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Effect of anion interaction on the removal efficiency of nanofilters for potable water treatment

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ABSTRACT

The interaction between the ions and the charge of membranes can affect the efficiency of pollutant removal. The present study investigated the removal efficiency of hexavalent chromium and nitrate ions from both actual and synthetic contaminated water via two different commercial spiral wound polyamide nanofilters. In addition, the interaction of ions under different experimental conditions was investigated by using a Box-Behnken design (BBD). The Box–Behnken design optimized the contributing factors which included pH (5-9), the initial concentration of Cr (VI) (0.05-5 mg/L) and the initial concentration of nitrate (40-160 mg/L). The maximum removal efficiency of both Cr (VI) and nitrate was achieved at a pH of 9.0, as 99 % and 90 % for the Iranian nanofilter (NF-I) and 98 % and 82 % for the Korean nanofilter (NF-K), respectively. The results also indicated that as the initial concentration of Cr (VI) increased, the removal efficiency was enhanced while the removal efficiency of nitrate decreased according to the pH. However, by increasing the initial concentration of nitrate, the removal efficiency of both the Cr (VI) and nitrate increased. For actual water samples at an optimum pressure of 0.6 Mpa (NF-K) and 0.8 Mpa (NF-I), the removal efficiency of Cr(VI) and nitrate obtained was 95% and 76 % for the NF-K and 97 % and 86 % for the NF-I, respectively.

1. Introduction

Recently, the extensive application of nitrogen-rich fertilizers as well as utilizing municipal wastewater in the agriculture industry has resulted in severe water contamination by nitrate [1], turning many of the wells into stand-by ones [2]. Since the excessive concentration of nitrate causes various health problems and diseases such as methemoglobinemia [3], many researchers have focused on the removal of nitrate from water resources. On the other hand, the presence of heavy metals in water and wastewater has always been a matter of concern for environmentalists, who promote practical methods in an attempt to remove them. Of the various water polluting ions, hexavalent chromium is the most frequently found toxic agent in water and wastewater, originating mainly from industries such as mining, tanning, cement,

photography, metal manufacturing and electroplating [4]. This carcinogenic element can cause a number of illnesses affecting the kidneys, lungs, and liver [5]. Therefore, developing a novel pragmatic approach to remove these contaminating ions is of crucial importance. The World Health Organization (WHO) has reported a maximum contamination level (MCL) of 45 and 0.05 as mg/L for nitrate and Cr (VI), respectively [6]. However, the amount of these ions is usually higher. In Iran, there is also an increased potential for the presence of both nitrate and hexavalent chromium in water resources due to agricultural and industrial activities. Although a number of methods such as membrane filtration [7], adsorption [8], ion exchange [9], electrodialysis [10] and biosorption [11-12] are available for ion removal from contaminated water, most of them are unable to thoroughly eliminate such impurities. Furthermore, these methods suffer from several



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disadvantages such as requiring expensive equipment, monitoring systems and energy as well as the management of the produced toxic sludge [13]. Nanofiltration(NF) is not only an effective method to remove both the Cr (VI) (ionic radius for HCrO₄= 0.242 nm) [14] and nitrate (ionic radius= 0.189 nm) [15], it is also cost-effective and environmentally friendly. The separation of ionic species by the nanofilter membrane depends on both the charge and size effects [16]. Besides, nanofiltration can simultaneously remove a broad range of other impurities such as salts, dyes, viruses, bacteria and parasites. Yu Y., et al. [17] investigated the effect of ion concentration and natural organic matter on arsenic removal by nanofiltration. Recently, Li K., et al. [18] used NF to reuse wastewater by operational optimization and analysis of the membrane fouling. Since the removal of nitrate and hexavalent chromium from water has not been studied extensively, this study aims to compare the efficiency of two different nanofilter membranes in removing nitrate and hexavalent chromium from both actual and synthetic drinking water. In addition, the interaction of ions under different experimental conditions including the pH and the initial concentration of nitrate and hexavalent chromium was investigated by using a Box-Behnken design. The removal of both nitrate and chromium were first tested by nanofilters using synthetic water samples. Then, the experiments were repeated for the actual water samples.

2. Materials and methods

All the chemicals used in this study were supplied by the Merck Company, Germany, and included potassium dichromate (K₂Cr₂O₇), potassium nitrate (KNO₃), sulfuric acid, hydrochloric acid, and sodium hydroxide. The nitrate and hexavalent chromium solutions were also prepared using distilled water. Additionally, the polyamide spiral wound nano-filter membranes used in the experiments were selected from two different brands, one developed by the Noshirvani University of Technology, Iran (NF-I), and the other by the TFC Company, Korea (NF-K). Their characteristics are defined in Table 1. The actual water

samples were taken from the city of Isfahan's potable water (Table 2).

