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The effects of operating factors on the removal of total ammonia nitrogen and florfenicol antibiotic from synthetic trout fish farm wastewater through nanofiltration

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ABSTRACT

An aquaculture system can be a potentially significant source of antibacterial compounds and ammonia in an aquatic environment. In this study, the removal of total ammonia nitrogen and florfenicol antibiotic from synthetic aqueous wastewater was assessed by applying a commercial TFC (thin film composite) polyamide nanofilter. The effects of pH (6.5-8.5), pressure (4-10 bar), concentration of total ammonia nitrogen (1-9 mg/L), and florfenicol (0.2-5 mg/L) on the removal efficiency of the nanofilter were studied at a constant 70% recovery rate. It was found that by increasing the pH within the range of 6.5 to 8.5, it enhanced the removal efficiency by up to 98% and 100% for total ammonia nitrogen and florfenicol, respectively. With an increase in pressure from 4 to 7 bar, the removal percentage increased and then, it decreased from 7 to 10 bar. The interactions factors did not have significant effects on the both pollutants removal efficiencies. To obtain optimal removal efficiencies, an experimental design and statistical analysis via the response surface method were adopted.

1. Introduction

Freshwater fish production may environmentally impact surface waters because of organic carbon pollution and eutrophication [1, 2]. The introduction of foreign species, parasites, and pathogens [3, 4] as well as harmful chemicals including antibiotics and pesticides [5, 6] also pollute the environment. According to an FAO report [7], the aquaculture total fish production by weight has consistently grown from 13.4% in 1990 to 25.7% in 2000 and to 42.2% in 2012. Recently, antibiotic residue in the aquatic environment is of major concern due to their large-scale use and long-term adverse effects [8]. Antibiotics lose their efficiency over time because of increased resistance among bacterial pathogens [9]. In 2010, florfenicol (Flo) was the most important antibiotic employed in the aquaculture (52%) followed by oxytetracycline, flumequine, and oxolinic acid (44%, 1% and 1%, respectively) [10]. Flo (2, 2- dichloro-N- [(1 R, 2 S) - 3- fluoro- 1- hydroxy- 1- (4-methylsulfonylphenyl) propan- 2- yl] acetamide; $C_{12}H_{14}Cl_2FNO_4S$;CAS No: 73231-34-2) is a fluorinated synthetic analog of thiamphenicol that belongs to the amphenicol [11, 12] class of antibiotics. In addition to pharmaceutical compositions, total ammonia nitrogen (TAN), nitrite, and nitrate are other major pollutants in aquaculture wastewater [13, 14]. Among these, ammonia is a toxic waste that is produced by fish through their gills and feces. These are all byproducts from metabolizing protein. An increase in feeding times enhances the production of ammonia. Likewise, the bacterial decomposition of organic waste solids such as uneaten feed and dead algae leads to the production of ammonia [15, 16]. There are various techniques for the treatment of fish farming wastewater including ion exchange, membrane and adsorption process [14, 17]. Biological systems such as membrane bioreactors [18] and sand biofilters [19] have also been used. Biological

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systems are impaired in situations with high loads of antibiotics. Antibiotics are also expected to inhibit the nitrification process [20, 21]. Recently, researchers are paying more attention to chemical oxidation processes. Their results showed that the UV/H_2O_2 process may not be an effective disinfection process which can limit or minimize the potential spread of antibiotic resistance under realistic conditions at a high flow rate and low concentrations of contaminants [22]. One of the most effective treatment methods for wastewaters containing ammonia and Flo antibiotic is membrane nanofiltration (NF). Simultaneous removal of bacteria and contaminants, ease of operation, low energy consumption, and the ability to operate at high rate applications are among the advantages of employing NF [23]. The NF permeate can be consumed in households, industrial processes or as irrigation water. The NF concentrate could be discharged to surface waters or landfills, while it has serious environmental impacts and remains the bottle neck of this application. The contaminants in the NF concentrate can be eliminated using such methods such as the advanced oxidation process and electrochemical technology [14, 24]. Particles, molecules and ions could be rejected due to the charge and size differences in the nanofiltration process [25]. The ion charge rejection depends on the membrane charge, ion valence and ionic force. Ionic force and ion valence influence the membrane charge density and the isoelectric point. The membrane charge is negative above the isoelectric point and positive below it [26]. Thus, charge exclusion or separation is mainly related to the charge differences of the species to be separated (Donnan effect). The removal efficiency of these compounds depends on the type and characteristics of the membrane [27] and operating factors like pH and pressure [27, 28]. The aim of this study was to assess the effects of pressure, pH, and the initial concentrations of Flo and TAN on the removal efficiencies for these two pollutants lo from synthetic trout fish farming wastewater samples by applying a nanofiltration technique.

