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Optimization of ammonia removal in an integrated fix-film activated sludge using response surface methodology

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Original Article

Abstract

In this work, removal of ammonia from synthetic wastewater using integrated fixed-film activated sludge (IFAS) process was optimized using response surface methodology (RSM). The main operating parameters such as ammonia concentration rate (ALR) and hydraulic retention time (HRT) were optimized to acquire the maximum removal efficiency. The linear, 2FI, quadratic, mean, and cubic models were utilized for modeling of the parameters. Residual nitrate and nitrite were determined as the byproducts. The results showed that the actual data fitted well with the predicted results. The maximum ammonia removal achieved using mean, linear, 2FI, quadratic, and cubic models were 59.88, 79.05, 79.32, 77.11, and 78.65%, respectively. Nitrate and nitrite were determined in ammonia concentrations of higher than 100 mg/l. The obtained results showed that RSM is a suitable technique for the optimization of conditions for the maximum removal of ammonia.

KEYWORDS: Ammonia, Wastewater, Optimization, Biofilms, Optimization

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Introduction

Nitrogen compounds such as ammonium/ammonia ions are the main pollutants in water and wastewater. Discharge of ammonia into environmental resources can lead to various health and environmental problems such as eutrophication, oxygen depletion, and toxicity.[1] Water and wastewater containing large quantities of ammonium/ammonia ions can have adverse effects on human health (metabolic diseases) and the environment (such as eutrophication and overgrowth of plants).[2] Ion exchange, electrodialysis (ED), reverse osmosis, electrocoagulation, and biological treatments are proposed for the removal of ammonia from aqueous sources.[3] Among the proposed techniques, biological processes have various advantages such as their low cost, low operation handling, reliability, and efficacy, and being environmentally friendly. Conventional biological removal of nitrogenous compounds is performed using a two-step process involving nitrification and denitrification.[4] The two-step nitrification–denitrification process using ammonia and nitrite oxidizing biomass is preformed via conversion of ammonium (NH^{4+}) to nitrate (NO^{3-}), and finally, to N_2 gas.[5-7] These two stages are illustrated as the following reactions:

$$NH_4^+ + \frac{3}{2}O_2 \xrightarrow{\text{Ammonia oxidiziers biomass}} NO_2^- + 2H^+ + H \quad (1)$$

$$No_2^- + \frac{1}{2}O_2 \xrightarrow{\text{Nitrite oxidiziers biomass}} NO_3^- + 2H^+ + H \quad (2)$$

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Denitrification pathway can be summarized by the following reactions:

$$\frac{1}{5}No_3^- + \frac{5}{6}H^+ + e^- \xrightarrow{\text{Denitifying biomass}} \frac{1}{10}N_2 + \frac{3}{5}H_2O \quad (3)$$

$$\frac{1}{3}No_2^- + \frac{4}{3}H^+ + e^- \xrightarrow{\text{Denitifying biomass}} \frac{1}{6}N_2 + \frac{2}{5}H_2O \quad (4)$$

Reactions 3 and 4, respectively, show anoxic growth on nitrate and anoxic growth on nitrite. Nitrification and denitrification are conducted simultaneously for nitrogen removal, but efficient and reliable nitrogen removal requires long solid residence time. Fixed-film processes such as integrated fixed-film activated sludge (IFAS) or moving bed biofilm reactors (MBBR) have been shown to be successful in simultaneous nitrification and denitrification.[8] The enhanced removal of chemical oxygen demand (COD) and biological nutrient (nitrogen and phosphorus) removal have been well demonstrated using IFAS.[9] Optimization of operating parameters is an important method in various fields of sciences. Presently, response surface methodology (RSM) is applied successfully in many scientific fields such as biology, chemistry, medicine, and economy.[10] RSM was proposed by Box et al. in the 1950s.[11] RSM is based on an experimental design with the final goal of evaluating optimal functioning of industrial facilities, using minimum experimental effort.[10]. The aim of the present study was to optimize ammonia concentration and hydraulic retention time (HRT) for the determination of the best conditions of ammonia removal through IFAS process. To the best our knowledge and according to the literature review, the optimization of operating factors of ammonia removal through IFAS process has not been reported.