Table 1. Physicochemical characteristics of the commercial polyamide nanofilter membranes

Specification	Allowed range			
Specification	NF-I	NF-K		
Maximum operating pressure (bar)	20	9		
Maximum operating temperature (ºC)	50	-		
pH range	3-12	2-11		
Active surface (m ²)	0.35	0.35		
Isoelectric point	4.6	4.5		
Surface charge	Negative	Negative		

Fable 2. Isfahan's pota	able water	characteristics
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Characteristics	Measured value
K ⁺ (mg/L)	1
Na+ (mg/L)	11
Ca ²⁺ (mg/L)	38
Mg ²⁺ (mg/L)	13
HCO₃⁻ (mg/L)	173
NO ₃ - (mg/L)	10
Cl⁻ (mg/L)	15
SO ₄ ²⁻ (mg/L)	19
рН	8.1
EC*(µS/cm)	310
TDS (mg/L)	205

*Electric conductivity

2.1. Experimental set-up

A schematic picture of the apparatus is illustrated in Figure 1. The setup included a temperature control device and two diaphragm pumps with a capacity of 1.6 liters per minute at a maximum outlet pressure of 8.5 bars.



Fig. 1. Schematic picture of the experimental setup.

2.2. Experimental procedure

The experiments were conducted in 15, 30, 45 and 60 minute intervals after the startup time. The sampling analysis indicated that the system had the maximum removal efficiency at the 15 minute interval after the startup. In fact, by increasing the time interval, the removal efficiency remained constant. In order to achieve an efficiency rate of 75 %, the pressure was adjusted using the pressure valves on permeate and the concentrate stream. In addition, to avoid both measurement and human errors, the sampling and all the experiments were triplicated and duplicated, respectively. The data were introduced as the mean value to the Design Expert software. The feed concentration was also measured to obtain more accuracy in calculating the contaminant removal efficiency. During the experiments, the feed temperature and optimum pressure were kept constant at 20±1 °C and 0.8 (NF-I) and 0.6 Mpa (NF-K), respectively. According to the standard methods of 4500B and 3111B [19], the nitrate and chromium concentrations were determined using UV spectrophotometry (Jasco V-570, Japan) and atomic spectrophotometry (Philips absorption PU-9100, Netherlands), respectively. While the initial concentration of Cr (VI) was designated as 0.05, 0.5 and 5 mg/L, the nitrate concentration was selected as 40, 80 and 160 mg/L at three pH values of 5, 7 and 9. The removal efficiency of Cr (VI) and nitrate by the nanofilter membrane were determined by Eq. 1 [20]:

$$R\% = [1 - (\frac{C_p}{C_0})] \times 100$$
 (1)

where *R* represents the removal percentage and C_{ρ} and C_{0} are the concentrations of the pollutant in the permeate and the feed water, respectively.

2.3. Design of experiment (DOE)

The response surface method (RSM) is an effective method for response optimization [21]. Therefore, it was employed in this study to maximize the removal of nitrate and hexavalent chromium. In order to determine the effective variables of the experiments and develop a RSM for optimization, the main factors mentioned above were further studied via BBD which is an accurate method in the case of water and wastewater treatment processes. Eq. 2 was used to calculate the number of experiments:

$$N = 2K \times (k - 1) + C$$
⁽²⁾

where k and C_0 denote the number of factors and central points, respectively [22]. On the other hand, Eq. 3 represented a second order polynomial [21]:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_{12} + b_{22}X_{22} +$$
(3)
$$b_{33}X_{32}^2 + b_{12}X_1X_2 + b_{13}X_{13}X_3 + b_{23}X_2X_3$$

where Y, $[X_1, X_2, X_3]$ and $[b_0, b_i, b_{ij}]$ represent the responses, coded parameters and the estimated model coefficients, respectively. It is worth mentioning that the response can be analyzed by applying contour diagrams. The contour line plot is two dimensional, illustrating fixed responses. The RSM used the contour plots to analyze the results. According to the number of factors and by employing the RSM method via Design Expert software (8.0.1), it was determined that 15 experiment runs should be conducted.

3. Results and discussion

The levels of independent variables according to the BBD method and the rejection percent of hexavalent chromium (Y_1) and nitrate (Y_2) responses for all the experiments done by both membranes are presented in Table 3.