2. Materials and methods

2.1. Materials

The NH_4Cl (CAS No. 12125-02-9), HCl (%37, CAS No.7647-01-0) and NaOH (CAS No. 1310-73-2) were purchased from Merck (Germany) and the commercial Flo antibiotic (pure powder, CAS No. 333-41-5) was supplied by Iranian science laboratories.

2.2. Experimental set-up

A schematic diagram of the system is shown in Figure 1. All experiments were performed in a continuous manner. The feed and concentrated vessels were made of polyethylene (LLDPE) with a capacity of 100 liters per vessel. Two diaphragm pumps (Soft Water, Taiwan) were applied. The pump flow was set at 1.6 L/min with the output pressure of 8.5 bar. A commercial NF membrane (spiral wound polyamide membrane, TFC, Korea) was placed in the NF module. The NF membrane specifications were of a fine film composite for operation at a pH range of 2 to 11 with a maximum tolerable pressure of 20 bar. The membrane specifications are shown in Table 1.

Table 1. Commercial polyamide TFC membrane features

Provider	**TFC company of Korea**
Material	Polyamide
Maximum tolerable pressure	20
pH range (bar)	2-11
Isoelectric point	4.5
Active surface (m^2)	0.35
Surface electrical charge	Negative
MWCO (da)	300

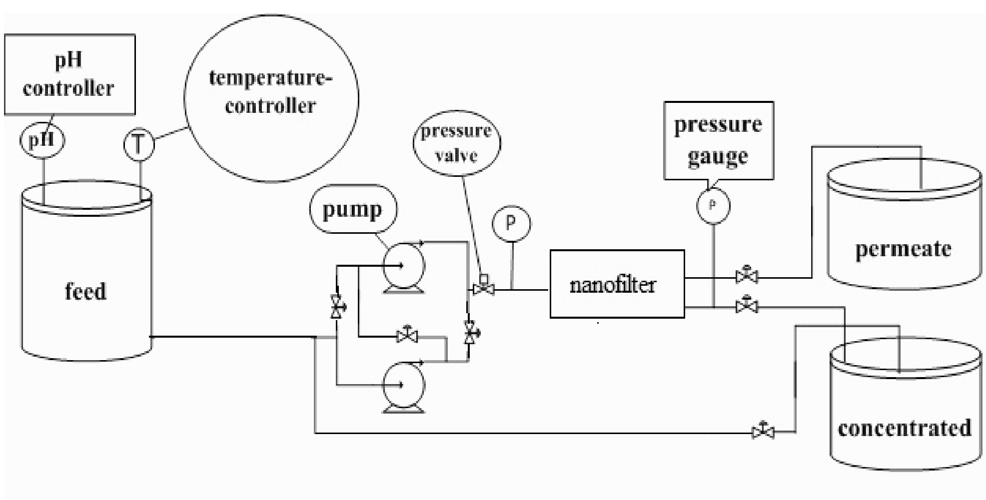

Fig. 1. Schematic set-up of nanofiltration system.

2.3. Experimental procedure

The stock solutions containing 1000 mg/L of Flo and TAN were prepared in distilled water and suitably diluted to give 0.2, 2.6 and 5 mg/L solutions of Flo and 1, 5 and 9 mg/L solutions of TAN. The solution pH was adjusted by NaOH (0.1 M) and HCl (0.1 M) and measured by a pH meter (827 pH Lab Metrohm). The experiments were conducted at a constant temperature of 15 ± 1°C with a recovery rate of 70±5%. The factors levels were selected based on their real ranges in Iranian trout fish farms and firsthand experience. The measurements were carried out according to water and wastewater standard procedures. The residual TAN concentrations were evaluated by measuring the solutions absorbance at a 410 nm wavelength based on the Nessler method [29] by applying a JASCO V-570 spectrophotometer. The Flo had a peak of absorbance of around 226 nm [30]. The NF contaminant removal percentage was calculated through the following equation:

$$\mathrm{R}(\%) = [1 - (\mathrm{C_P}/\mathrm{C_O}) \times 100] \tag{1}$$

where, R denotes the removal percentage, and $\boldsymbol{C_p}$ and $\boldsymbol{C_0}$ represent contaminant concentrations in the permeate and feed water, respectively [31].

