Discharge	A
pH	6.8 ± 0.03	6.29-6.96	7.3	-	6.54		5.8 – 6.5	6 – 9	5.5 – 9	7 – 9	5.5 – 9	6 – 8.5
Turbidity (NTU)	-	-	-	-	328	920	16.1 – 90.0					-
TSS (mg/L)	0.7 ± 0.15	27 - 690	100	25.6 – 11490	216		-	50	100	-	≤100	20 – 30
Nitrate (mg/L)	8.5 ± 0.06	0.36 - 1.22	110		167	8.43	-	-	-	-	-	2 – 5
Ammonia (mg/L)	0.08 ± 0.01	0.55 – 3.23	7	0.81 – 4.97	-	3.46	7.84 – 16.8	5	10	≤0.3	-	0.3
N total	-	2.08 – 24.68	-	1.7 – 10.0			-	20	40	-	-	-
Phosphate (mg/L)	2.5 ± 0.08	0.01 – 0.07	-	-	62		6.87 – 33.88	-	-	-	-	0.1 – 0.2
P total (mg/L)	-	0.26 – 3.67	-	2.9 – 14.2	-		-	4	6			-
DO (mg/L)	4.17 ± 0.08	0.86 – 7.38	-				-			≥2		≥ 6 – 5
COD (mg/L)	108.7 ± 6.66	19.25 – 104.7	240	4 – 250	700	452.04	60.8 – 480	75	150	-	≤150	10 – 15
BOD₅ (mg/L)	46.8 ± 0.88	6.98 – 49.2	-	2.2 – 198	340			30	50	-	≤50	4 – 6
Coliform (CFU/100 mL)	-	-	-	1200 – 580000	-	3.6×10⁴	42863 – 2233333	3000	5000	-	≤5000	2500 – 5000

*QCVN 40:2011/BTNMT - National technical regulation on industrial wastewater
**QCVN 02-20:2014/BNNPTNT - National technical regulation on Striped catfish (Pangasianodon hypophthalmus Sauvage, 1878) culture farm in pond - Conditions for veterinary hygiene, environmental protection and food safety
***QCVN 08-MT:2015: National technical regulation on surface water quality

3.2. Aquaculture wastewater treatment by ferrate

3.2.1. The results of experimental data

The results of the aquaculture wastewater characteristics in Section 3.1 indicated that the pollutants in the wastewater of the IU catfish tank were at higher concentrations than those from the VL and AG ponds. Hence, the wastewater from the IU catfish tank was selected for evaluating the ferrate treatment. Three wastewater samples (S1, S2, and S4) taken from the IU tank on different days (Table S1) were treated by ferrate using the experimental layout of the 21 experiments designed by the Face Centered Composite Central (FCCD). Sample S3 was not used for ferrate treatment since the amount of ferrate at the time of sampling was not enough for conducting all 21 experiments. The results of these experiments are shown in Table 3.

Accordingly, superior regression models were proposed while statistical regression coefficients including R-squared, Adjusted R-squared (Adj. R-squared), and the probability "Prob > F-value" (p-value) of the responses were evaluated to determine the accuracy of the model (Table S2). The regression equations are given in Table S3 and the suggested optimum solutions to achieve the minimum values of each response are reported in Table S4.

Table 3. FCCD design and the experimental results.

Standard order	Factor		Response							
	X1: pH	X2: Fe(IV) dose	COD out (S1)	COD out (S4)	Turbidity out (S1)	Turbidity out (S4)	Log reduction (S2)*	PO_4^{3-} out (S2)	TKN out (S2)	NH_4^+ out (S1)
	-	mg/L	mg/L	mg/L	NTU	NTU		mg/L	mg/L	mg/L
1	3	1	44.8	99.2	3.7	7.1	1.445	27.1	8.4	2.8
2	3	1	38.4	102.4	3.28	8.1		28.86	22.4	3.36
3	11	1	24	99.2	1.8	11.2	3.6068	0	19.6	3.36
4	11	1	19.2	102.4	3.84	11.6		0	22.4	3.92
5	3	20	12.8	83.2	4.69	13.35	3.3032	8.49	14	4.48
6	3	20	12.8	83.2	6.32	12.7		7.91	14	4.48
7	11	20	35.2	108.8	109	68	3.3051	0	44.8	3.36
8	11	20	38.4	112	32	71.8		0	50.4	2.24
9	3	10.5	22.4	60.8	14.9	2.2	3.1293	17.28	16.8	3.92
10	3	10.5	28.8	57.6	7.43	3.4		18.22	11.2	3.92
11	11	10.5	32	99.2	54.6	31.2	3.6068	0	30.8	4.48
12	11	10.5	32	102.4	6.98	33.7		0.99	14	3.36
13	7	1	59.2	121.6	2.96	5.8	0.4544	27.51	16.8	5.6
14	7	1	54.4	118.4	2.98	6.8		27.25	14	5.6
15	7	20	28.8	89.6	6.29	23.4	3.0044	1.99	28	4.48
16	7	20	35.2	92.8	10.4	23.9		2.08	16.8	4.48
17	7	10.5	35.2	112	10.2	15.4	2.6055	9.55	14	5.6
18	7	10.5	33.6	108.8	8.99	15.28	2.3054	9.17	19.6	3.92
19	7	10.5	32	102.4	9.79	16.3	2.4022	9.36	33.6	4.48
20	7	10.5	36.8	105.6	11.7	16.1	2.6063	8.17	14	5.04
21	7	10.5	35.2	96	9.26	16.3	2.8282	10.78	14	4.48

*Note: Coliform effluent concentrations from two replicates were averaged before entering into the Design Expert for data processing due to the fact that some concentrations were zero CFU/100 mL (i.e. coliform was totally eliminated in the effluents) and their logarithmic values were undefined.