Nitrate				NF-I		NF-K	NF-K	
Run	concen. (mg/L)	Cr (VI) concen. (mg/L)	рН	Cr (VI) Removal Y1 (%)	Nitrate Removal	Cr (VI) Removal Y1 (%)	Nitrate Removal	
1	80±3 (0)	0.5±0.1 (0)	7±0.1 (0)	93.2	76.3	90.4	72.2	
2	40±2 (-1)	0.5±0.1 (0)	5±0.1 (-1)	86.4	73	87.4	67.8	
3	40±2 (-1)	0.5±0.1 (0)	9±0.1 (1)	95.2	89.7	93.2	81.5	
4	40±2 (-1)	5±0.5 (1)	7±0.1 (0)	93.5	75.4	91.2	70.3	
5	40±2 (-1)	0.05±0.02 (-1)	7±0.1 (0)	91.4	83.1	88.7	75.9	
6	160±5 (1)	0.5±0.1 (0)	5±0.1 (-1)	89	65.4	87.4	66.7	
7	160±5 (1)	0.5±0.1 (0)	9±0.1 (1)	98.8	86.9	96.8	77.1	
8	80±3 (0)	0.05±0.02 (-1)	9±0.1 (1)	97.2	90.4	96.2	80.6	
9	80±3 (0)	0.5±0.1 (0)	7±0.1 (0)	92.6	79.1	90.4	72.2	
10	80±3 (0)	5±0.5 (1)	9±0.1 (1)	98.5	86	97.9	77.8	
11	80±3 (0)	5±0.5 (1)	5±0.1 (-1)	91	66.2	91.4	64	
12	80±3 (0)	0.5±0.1 (0)	7±0.1 (0)	93.8	78	91.5	71.6	
13	80±3 (0)	0.05±0.02 (-1)	5±0.1 (-1)	86.2	77.5	83.6	72	
14	160±5 (1)	0.05±0.02 (-1)	7±0.1 (0)	93.6	77.6	92.2	76.6	
15	160±5 (1)	5±0.5 (1)	7±0.1 (0)	95	70.8	94.6	66.9	
AWS*	80±3	0.5±0.1	8±0.1	97.3	86	95	76.4	

*Actual Water Samples

3.1. ANOVA study

The results of the analysis of variance (ANOVA) for Cr(VI) and nitrate removal are presented in Table 4. Since the confidence level was taken as 95%, the effect of any factor was only significant if its P-value was less than 0.05. This meant that there was only a 5% probability of error to consider a non-significant factor as significant. The greater F-value showed a greater effect of the factor on the response. The F-value was defined as the ratio of the mean square of regression (MRR) to the mean square of error (MRe) (F = MRR/MRe). This implied that the linear effects of $pH(X_2)$, Cr (VI) concentration(X_1), nitrate concentration (X_3) and interactive effect of pH and Cr (VI) concentration were more significant. Table 4 also indicates that the interactive effects of pH and nitrate concentration as well as Cr (VI) and nitrate concentration had no significant influence on the removal efficiency of Cr (VI) and nitrate. It is worth mentioning that the interactive effects between Cr (VI) concentration and pH on the response can be adjusted by pH. In fact, as the pH increased from 5 to 9, the concentration of the chromium ion which was in the form of HcrO⁴⁻ shifted to other forms like CrO₄²⁻ and Cr₂O₇²⁻ [23-24]. Therefore, their electrical charge and ionic radius

changed, thus affecting the contaminants removal efficiency. The mathematical model based on actual values for hexavalent chromium and nitrate removal percentages are expressed by Eqs. 4 and 5 for the NF-I and Eq. 6 and Eq. 7 for the NF-K, respectively:

$$R_1(\%) = 93.2 + 1.25X_1 + 4.6375X_2 + 1.2875X_3 \quad (4) - 0.875X_1X_2$$

$$R_2(\%) = 77.8 - 3.775X_1 + 8.862X_2 - 2.5625X_3 \quad (5) + 1.725X_1X_2 + 2.125X_2^2$$

$$R_1(\%) = 91.3 + 1.825X_1 + 4.925X_2 + 1.925X_3 \quad (6) - 1.525X_1X_2 + 1.3375X_1^2$$

$$R_2(\%) = 72.27 - 3.2625X_1 + 5.8125X_2$$
(7)
- 1.025X_3 + 1.30X_1X_2

The regression parameter R^2 was applied to determine the agreement in comparison of the experimental responses to the ones estimated by the BBD method. The R^2 value for Eq. 4 and Eq. 5 was found to be 0.9910 and 0.9906, respectively, and 0.9840 and 0.9874 for Eq. 6 and Eq. 7, respectively. Thus, there were good agreements between the experimental and the predicted removal efficiency (Figure 2).