2.4. Response surface methodology

The response surface methodology (RSM) is a productive method used to optimize the response. The Box-Behnken statistical design was used to analyze and optimize the responses [32]. This design included three trihedral factors with 15 tests to be run. The experiments were performed on a random basis. The confidence level (C.L) of 95% was considered to prevent possible errors due to systematic bias. The factors and their selected levels are tabulated in Table 2. This design included three level factors and three times implementation of the experiments in the central surface in order to obtain the experimental error. A second order polynomial is presented by the design method to fit the experimental data as [32]:

$$\mathrm{Y} = \mathrm{A_0} + \mathrm{A_1X_1} + \mathrm{A_2X_2} + \mathrm{A_3X_3} + \mathrm{A_{12}X_1X_2} + \mathrm{A_{13}X_1X_3} + \mathrm{A_{23}X_2X_3} + \mathrm{A_{11}X_1^2} + \mathrm{A_{22}X_2^2} + \mathrm{A_{33}X_3^2} \tag{2}$$

where, Y is the removal percentage response and X_1, X_2, X_3 represent the coded levels of the independent variables. The coefficients A_0, A_i, A_{ij} (i,j=1,2,3) were determined by best fitting the experimental results. The contour plots and the analysis of variance (ANOVA) evaluation were used to analyze the results. The contour plots and the analysis of variance (ANOVA) evaluation were used to analyze the results.

Table 2. Factors and selected levels

Factors	Level 1	Level 2	Level 3
Flo concentration (ppm)	0.2	2.6	5
TAN concentration (ppm)	1	5	9
pH	6.5	7.5	08.5
P (bar)	4	7	10

3. Results and discussion

The experimental design data and the results for the Flo and TAN removal are presented in Tables 3 and 4.

3.1. Analysis of experimental data

The analysis of variance are shown in Tables 5 and 6. A factor was significant when its effect on response was important and could not be neglected. The effect of any factor was considered significant when its *P*-value was less than 0.05, which meant that there was only a 5% probability for error to consider a non-significant factor as significant. The greater *F*-value showed a greater effect for the factor on the response. The Flo and TAN concentrations factors (A), pH of the solution (B), and pressure (C) followed in rank order of importance on the Flo and TAN removal from the synthetic wastewater. In addition, there were no interactions effects among the mentioned factors. The mathematical model based on actual values for Flo and TAN removal percentages are expressed through Eqs. 3 and 4, respectively.

$$\mathrm{R_1}(\%) = 58.194 - 2.3437 \times \mathrm{A} + 5.106 \times \mathrm{B} + 3.999 \times \mathrm{C} + 0.081 \times \mathrm{A} \times \mathrm{B} + 0.0069 \times \mathrm{A} \times \mathrm{C} - 0.1125 \times \mathrm{B} \times \mathrm{C} - 0.0427 \times \mathrm{A}^2 - 0.2187 \times \mathrm{B}^2 - 0.2065 \times \mathrm{C}^2 \tag{3}$$

$$\mathrm{R_2}(\%) = 148.709 - 3.598 \times \mathrm{A} - 17.715 \times \mathrm{B} - 1.462 \times \mathrm{C} + 0.081 \times \mathrm{A} \times \mathrm{B} - 0.154 \times \mathrm{A} \times \mathrm{C} + 1.058 \times \mathrm{B} \times \mathrm{C} + 0.286 \times \mathrm{A}^2 + 1.108 \times \mathrm{B}^2 - 0.535 \times \mathrm{C}^2 \tag{4}$$

where, R_1 and R_2 denote the Flo and TAN removal percentages, respectively. The regression parameter R^2 was used to determine the comparison agreement of the experimental responses to that estimated by the Box-Behnken method. For the Flo and TAN rejection, the R^2 statistic parameter was equal to 92.8.6% and 95.10%, respectively. Because of its proximity to unity, the proposed models are acceptable and accurate.