Materials and Methods

Bench-scale experiments were conducted using a plexiglass reactor with total volume of 13 l (100 × 10 × 15 cm dimensions) (Figure 1). All chemicals used in this work were analytical reagent grade and they were used without further purification. A general medium containing 500 mg/l dextrose, 12 mg/l potassium dihydrogen phosphate, 16 mg/l dipotassium phosphate, 18 mg/l calcium chloride, and 24 mg/l magnesium sulfate was used at the start-up. The synthetic wastewater was continuously pumped to the reactor for 42 days. The HRT of the reactor was adjusted at 12 hours. The pH was adjusted normally at 7 ± 0.2. The mixed liquor suspended solids (MLSS) was adjusted at 2.5 g/l with HRT of 24 hours start-up period. All experiments were performed at room temperature (25 ± 1 °C). Ammonia, nitrite, nitrate, and COD were analyzed according to standard methods. Nitrate was determined using spectrophotometer at λmax of 220 nm. The Nitrite content was analyzed through colorimetric method and sulfanilamide and naphthylethylendiamine dihydrochloride regents at λmax of 543 nm. The determination of ammonia content was conducted through phenate method.

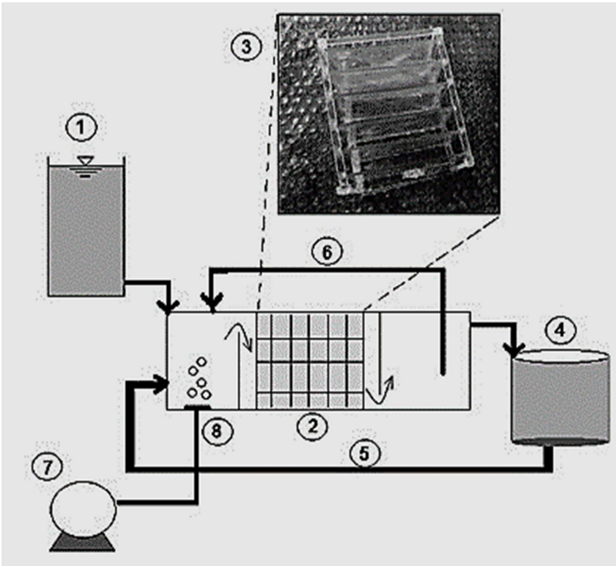

Figure 1. Schematic representation of experimental setup for integrated fixed-film activated sludge (IFAS) process [1) feed tank, 2) fixed film, 3) media, 4) sedimentation tank, 5) returne active sludge, 6) internal recirculation, 7) blower, 8) air diffuser]

RSM offers an empirical relationship between the response function and the independent variables. In this study, the coefficients of the response functions for various dependent variables were determined with the response functions using the Design-Expert regression software (trial version, Stat-Ease Inc., Minneapolis, MN, USA) regression program. The least squares technique was used to evaluate polynomial approximation. The central composite design (CCD) was used to analyze the main parameters (x_1: ammonia concentration, x_2: HRT). Wastewater was prepared with COD of 500 mg/l and different concentrations of ammonia (20, 43, 60, 88, and 100 mg-N/l). According to the primary design, HRT was adjusted in 4, 5.75, 10, 14.25, and 16 hours for -α, -1, 0, +1, +α, respectively. Based on the experimental runs, a total of 13 runs of the CCD experimental design and response are presented in table 1.

Results and Discussion

During the start-up period, ~89.5% ammonia removal was achieved at a constant ammonia load of about 32 mg-N/l and HRT of 16 hours. The percentage of COD removal was determined between 66.8 to 94.86% during 42 days since the start-up.