Table S2(a) shows the fitting models and R-square (R^2) for the responses. The quadratic models of COD effluent concentrations from S1 and S4 samples owned adequate fitting levels, in which R-squared were 0.82 and 0.71, and the adj. R-squared were 0.76 and 0.62, respectively. The R-squared and adjusted R-squared of coliform log reduction were 0.85 and 0.84, respectively. While the two-factor interaction (2FI) model of the sample S1 was adequate with 0.53 of R-square and 0.45 of adjusted R-square, the quadratic model of S4 turbidity output concentration was satisfactory with 0.96 of R-square and 0.95 of adjusted R-square (Table S2(a)). The low R-square from S1 would be due to the strong fluctuations in turbidity concentration at the high pH and ferrate values. For example, working at pH 11 and 20 mgFe(VI)/L resulted in the strong variation and highest values of turbidity between two replicates (i.e., 32 and 109 NTU) for the sample S1, which was even higher than the input (16.1 NTU). It is possibly due to the excess ferrate amount added. These additional iron flocs would be easily broken, resulting in a strong variation of turbidity values. A similar trend was found for sample S4 at the same working conditions, resulting in the highest output turbidity of 68.0 - 71.8 NTU. The 2FI model also fitted well for both phosphorus and TKN effluents while ammonium effluents followed the quadratic model. R-squared and adjusted R-squared of those parameters varied from 0.55 to 0.87. As p-values from the models were less than 0.05 (Table S2(b)), the models were statistically significant for demonstrating the responses.

3.2.2. Removal of pollutants

COD removal

Figures 2(a) and 2(c) show the effect of pH and ferrate dose on the effluent COD concentrations while contour plots (2D) of the interaction effects of pH and ferrate dose are visualized in Figures 2(b) and 2(d). Even though the COD inputs of S1 and S4 samples were different, the tendencies of the effect of pH and ferrate dose on their COD outputs were similar in which COD was best removed at an acidic pH range of 3 - 4 with a sufficiently high range of ferrate dose of above 10.5 mg/L. The regression equations of COD outputs from both S1 and S4 suggest that the increase in ferrate dose and the reduction in pH value would lead to lower COD output concentrations (Table S3). It is reasonable since Fe(VI) is a powerful oxidizing agent with a reduction potential varying from +2.2 to +0.7 V in acidic and basic solutions, respectively [19]; which can oxidize organic pollutants very quickly [28] in acidic environments.
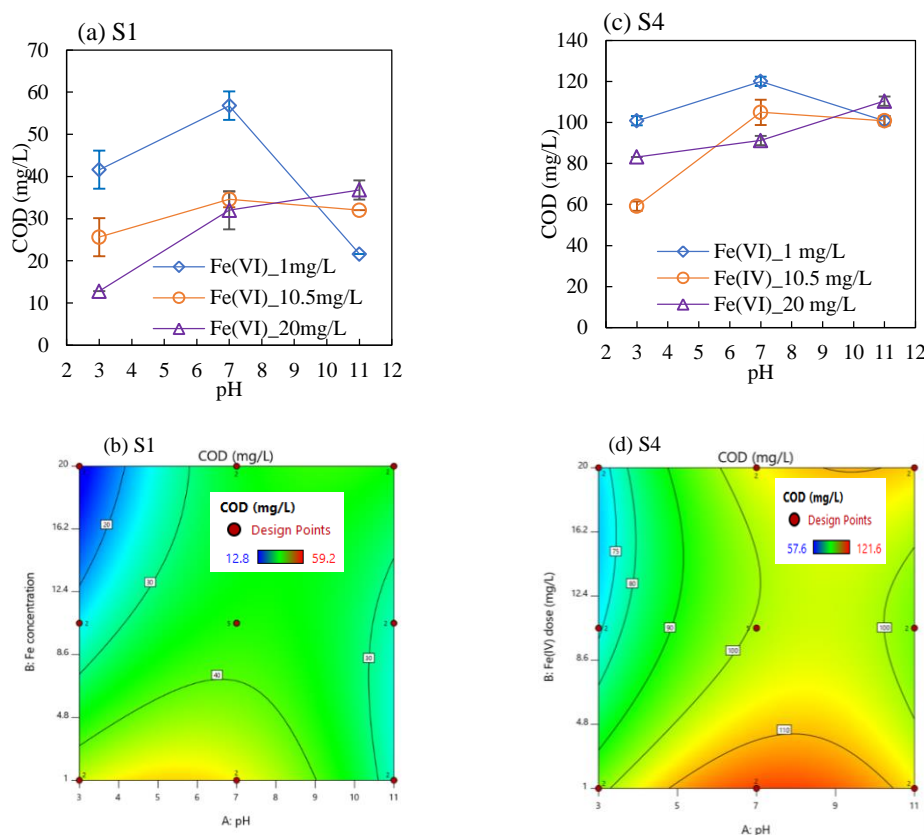