Table 3. Box-Behnken method results for Flo

Experiment No.	Flo concentration (ppm)	pH (±0.1)	P (±0.5) (bar)	Flo removal (%)
1	2.6±0.08	7.5	7	97.3
2	5±0.2	7.5	4	96.04
3	2.6±0.08	8.5	4	95.39
4	5±0.2	7.5	10	97.15
5	2.6±0.08	8.5	10	97.09
6	0.2±0.01	8.5	7	97.71
7	2.6±0.08	6.5	4	93.22
8	2.6±0.08	7.5	7	97.69
9	2.6±0.08	6.5	10	96.27
10	0.2±0.01	7.5	10	94.79
11	0.2±0.01	6.5	7	94.6
12	2.6±0.08	7.5	7	97.72
13	5±0.2	6.5	7	96.11
14	0.2±0.01	7.5	4	93.88
15	5±0.2	8.5	7	100

Table 4 Box-Behnken method results for TAN

Experiment No.	TAN concentration (ppm)	pH (± 0.1)	P (± 0.5) (bar)	TAN removal (%)
1	5±0.1	6.5	10	62.29
2	9±0.3	7.5	10	71.79
3	1±0.05	6.5	7	89.29
4	9±0.3	8.5	7	90.99
5	5±0.1	7.5	7	82.79
6	1±0.05	7.5	4	92.29
7	9±0.3	6.5	7	80.89
8	5±0.1	8.5	4	92.19
9	5±0.1	6.5	4	81.09
10	9±0.3	7.5	4	84.49
11	1±0.05	7.5	10	86.99
12	5±0.1	7.5	7	86.29
13	1±0.05	8.5	7	98.09
14	5±0.1	7.5	7	83.29
15	5±0.1	8.5	10	86.09

Table 5. Analysis of variance for Flo removal efficiency

Model terms	Mean square error	Degree of freedom	Sum of the error squares	*F*-value	*P*-value	Status
Model	40.29	9	4.48	7.18	0.0214	significant
A:Flo concentration (ppm)	8.65	1	8.65	13.88	0.0136	significant
B: pH	12.48	1	12.48	20.02	0.0066	significant
C: P	5.73	1	5.73	9.19	0.029	significant
B×A	0.15	1	0.15	0.24	0.6422	not significant
C×A	1.00E-02	1	1.00E-02	0.016	0.9041	not significant
C × B	0.46	1	0.46	0.73	0.4316	not significant
A ×A	0.22	1	0.22	0.36	0.575	not significant
B× B	0.18	1	0.18	0.28	0.6172	not significant
C × C	12.76	1	12.76	20.47	0.0063	not significant
Lack of fit	3.01	3	1.00	18.25	0.0524	not significant
Pure Error	0.11	2	0.055			

Table 6. Analysis of variance for TAN removal efficiency

Model terms	Mean square error	Degree of freedom	Sum of the error squares	*F*-value	*P*-value	Status
Model	1013.11	9	112.57	10.79	0.0087	significant
A:TAN concentration (ppm)	185.28	1	185.28	17.76	0.0084	significant
B: pH	361.8	1	361.8	34.69	0.002	significant
C: P	230.05	1	230.05	22.06	0.0054	significant
B×A	0.42	1	0.42	0.041	0.8484	not significant
C×A	13.69	1	13.69	1.31	0.3038	not significant
C × B	40.32	1	40.32	3.87	0.1064	not significant
A ×A	77.56	1	77.56	7.44	0.0414	not significant
B× B	4.54	1	4.54	0.43	0.5388	not significant
C × C	85.66	1	85.66	8.21	0.0352	significant
Lack of fit	44.98	3	14.99	4.18	0.1989	not significant
Pure Error	7.17	2	3.58			