Based on the experimental runs, a total of 13 runs of the CCD experimental design were conducted. The coefficient of variation (CV) is the value of the reproducibility of the model and should be lower than 10%. The predicted R-squared amount was agreed with the adjusted R-squared. The difference between R-squared and adjusted R-squared values should not be more than 0.2. The analysis of variables with statistical values and constant are presented in table 2. A significant lack of fit implies that there may be some systematic variation unaccounted for in the hypothesized model.[12] Ammonia removal efficiency was predicated based on the final equation for coded and actual factors. The final first-order and second-order (polynomial) regression in terms of coded and actual factors for all applied models are represented by the following equations.

Final equations in terms of coded factors:

$$Ra_{Mean} = +66.06 \quad (5)$$

$$Ra_{Linear} = +66.06 - (2.50 \times x_1) + (13.25 \times x_2) \quad (6)$$

$$Ra_{2FI} = +66.06 - (2.50 \times x_1) + (13.25 \times x_2) + (2.28 \times x_1 \times x_2) \quad (7)$$

$$Ra_{Quadratic} = +65.79 - (2.50 \times x_1) + (13.25 \times x_2) + (2.28 \times x_1 \times x_2) - (0.32 \times x_12) + (0.76 \times x_22) \quad (8)$$

$$Ra_{Cubic} = +65.79 - (1.82 \times x_1) + (10.77 \times x_2) + (2.28 \times x_1 \times x_2) - (0.32 \times x_12) + (0.76 \times x_22) + (4.96 \times x_12 \times x_2) - (1.35 \times x_1 \times x_22) \quad (9)$$

Table 1. The central composite design (CCD) using natural and coded factors

Run	Precedence	Ammonia concentration (mg-N/L)	HRT (hour)	X1	X2
1	11	88	5.75	1	-1
2	4	60	10	0	0
3	5	60	10	0	0
4	12	88	14.25	1	1
5	13	100	10	2	0
6	10	60	16	0	2
7	6	60	10	0	0
8	7	60	4	0	-2
9	3	32	14.25	-1	1
10	8	60	10	0	0
11	9	60	10	0	0
12	2	32	5.75	-1	-1
13	1	20	10	-2	0

HRT: Hydraulic retention time; X1: Minimum level; X2: Maximum level

Table 2. Statistical analysis of models

Type	Source	df	F-Value	P-value Prob > F	Result
Mean	Model	0	-	-	-
	Lack of Fit	8	46.04	0.0011	
	R2			0	
	Adjusted R2			0	
	Predicted R2			-0.17	Significant
	Adequate Precision			-	
	SD			11.46	
	C.V. %			17.35	
Linear	Model	2	58.87	< 0.0001	Significant
	Lack of Fit	6	4.19	0.0934	
	R2			0.92	
	Adjusted R2			0.90	
	Predicted R2			0.84	Not Significant
	Adequate Precision			22.19	
	SD			3.51	
	C.V. %			5.32	
2FI	Model	3	43.04	< 0.0001	Significant
	Lack of Fit	5	4.05	0.0999	
	R2			0.93	
	Adjusted R2			0.91	
	Predicted R2			0.78	Not Significant
	Adequate Precision			19.98	
	SD			3.38	
	C.V. %			5.11	
Quadratic	Model	5	21.24	0.0004	Significant
	Lack of Fit	3	6.34	0.0532	
	R2			0.93	
	Adjusted R2			0.89	
	Predicted R2			0.62	Not Significant
	Adequate Precision			14.92	
	SD			3.73	
	C.V. %			5.65	
Cubic	Model	7	24.51	0.0014	Significant
	Lack of Fit	1	6.54	0.0628	
	R2			0.97	
	Adjusted R2			0.93	
	Predicted R2			-0.14	Not Significant
	Adequate Precision			16.12	
	SD			2.99	
	C.V. %			4.52	

Final equations in terms of actual factors: Ra_{Mean} = +66.065 (10)

Ra_{Linear} = +40.15 – (0.088 × ammonia concentration) + (3.12 × HRT) (11)

Ra_{2FI} = +51.52 – (0.28 × ammonia concentration) + (1.98 × HRT) + (0.019 × ammonia concentration × HRT) (12)

$Ra_{Quadratic}$ = + 54.06 – (0.23 × ammonia concentration) + (1.14 × HRT) + (0.019 × ammonia concentration × HRT) – (3.94 E-004 × ammonia concentration2) + (0.042 × HRT2) (13)

Ra_{Cubic}= Not available for aliased models. (14)

Predicated efficiencies were calculated using equations 4-14. It was found that the calculated values were similar to experimental removal data. According to the obtained results, a uniform removal efficiency pattern was provided for each run (Figure 2).