Fig. 2. Regression parameter of nanofilters a) Cr(VI) removal with NF-I; b) Ni removal with NF-I; c) Cr (VI) removal with NF-K; d) Ni removal with NF-K.

Table 4.	ANOVA res	ilts of Ci	r (VI) (A)	and nitrate	(B) removal	for NF-I and NF-K.
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Sours d.f. Methods by per Adj MS Seq SS F-value (A) Cr (V) removal									
(A) Cr (VI) removal NF-I 203.74 22.64 60.29 0.0001 X-Cr (VI) NF-K 271.98 30.22 34.03 0.0005 X-Cr (VI) NF-K 12.5 13.25 33.29 0.0022 Concentration NF-K 26.64 26.64 30.01 0.0028 XPH 1 NF-K 13.26 13.26 35.32 0.0001 X-Mitrate NF-K 29.64 33.38 0.0022 0.0023 0.0032 X.A NF-K 29.64 29.64 33.38 0.0022 0.0023 X.A NF-K 29.64 29.64 33.38 0.0022 0.023 X.Xi 1 NF-K 0.3 0.3 0.81 0.622 X.Xi 1 NF-K 0.65 0.66 0.61 0.414 X.Xi 1 NF-K 0.55 0.55 0.67 0.4316 X.Xi 1 NF-K 0.61 7.44	Sours	d.f.	typo	Adj MS	Seq SS	F-value	P-value		
LAD CLUY Demoval VI-I 203.74 22.64 60.29 0.0001 Model 9 NF-K 213.93 30.22 34.03 0.0006 Concentration 1 NF-K 215.64 25.64 30.01 0.0028 X-pH NF-K 172.05 455.91 0.0021 X-pHr 13.26 35.32 0.0011 x-Nitrate NF-K 13.26 35.32 0.0021 concentration NF-K 29.64 29.64 33.38 0.0025 X,X NF-K 0.0025 0.0025 0.0028 0.9597 X,X NF-F 0.30 0.3 0.61 0.4622 X,X 1 NF-K 0.0025 0.0028 0.0028 0.9391 X,X 1 NF-K 0.59 0.59 0.4930 0.59 0.4930 X,X 1 NF-K 0.49 0.49 0.50 0.4930 X,X 1 NF-K 0.49 0.59 </th <th colspan="9"></th>									
Model9Nr=K203.742.6.9400.2300.001XCr(V)1Nr=K271.9830.2230.300.0002concentration1Nr=K26.6426.6430.010.0028XpH12.626.6430.600.0001XWirtate1Nr=K124.05124.05218.52<0.0001	(A) Cr (VI) removal								
N-Cr (V) N-FA 21.95 30.22 34.05 0.0008 concentration 1 NF-K 26.64 26.64 30.01 0.0028 X-pH 1 NF-K 172.05 455.19 <0.0001	Model	9		203.74	22.04	00.29	0.0001		
Ar-L concentrationNNL L L L NL L L L L L L L L L NNL L L L L L L L L NNL L L L L L L S L NNL L L L L S L S L S NN <b< td=""><td></td><td></td><td></td><td>271.98</td><td>30.22</td><td>34.03</td><td>0.0000</td></b<>				271.98	30.22	34.03	0.0000		
concentration NF-K 26.84 30.01 0.0028 Xr-pH 1 NF-K 194.05 124.05 218.52 0.0001 Xr-Witrate NF-K 132.65 132.05 33.38 0.0022 concentration 1 NF-K 29.64 29.64 33.38 0.0025 XiX 1 NF-K 29.64 29.64 33.38 0.022 XiX 1 NF-K 9.3 9.3 10.48 0.0356 XiX 1 NF-K 0.0025 0.0025 0.0028 0.9597 XiX 1 NF-K 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.56 0.4930 0.49 0.4930 0.49 0.4930 0.49 0.4930 0.55 0.4930 0.55 0.4930 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.55	X1-Cr (VI)	1		12.5	12.5	33.29	0.0022		