Figure 2. (a) Effect of pH and ferrate dose on COD effluent concentrations from S1 (COD_{in}: 61 mg/L) and (b) the contour plots (2D) with factors' interaction; (c) Effect of pH and ferrate dose on COD effluent concentrations from S4 (COD_{in}: 480 mg/L) and (d) the contour plots (2D) with factors' interaction.

In the case of a ferrate dose of 1 mg/L, the trend of the effect of pH was a little different because the effluent COD concentration was lowest at pH 11 (for the S1 sample, Figure 2(a)) and both pH 3 and 11 (for S4 sample, Figure 2(c)). This finding is partially similar to Wang Hongbo *et al.* [29] who claimed that COD was mainly removed through the oxidation process,

which was best at pH 10.31, while coagulation and flocculation processes would have a minor contribution. The optimization conditions suggested for the samples S1 and S4 to minimize their COD in the effluents were close, i.e., pH 3.1 and 18.9 mgFe(VI)/L, and pH 3.0 and 16.3 mgFe(VI)/L, respectively. Application of these two conditions may result in the S1 effluent COD of 12.3 mg/L and the S2 effluent COD of 70.1 mg/L, corresponding to the removal efficiencies of 79.8 and 85.4 %, respectively (Table S4). The COD removal efficiencies from this study are higher than those in some previous studies with a maximum of 55 % obtained at pH 5 and 15 mgFe(VI)/L for produced water [30], 71.3 % at pH 7.5 for polycyclic aromatic hydrocarbons (PAHs) removal from the produced water [31], and 79 % from municipal secondary effluents using 7 - 15 mgFe(VI)/L at pH 7.58 - 7.61 [32]. Also, the optimal pH value on COD reduction of this study differs from previous studies, possibly due to the influence of other pollutants existing in the wastewater on the treatment ability of ferrate for COD [31], and the water matrix [32]. Increasing the ferrate dose would be necessary to enhance COD removal efficiency in wastewater, and a large amount of ferrate can result in strong flocs formation which settled easily by gravity [33]. Therefore, determining a sufficient dose of ferrate for COD removal which depends on wastewater characteristics is necessary.

The data from the 21 experiments reported that the effluent COD concentrations were in the range of 57.6 - 121.6 mg/L. Clearly, all COD effluent concentrations were lower than those from QCVN 40:2011/BTNMT (column B) and QCVN 02-20:2014/BNNPTNT, but some effluents contained higher COD concentrations compared to the allowable value of QCVN 40:2011/BTNMT (column A). To achieve an effluent COD equal to or lower than 75, pH 3.1 - 3.4 with a ferrate dose of 10.0 - 18.6 mg/L is suggested (Figure 2(d)).

Coliform log reduction

Fe(VI) has been found to effectively inactivate bacteria and other pathogens in synthetic buffer solutions and secondary effluents [34]. In this study, coliform removal was evaluated by its log reduction. As can be seen from Figure 3(a), the log reduction reached higher values in acidic and basic environments compared to the neutral conditions and the effect level of pH depended on the ferrate dose. Clearly, the effect of pH on the log reduction at the low dose of ferrate (1 mg/L) was stronger than that at higher doses (10.5 and 20 mg/L). This result is partially consistent with the findings from Jiang *et al.* [35] in which the disinfection rate constant of ferrate(VI) was slightly affected by pH at lower doses (4 and 6 mgFe/L) but was not affected by pH at higher dose (8 mgFe/L). In addition, the effect of pH and ferrate dose on coliform removal was statistically proved by the ANOVA results in which pH, ferrate dose, and their interaction significantly affected the log reduction (Table S2(b)). Figure 3(b) visualizes that to achieve a high log reduction, an acidic working environment required a sufficiently high ferrate dose while this dose can be lower in the basic environment. According to Nguema and Jun [34], the water treatment for various natural water sources to achieve 99.9 % of total coliform removal in the pH range from acidic to neutral conditions (3.5 - 7.5) required the ferrate doses from 0.5 to 3.1 mg/L, which was lower than the ferrate dose required in this study in the acidic region. However, it is reasonable since other parameters such as NH_4^+, phosphorus, and COD in this study, which would also consume ferrate for their treatment, were significantly higher than those from Nguema and Jun [34].