The adequacy of a model can be evaluated by diagnostic plots such as a normal probability plot of the studentized residuals and a plot of predicted versus actual values.[10]

Figure 3 illustrates three dimensional graphics response surface plots of the main parameters and their interactions for ammonia removal efficiency.

The mean model did not change in efficiency for different amounts of ammonia concentration and HRT (Figure 4a). However, in the other models, the ammonia efficiency increased with the increasing of HRT at lower ammonia concentrations (Figures 4b-e). To create favorable conditions for nitrification and denitrification, continuous operation and a relatively long HRT are required.[13] HRT is the main operating variable for biological stabilization. Moreover, solid retention time (SRT) is one of the major factors that contribute to different treatment performances and biomass characteristics.[13] It has been reported that complete nitrification occurred when HRT was longer than 3 hours. The total nitrogen removal rate was low at HRT of less than 3 hours due to limited partial nitrification.[14] Rostron et al. similarly reported low nitrification at HRT of less than 3 hours. In this condition, very little nitrate was produced.[15] In the numerical optimization, a minimum and a maximum level have to be provided for each parameter.[16] The level of all parameters within the range of investigation was optimized for maximum ammonia removal. Under optimal conditions, maximum ammonia removal was predicted for each model.

In the numerical optimization, a minimum and a maximum level must be provided for each parameter. For several responses, the goals are combined into an overall desirability function.[16] Desirability is defined as an objective function that ranges from zero (0.00), outside of the limits, to one (1.00), at the goal. The program seeks to maximize this function. By starting from several points in the design space, chances for finding the best local maximum improve.[17] Level of all parameters within the range of investigation was set for maximum ammonia removal. With regard to numerical optimization, at optimal conditions, the maximum ammonia removal value was predicted for each model (Table 3).