3.2. Effect of contaminants concentrations

Based on the results, the removal efficiency of Flo increased at higher Flo concentrations. This indicated that the pores of the membrane were able to pass a certain amount of molecules due to their capacity [33]. As the number of antibiotic molecules per unit volume increased, passing through the pores of membrane became more difficult. Therefore, increasing Flo concentration enhanced the removal efficiency which is illustrated in Figures 2(a) and 2(b). These results confirm the findings of other researchers [34]. The effect of TAN concentration on the removal efficiency are shown in Figures 3(a) and 3(b). With an increase of TAN concentration from 1 to 9 mg/L, its removal efficiency decreased. This effect can be explained by the fact that an increase in NH_4^+ concentration led to a higher ionic force, followed by a decrease in the surface charge of the membrane. This behavior was in accordance

with the Donnan exclusion theory and has also been deduced by other researchers [35, 36]. Another mechanism that could be inferred was the formation of a positively charged surface layer by adsorption of the NH_4^+ ions on the active layer of the membrane. Those charged functional groups attracted ions of the opposite charge which controlled the repulsion of other ammonium ions [37, 38].

3.3. Effect of pH

According to the obtained results, with the enhancement of pH, the membrane water wettability increased and the thin polyamide layer swelled and its pores started to shrink. Also by increasing the pH, the hydroxyl group in antibiotic molecules structure was deionized which led to an increase in the electrical repulsive between the membrane surface and antibiotic molecules. However, it was reported that the membrane water wettability mechanisms did not have a significant effect on the removal efficiency [33]. As presented in Figures 2(a) and 2(c), with an increase in pH, the removal efficiency of Flo increased. The results showed that by increasing pH from 6.5 to 8.5, the Flo removal efficiency was enhanced from 94 to 99%, respectively. The isoelectric point of the NF membrane was 4.5. Therefore, as long as the pH value was greater than 4.5, the membrane was negatively charged; this was followed by an increase in the adsorption of the ammonia cation as well as enhanced TAN removal efficiency. With increasing pH, the TAN removal efficiency improved from 81.06 to 97.03 % as demonstrated in Figure 3(a). These results are in agreement with the other researchers' findings [23, 37, 39, 40]. The experiments showed that an appropriate operating pH for the removal of Flo and TAN was observed at 8.5. Among the influenced factors, the pH effect was more significant on the removal efficiencies of TAN and Flowith *P*-values of 0.0020 and 0.0066, respectively. In other words, increasing pH had a greater influence on the removal efficiency.