The optimization conditions of pH and ferrate dose suggested that the maximum log reductions at three pH areas were gained at conditions of pH 3.0 and 19.5 mg/L, pH 7.0 and 15.6 mg/L, and pH 11.0 and 9.8 mg/L for acidic, neutral, and basic environments, respectively. These conditions would result in log reductions of 3.624, 2.681, and 3.907, respectively, and their

corresponding removal efficiencies of 99.976, 99.792, and 99.988, respectively. To reach the allowable values given in the standards, various optimum conditions can be suggested such as pH 6.8 and 9.0 mgFe(VI)/L for log reduction of 2.351 (i.e., the output of 3000 CFU/100 mL, QCVN 40:2011/BTNMT) or pH 6.8 and 7.0 mgFe(VI)/L for log reduction of 2.129 (i.e., the output of 5000 CFU/100 mL, QCVN 02-20:2014/BNNPTNT) (Table S5 and S6).
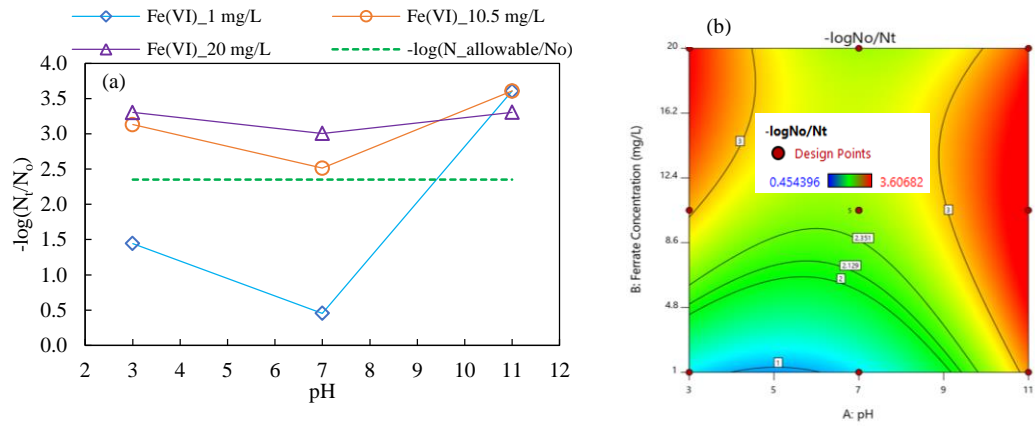

Figure 3. (a) Effect of pH and ferrate dose on log reduction of coliform from S2 (input concentration: 67333 CFU/100 mL) and the (b) contour plots (2D) with factors' interaction.

Turbidity removal

Turbidity can be removed by ferrate treatment due to the conversion of ferrate to ferric ion and ferric hydroxide, resulting in the prominence of coagulation and precipitation processes [36]. Hence, ferric ions and ferric hydroxides act as coagulants that assist colloidal particles to adhere together to form flocs and are eliminated by gravity [37]. In contrast, ferrate overdose under basic conditions was the major cause of increasing turbidity concentration because of the increase in residual iron (III) precipitation formation leading to the increase of iron flocs in water. Therefore, finding an appropriate ferrate dose is necessary.

As can be seen from Figure 4, the effects of two factors on turbidity outputs were quite similar for both samples of S1 and S4. For high ferrate doses of 10.5 and 20 mg/L, turbidity was best handled in acidic and neutral environments (pH 3 and 7, respectively). It is possibly due to the main removal mechanism of turbidity, which would be similar to the suspended solid, being coagulation and flocculation and the best in an acidic environment (pH 3.28) [29]. Nevertheless, in a basic condition (pH 11), the ability to treat turbidity by using ferrate at 10.5 and 20 mg/L was depreciated. Interestingly, the difference in turbidity from the three pH values was insignificant when the treatment was conducted at the ferrate dose of 1 mg/L, resulting in low effluent turbidity (1.8 - 3.8 NTU for S1 and 5.8 - 11.6 NTU for S4). The effect of pH and ferrate dose on the turbidity in the effluent was also proved by ANOVA results (Table S2(b)). Obviously, both pH and ferrate dose, and their interaction significantly affected the values of turbidity in the effluents. In addition, the regression equations for turbidity suggested reducing both pH and ferrate dose to minimize turbidity in the effluents (Table S3). The optimum conditions of pH and ferrate dose for S1 and S4 were quite consistent in which the ferrate required higher doses (i.e., 14.5 and 10.2 mg/L for S1 and S4, respectively) at pH ~ 3, but lower