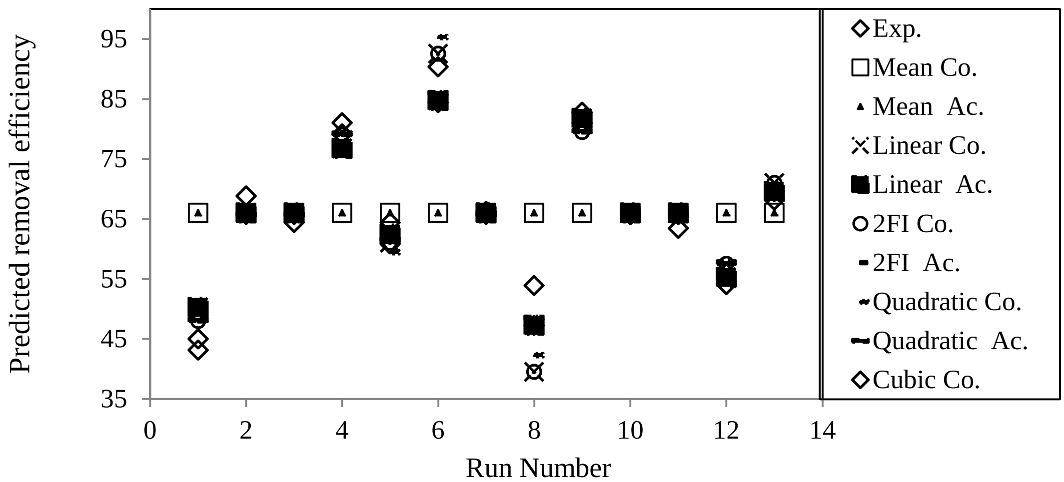

Figure 2. Ammonia removal efficiency pattern for applied models

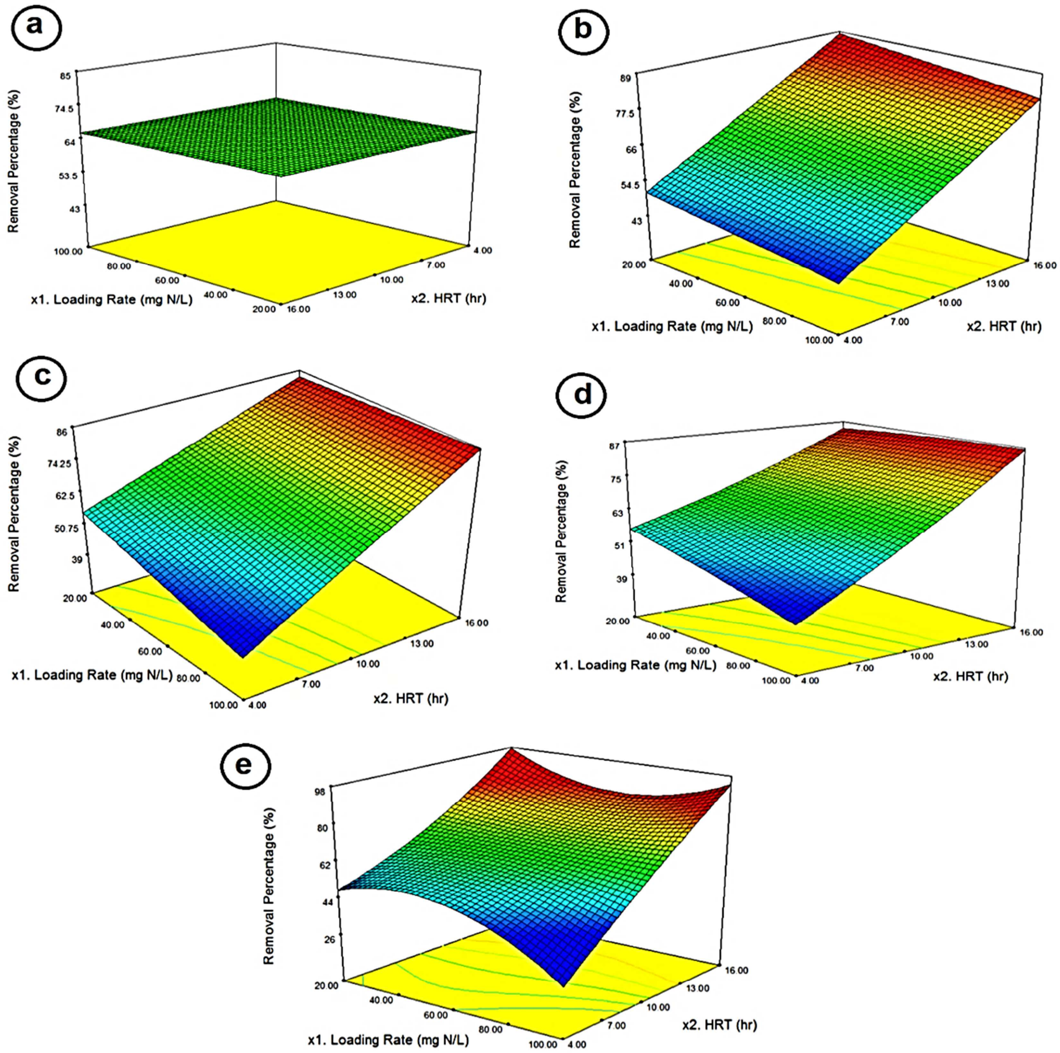

Figure 3. Ammonia byproducts from integrated fixed-film activated sludge (IFAS) process at different loading rates of ammonia

To approve the validity of the optimized points, an experiment was carried out with the parameters suggested by the model. The obtained result shows 95% similarity. The results confirmed the validity of the model, and the experimental values were determined and found to be quite close to the predicted values. Under these conditions, the experimental value for ammonia removal was found to be 59.88, 79.05, 79.32, 77.11, and 78.65% for mean, linear, 2FI, quadratic, and cubic models, respectively. The obtained results showed that an efficient nitrification potential (79.32% for 2FI model) is provided by IFAS reactor. Similar to the current study, many researchers have studied the potential of nitrification using different biosystems that can be seen in table 4.[15, 18-21]