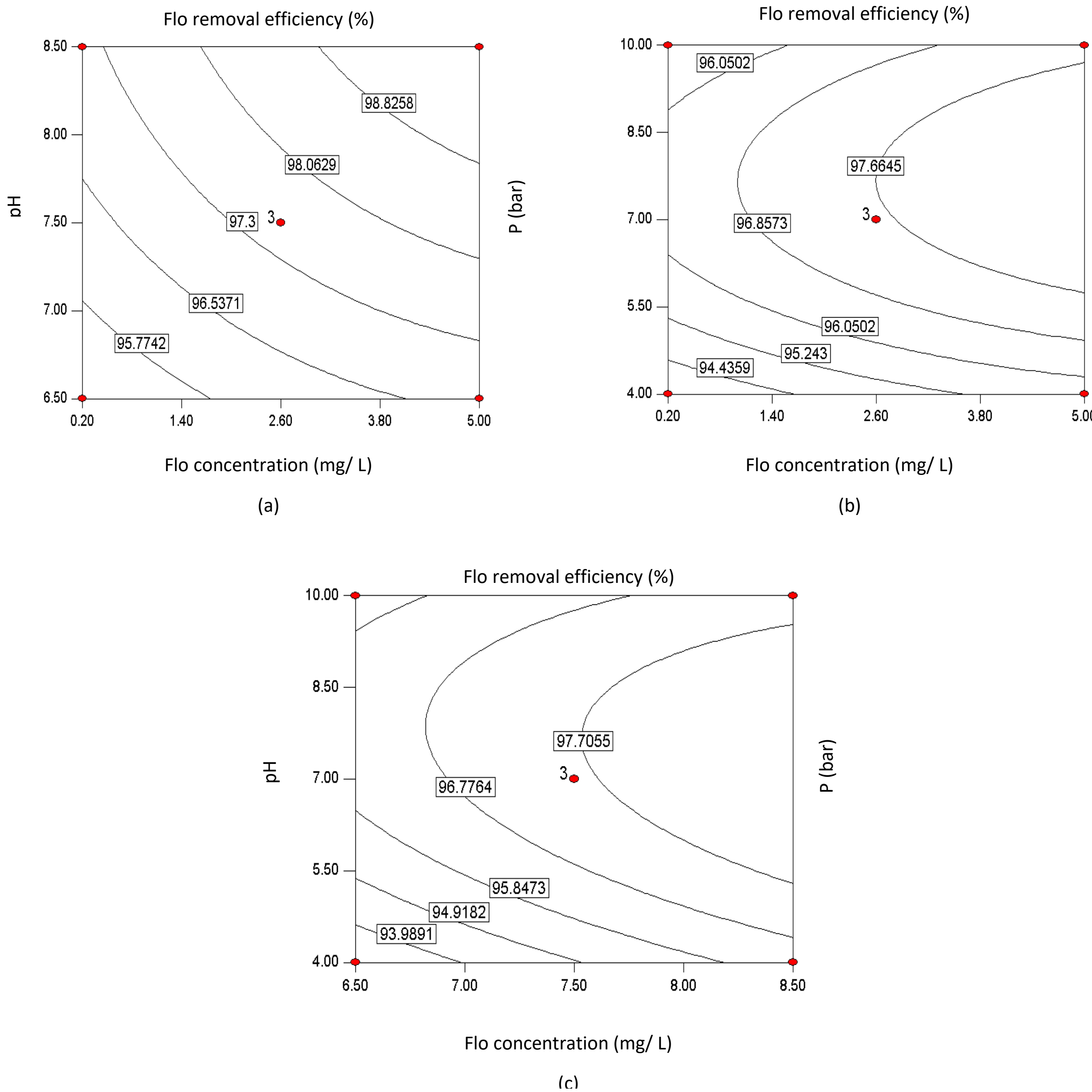

Fig. 2. Contour plots of the Flo removal efficiency; (a): the effect of concentrations and pH on the removal efficiency of Flo at a constant pressure. (b): the effect of pressure and concentration on the removal efficiency of Flo at a constant pH (c): the effect of pH and pressure on the removal efficiency of Flo at a constant concentration**.**