dose (1 mg/L) at neutral and basic pH by which the corresponding turbidity removal efficiencies were from 81.8 to 98.6 % (Table S4).
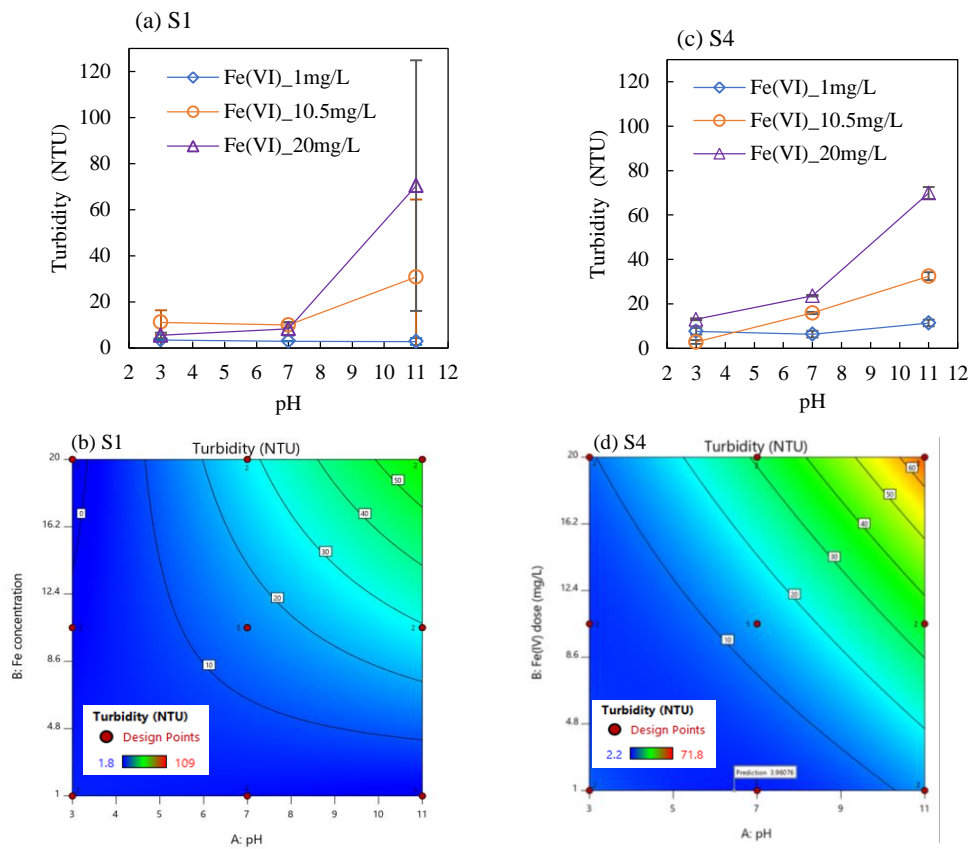

Figure 4. (a) Effect of pH and ferrate dose on turbidity output from the sample S1 (input: 16.1 NTU), (b) contour plots (2D) with interactions; (c) effect of pH and ferrate dose on turbidity output from the sample S4 (input: 90 NTU), (d) contour plots (2D) with factors' interaction.

Phosphate, TKN, and NH_4^+-N removal

We further considered the treatment efficiency of ferrate for nutrient components in aquaculture wastewater. While pH, ferrate dose, and their interaction affected phosphorus and TKN output concentrations significantly, only their interaction affected NH_4^+-N output concentration (Table S2(b)). As described in Figures 5(a) and 5(d), the increase in ferrate dose resulted in a better treatment of phosphate, and the basic condition was more favorable than acidic and neutral conditions. The high phosphate removal efficiency of ferrate is due to its ability to provide precipitation, coagulation, and flocculation [32] or adsorption mechanisms on the resultant iron hydroxide particles [38]. Compared to other parameters, phosphate was the only one able to achieve total elimination under a basic environment of pH 11 at all three ferrate doses, resulting in effluent phosphate concentrations of 0 - 0.6 mg/L. Under the neutral condition (pH 7 and 20 mgFe(VI)/L), the output concentration was 1.99 - 2.08 mg/L. Though both QCVN 40:2011/BTNMT and QCVN 02-20:2014/BNNPTNT do not regulate the phosphate concentration, their regulation for total phosphorus concentration can be used as a reference (i.e.,