In order to monitor ammonia conversion to N_2 gas and nitrate, residual nitrate/nitrite (sum of NO_2^- and NO_3^-) was determined for high ammonia concentrations (20-100 mg-N/l) and HRT of 14.25 hours. High amounts of byproducts were seen at 100 mg-N/l of ammonia (Figure 3). At this ammonia concentration, nitrate and nitrite values were

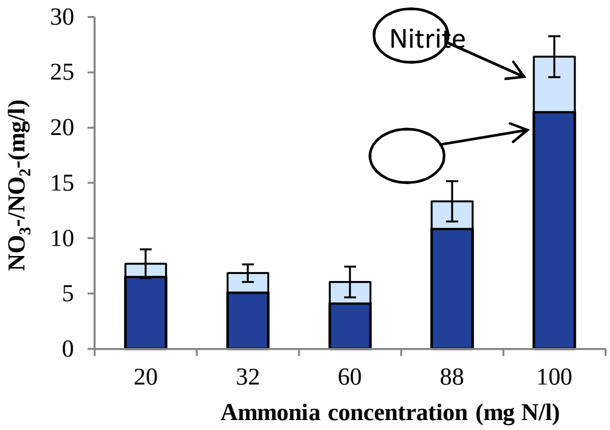

Figure 4. Three-dimensional graphics of response surface for ammonia removal efficiency in (a) mean, (b) linear, (c) 2FI, (d) quadratic, and (e) cubic models

determined at ~26.42 mg/l. In most wastewater treatment plants, nitration is presented by nitrogen oxidizing bacteria such as the genus Nitrospira and Nitrobacter.[7] From the results it can be seen that a long HRT is required to treat the higher ammonium concentrations. This can occur due to the very slow growth of autotrophic nitrifiers. In the case of Nitrobacter sp. (as a dominant species of nitrite oxidizing bacteria), generation times have been reported at about 18 and 69 hours, and this can provide a low cell yield.[2] On the other hand, during short HRTs, a small amount of ammonia is converted to nitrite and other intermediates, which implies that the denitrifying bacteria has limited access to electron sources.[2]

Conclusion

The results of this study showed that maximum ammonia removal was acquired at 59.88, 79.05, 79.32, 77.11, and 78.65% in the mean, linear, 2FI, quadratic, and cubic models, respectively. High correlation coefficient (r^2) was observed for linear (0.92), 2FI (0.93), quadratic (0.93), and cubic models (0.97). Therefore, the actual data fitted well with the predicted results. A higher amount of ammonia byproducts were observed at 100 mg-N/l of ammonia. At this ammonia concentration, total concentrations of nitrate/nitrite were determined at about 26.42 mg/l.

Conflict of Interests

Authors have no conflict of interests.

Table 3. Numerical optimal conditions and maximum predicted removal

Model	Ammonia concentration (mg-N/l)	HRT (h)	Removal Efficiency (%)	Desirability
Mean	60	8.06	66.06	0.55
Linear	32	14.25	81.81	0.93
2FI	32	14.25	79.53	0.88
Quadratic	50	14.25	79.84	0.89
Cubic	32	14.25	82.86	0.96

HRT: Hydraulic retention time

Table 4. Literature review

Wastewater type	Reactor	Nitrification rate (%)	References
Synthetic feed	IFAS	79.32 for 2FI% model	Current study
Synthetic feed	Linpor and Kaldnes	35-40%	Rostron et al.[15]
Refinery wastewater	Activated sludge	over 90%	Fang et al.[18]
Synthetic feed	Activated sludge	nearly 100%	Campos et al.[19]
Synthetic feed	Activated sludge	98%	Ruiz et al.[21]
Domestic wastewater	IFAS	over 87%	Regmi et al.[20]

IFAS: Integrated fixed- film activated sludge

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