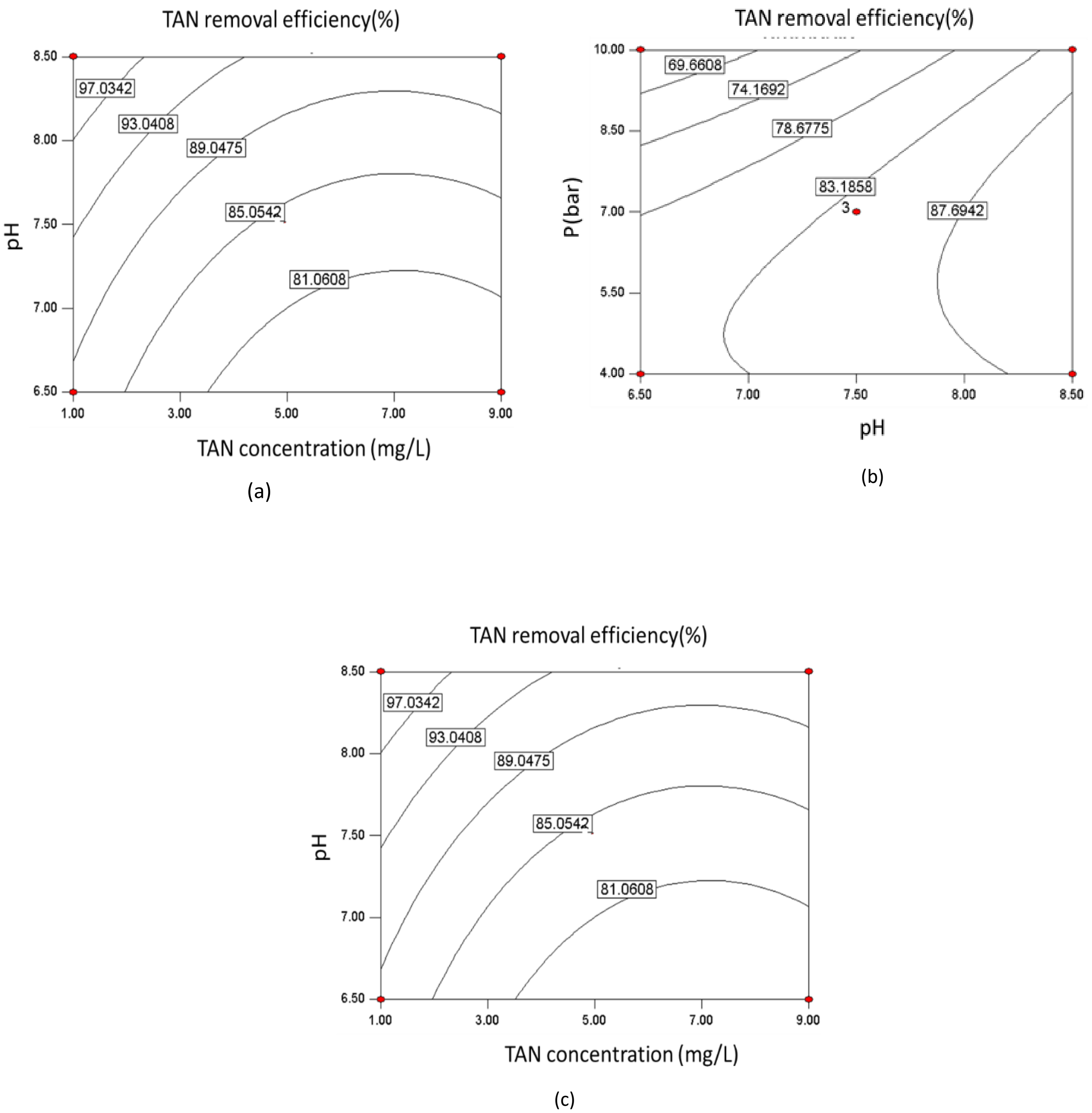

Fig. 3. Contour plots of the TAN removal efficiency; (a): the effect of concentration and pH on the removal efficiency of TAN at a constant pressure. (b): the effect of pressure and concentration on the removal efficiency of TAN at a constant pH (c): the effect of pH and pressure.

3.4. Effect of pressure

The results demonstrated that the TAN and Flo removal efficiencies increased with an increase in pressure from 4 to 5 bar and to 7 bar, respectively (Figures 3(c) and 2(c)). According to the Darcy law, by an increase in pressure, the membrane effluent flux reached a maximum amount which led to a decrease in the pollutant concentrations in the filtrate stream due to constant concentrations of the TAN and Fl in the feed [41]. By increasing the operating pressure above 7 and 5 bar for Flo and TAN, respectively, a negative impact on the nanofiltration performance was observed. Since various electrochemical forces overcome pressure forces at the pressures beyond the optimum value [23], it causes the TAN and antibiotic molecules to pass through the membrane pores beyond the optimum pressure. These results were in agreement with the findings of other researchers [31].

3.5. Optimum conditions

The optimum conditions based on the maximum removal efficiencies were predicted through Eqs. (3) and (4) via Design Expert software (version 8.0.1). The optimum operating conditions for the Floand TAN removal are presented in Table 7. The membrane optimum operating conditions offer significant energy savings for industrial scale applications.

Table 7. Optimum condition for TAN and FLO.

Contaminant	Concentration (ppm)	pH	P (bar)	Removal efficiency (%)
TAN	1.07	8.23	7.35	98.35
Flo	5	8.5	7.44	99.61

4. Conclusion

The effect of pH, pressure and concentration on the TAN and Flo removal efficiencies from synthetic trout fish farm wastewater were assessed. Based on the obtained results, the pH and contaminants concentration had the most significant effect on the responses of TAN and Flo, respectively, while the factors interactions did not have a substantial effect on the removal efficiency of the Flo. The results also indicated that with an increase in pH and antibiotic concentration, the Flo removal efficiency increased. The design of experiments/response surface method was a suitable method for optimizing the number of experiments and analysis of the results within the selected factors levels. The results showed that applying a commercial spiral wound polyamide NF can be considered as an effective way of removing TAN and Flo antibiotics from trout fish farm wastewater.

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