4 - 6 mg/L, QCVN 40:2011/BTNMT). The results of phosphate output concentrations in this study were much lower than the allowable value given in QCVN 40:2011/BTNMT, indicating the great potential of ferrate for phosphate treatment. Optimal conditions of pH and ferrate dose for phosphate remediation at three pH conditions were proposed, including pH 10.9 and 15.8 mg Fe(VI)/L, pH 7 and 20 mgFe(VI)/L, and pH 3 and 20 mgFe(VI)/L by which the phosphate concentration would be 0.0, 2.7, and 6.7 mg/L, respectively (Table S4).
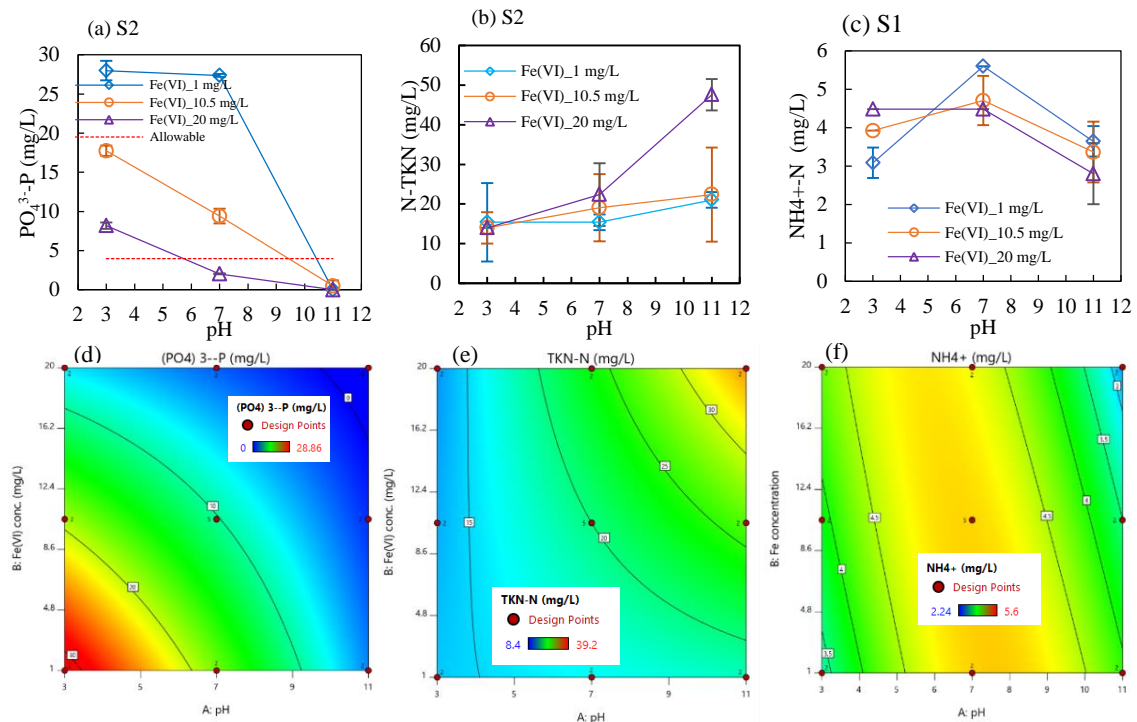

Figure 5. Effect of pH and ferrate dose on (a) PO_4^{3-}-P, (b) TKN, (c) NH_4^+-N effluent concentrations and the contour plots (2D) with factors' interactions of (d) PO_4^{3-}-P, (e) TKN, (f) NH_4^+-N effluent concentrations (PO_4^{3-}-P input from the sample S2: 25.39 mg/L, TKN input from the sample S2: 86.8 mg/L, NH_4^+-N input from the sample S1: 7.84 mg/L).

We finally considered the treatment ability of ferrate for two nitrogen species, including TKN and NH_4^+-N. The trend of pH and ferrate dose affecting TKN output concentrations was opposite to that of phosphate but quite similar to that of turbidity. As can be seen from Figures 5(b) and 5(e), the treatment seemed to be more favorable in the acidic and neutral environments than in the basic environment. In addition, increasing the ferrate dose had a negative impact on the removal efficiency. The pattern of pH and ferrate effect on NH_4^+ effluent concentrations was partially similar to those of COD and coliform (Figures 2(a), 2(c), 3(a), and 5(e)), possibly due to the three parameters' removal mechanism being contributed by the oxidation process from ferrate [39]. The treatment in either acid with a low ferrate dose or base with a high ferrate dose was better than that in a neutral environment. The ANOVA results in Table S2 further pointed out that though the main effect of either pH or ferrate dose on NH_4^+ effluent was insignificant, their interaction was significant. Compared to other parameters, ferrate treatment for NH_4^+ seemed to be less effective with the output concentration varying from 2.2 to 5.6 mg/L. As can be seen in Table S4, optimum conditions suggested for NH_4^+ removal were pH 3.5 and 1

mgFe(VI)/L or pH 11 and 20 mgFe(VI)/L by which the expected removal efficiencies were 57.29 and 64.60 %, respectively, with the output concentrations lower than the allowed value given in QCVN 40:2011/BTNMT (5 mg/L in column A) but was still higher than the recommended value for water supply in QCVN 02-20:2014/BNNPTNT (0.3 mg/L).

In summary, the findings above indicate that: (i) pH, ferrate dose, and their interaction affected complicatedly on the pollutant outputs; (ii) while the acidic condition was favorable for COD, turbidity, and TKN removal, the basic environment was the best for coliform, NH_4^+, and phosphate treatment; (iii) the level of pH effect on the pollutants' outputs varied depending on the ferrate dose since the interaction effects of pH and ferrate doses on the responses were statistically significant. In acidic conditions, high ferrate concentrations were preferred for COD and coliform removal, but low ferrate concentrations were preferred for turbidity and TKN removal. In basic conditions, the low ferrate doses were preferred for COD, coliform, and turbidity treatment, but phosphate and NH_4^+ removals were better at high ferrate doses; (iv) the aquaculture wastewater treatment by ferrate provided the best removal for phosphate, followed by coliform, turbidity, and TKN, but the moderate or low removals were found for COD and ammonia.

3.3. Optimization and validation of optimum condition

In the previous section, the optimum conditions to gain the lowest values of individual COD, turbidity, TKN, phosphate, and NH_4^+ and the highest value of log reduction were discussed. However, the fact is that all parameters generally occur in wastewater but their pollution level, and hence the level of treatment requirements are different. Though the S1, S2, and S4 samples were taken at different times and their input characteristics were also different, we added these parameters together into the software for data analysis and to find the optimum working condition for all parameters at the same time. Table 4 provides the constraints for the optimization process while the dependence of desirability on pH and ferrate doses as well as the results of suggested solutions with the desirability from 0.648 - 0.764 were reported in Figure S1 and Section 7 in Supplementary Data. The optimum conditions were suggested for acidic and basic environments, but not found for neutral environments. As adding ferrate increased the pH of the water after treatment [40], we referred to select the optimum condition at the acidic environment (pH 3 and 20 mgFe(VI)/L) so that the requirement of pH adjustment of effluents can be smaller compared to that of the optimum solutions at the basic environment. This acidic condition is also the one suggested by the software due to its highest desirability (0.764).

Sample S5 from the IU tank was collected for the validation of the selected optimum condition at pH 3 and 20 mgFe(VI)/L. The pollutants' concentrations in S5 raw wastewater and its effluents are illustrated in Figure 6. The influent concentrations of COD, turbidity, PO_4^{3-}, and TKN were within their ranges found from S1 to S4 while the S5 input concentrations of coliform and NH_4^+ were higher. The influent concentrations of COD, coliform, and NH_4^+ significantly exceeded their allowed values from QCVN 40:2011/BTNMT for discharging (column A) and the content of PO_4^{3-} was also above the reference value for total phosphorus, indicating the requirement of treatment before discharging. In comparison with the expected removal efficiencies (Table 4), the achieved removal efficiencies were significantly higher for NH_4^+ (61.7 %), coliform (99.985 %, log reduction of 3.826), turbidity (93.0 %), and PO_4^{3-} (96.8 %), slightly higher for COD (85.7 %), but lower for TKN (50.0 %). Since the samples used for the experiments in this study were actual aquaculture wastewater collected at different times from the IU tank, the variations in the input wastewater concentrations were reasonable, leading to the differences between the expected values and the values achieved from the validation test on S5

at the optimum condition. After being treated by ferrate, the COD, coliform, and PO_4^{3-} effluent concentrations were 38.5 mg/L, 333 CFU/100 mL, and 0.22 mg/L, respectively, which met the allowable values well. Similar to the result gained from the optimization experiments, the effluent concentration of NH_4^+-N (4.29 mg/L) from the validation test was also slightly lower than its allowable value regulated in QCVN 40:2011/BTNMT for discharging but was still higher than the required value for water supply in QCVN 02-20:2014/BNNPTNT. Hence, if the purpose of treatment is to recycle the treated water as the water supply for fish growth, the optimization constraints should be altered by adjusting to increase the weight or importance of NH_4^+ effluent concentration.

Table 4. Constraints for optimization, selected solution for optimization, and expected response values.

| Parameter		Constraints for optimization			Selected solution for optimization		
		Goal	*Lower Limit*	*Upper Limit*	*Optimum condition*	*Expected response value*	*Expected removal efficiency (%)*
Factors	A:pH	is in range	3	11	3		
	B:Fe(VI) conc. (mg/L)	is in range	1	20	20		
Desirability of selected optimum solution					*0.764*		
Responses	COD out (S4) (mg/L)	minimize	57.6	121.6		71.6	85.07
	NH_4^+-N out (S1) (mg/L)	minimize	2.2	5.6		4.3	45.56
	Log reduction (S2)	maximize	0.454	3.607		3.600	99.977
	Turbidity out (S4) (NTU)	minimize	2.2	71.8		9.4	89.58
	PO_4^{3-}-P out (S2) (mg/L)	minimize	0.0	28.9		6.7	73.75
	TKN out (S2) (mg/L)	minimize	8.4	50.4		11.4	86.90
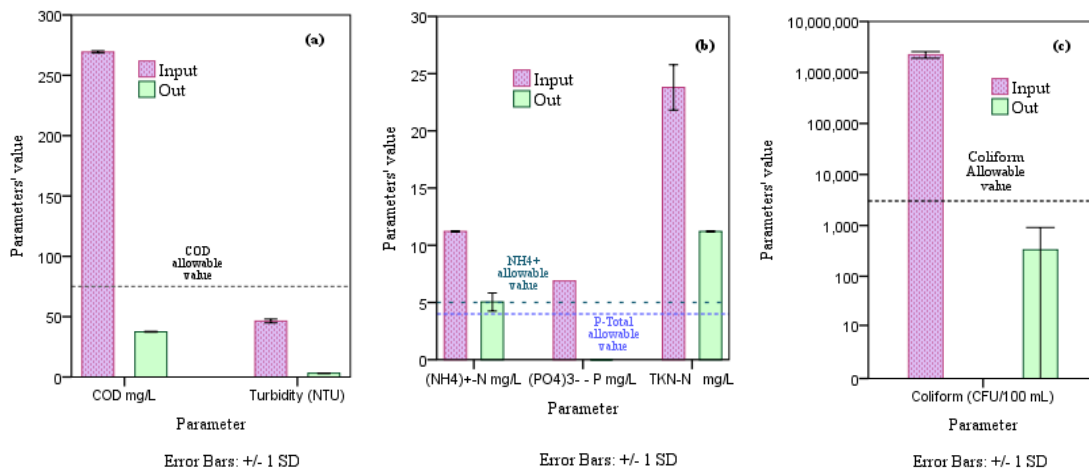
Figure 6. The results of the validation test: input and output concentrations (n = 3) of (a) COD and turbidity, (b) NH_4^+-N, PO_4^{3-}-P, TKN, (c) coliform. The allowable values for discharging in column A, QCVN 40:2011/BTNMT were presented.

Since adding ferrate would raise the iron concentration in the effluents, the ferrate and total iron concentrations in the wastewater influents and effluents were also considered. The result showed that the residual ferrate concentration after the treatment was 0.025 ± 0.002 mg/L (n = 3), indicating that residual ferrate concentration should be of no concern. The initial and residual total iron concentrations were 0.09 ± 0.01 and 1.43 ± 0.02 mg/L, respectively. Hence, this residual total iron concentration was approximately comparable to the allowable value from

QCVN 40:2011/BTNMT (1 mg/L, column A), while this parameter is not regulated in the catfish water supply in QCVN 02-20:2014/BNNPTNT. However, it was higher than the value from Khoi *et al.* [10] (0.029 mg/L) after the treatment of Saigon river water at 20 mgFe(VI)/L and pH 5, possibly due to the difference in pH values of the two studies. We further measured the pH of the sample after ferrate treatment and found a rise of pH to $3.6 - 3.8$. Despite this increase in pH, adjustment of pH after the treatment was necessary since the pH values required are from 6 to 9 for discharging, and from 7 to 9 for recirculating back to the fish tank (Table 2).

It is noted that the samples taken from three aquaculture sources in this study were limited in terms of sampling sites and frequency. Increasing the sampling frequency for various seasons with longer durations and enlarging the sampling sites in different areas would provide a comprehensive view of wastewater characteristics for both spatial and temporal variations. Additionally, since the number of samples used to test the ferrate treatment with RSM in this study was only two from either S1, S2, and S4 samples taken from the IU catfish tank, the results of optimization conditions achieved would be applicable to the aquaculture wastewater with the similar characteristics, but a trial test of ferrate treatment using RSM may be recommended for the new aquaculture sample containing very different pollutant contents. Enlarging the number of sample sites and frequency for both characteristics monitoring and testing ferrate treatment ability using RSM would be necessary for future studies to enhance the feasibility of the ferrate treatment technique for aquaculture wastewater.

4. CONCLUSIONS

In this study, the characteristics of various Pangasius catfish wastewater were first analyzed and the requirement of treatment for these wastewater sources was discussed. FCCD design was then applied to investigate ferrate treatment performance for the wastewater as well as to find optimal operation conditions of two independent variables (i.e., pH and ferrate dose) for six response variables, including the effluent concentrations of COD, turbidity, PO_4^{3-}, TKN, NH_4^+, and log reduction of coliform. The results showed that pH, ferrate dose, and their interaction had complicated effects on the pollutant outputs. While an acidic environment was best for removing COD, turbidity, and TKN, a basic environment was best for treating coliform, NH_4^+, and phosphate. The degree to which pH affected the outputs of pollutants varied depending on ferrate doses because the interaction effects of pH and ferrate doses on the responses were statistically significant. In acidic environments, high ferrate doses were preferred for COD and coliform removal, while low ferrate doses were favored for turbidity and TKN removal. In basic conditions, low ferrate doses were preferable for treating COD, coliform, and turbidity, but high ferrate doses worked better for removing phosphate and NH_4^+. In addition, phosphate was the contaminant with the best removal rate, followed by coliform, turbidity, and TKN whereas COD and ammonia had either moderate or low removal rates.

The optimum working conditions for minimizing the six pollutants were found at pH 3 and 20 mgFe(VI)/L. The results from validation test for the optimum conditions proved the potential of ferrate treatment for aquaculture wastewater in which the treatment efficiencies reached 99.985 % for coliform, 96.8 % for PO_4^3, 93.0 % for turbidity, 85.7 % for COD, 61.7 % for NH_4^+, and 50.0 % for TKN. The effluent concentrations of these parameters met the allowable values for discharging well while pH needed to be adjusted after the treatment. For recirculating the treated water for fish cultivation, a further study focusing on pH and NH_4^+ treatment was necessary. Moreover, increasing the number of sampling sites and frequency of aquaculture

wastewater sources in ferrate treatment experiments using RSM was recommended to enhance the feasibility of this technique application.

CRediT authorship contribution statement Authors Hoang Gia Phuc and Tran Tien Khoi: Ideas, Methodology, Experiment performing. Authors Dinh Kim Ngan, Dang Ngoc Quan, Tran Le Dang Khoa, Hoang Phi Hung, and Nguyen Huynh Bao Chau: Conducting experiments, Formal analysis, Culturing, Sampling. Author Nguyen Nhat Huy: Ideas, Revising manuscript, Critical review. Author Nguyen Thi Thuy: Supervision, Planning, Reviewing, Funding acquisition.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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