X ₂ -PH 1 NF-K 12/05 <th12 05<="" th=""> 12/</th12>	concentration		NF-K	26.64	26.64	30.01	0.0028		
N-F-K 194,05 128,52 40,001 concentration 1 NF-K 29,64 33,38 0.0022 X,X 1 NF-K 29,64 29,64 33,38 0.0025 X,X 1 NF-K 9,3 9,3 10,48 0.0356 X,X 1 NF-K 9,3 0,3 0,81 0,4106 X,X 1 NF-K 0,0025 0.0025 0.0028 0,9597 X,X 1 NF-K 0,025 0.75 0,451 0,4622 X,X 1 NF-K 0,75 0,75 1,99 0,2173 X,X 1 NF-K 0,49 0,49 0,55 0,4930 X,X 1 NF-K 1,46 7,28 - - X,X 1 NF-K 1,46 7,28 - - X,X 1 NF-K 1,46 7,28 - - X,X NF-K 1,46	X ₂ -pH	1	NF-I	1/2.05	1/2.05	458/19	<0.0001		
X-Mirate concentrationNF-K13.2613.2635.320.0019X.Xa1NF-K29.6429.6433.880.0022X.Xa1NF-K3.063.068.160.0356X.Xa1NF-K9.30.30.310.480.023X.Xa1NF-K0.00250.00250.00250.00250.05971X.Xa1NF-K0.560.560.670.4516X.Xa1NF-K0.560.560.630.4622X.Xa1NF-K0.616.617.440.0414X.Xa1NF-K0.590.591.570.2652X.Xa1NF-K0.590.591.570.0399X.Xa1NF-K3.793.793.700.4516X.XaNF-K1.467.28Lack of Fit3NF-I1.160.391.070.5159Pure Error2NF-K3.131.031.540.0002XCr(V)NF-K3.121.40.017.680.0003XCr(V)NF-K851.585.1587.620.0001XPH1NF-K270.28270.28278.11<0.0001	- r		NF-K	194.05	194.05	218.52	<0.0001		
concentration N F-K 29.64 29.64 33.38 0.0022 Xi,X N F-K 9.3 9.3 10.48 0.0356 Xi,X N F-K 9.3 9.3 10.48 0.023 Xi,X N F-K 0.0025 0.0025 0.0028 0.9597 Xi,X N F-K 0.0025 0.0025 0.663 0.4516 Xi,X N F-K 0.56 0.56 0.661 0.4622 Xi,X N F-H 0.83 0.83 2.22 0.1655 Xi,X N F-H 0.83 0.83 2.22 0.1655 Xi,X N F-H 0.83 0.83 2.22 0.1655 Xi,X N F-H 0.75 0.75 1.99 0.2173 Xi,X N F-H 0.36 1.57 0.2652 Xi,X N F-K 3.14 1.03 1.57 0.2652 Lack of Fit N F-H 1.46 7.28 - - Model	X₃-Nitrate	1	NF-I	13.26	13.26	35.32	0.0019		
X ₁ X ₂ 1N-I-I NF-K3.063.068.160.0356X ₁ X ₃ 1NF-I NF-K0.30.30.480.023X ₂ X ₃ 1NF-I NF-K0.250.00250.00280.9597X ₂ X ₃ 1NF-I NF-K0.550.560.670.4516X ₂ X ₄ 1NF-K0.560.560.630.4622X ₂ X ₂ 1NF-K0.560.560.630.4622X ₂ X ₂ 1NF-K0.6616.617.440.0414X ₂ X ₂ 1NF-K0.4900.550.4930X ₂ X ₃ 1NF-K0.590.591.570.939X ₂ X ₃ 1NF-K3.160.381.640.0021X ₂ X ₃ NF-I0.1667.28NF-K3.11.031.540.4166Pure Error2NF-I0.36NF-K3.10.36NF-K3.10.36NF-K3.10.311.540.0002X ₂ -PhNF-I0.720.5539.5070.0001X ₂ -PhNF-I0.282.5335.5070.0001X ₂ -PhNF-I13.40114.0114.0114.60X ₂ -PhNF-I13.4515.987.620.0002X ₂ -PhNF-I13.650.25.5335.070.0001X ₂ -PhNF-K<	concentration		NF-K	29.64	29.64	33.38	0.0022		
Number P NF-K 9.3 9.3 10.48 0.023 X ₁ X ₁ NF-K 0.0025 0.0025 0.0025 0.025 0.067 0.4316 X ₁ X ₃ NF-K 0.0025 0.025 0.067 0.4516 X ₁ X ₁ NF-K 0.56 0.56 0.63 0.4622 X ₁ X ₁ NF-K 0.656 0.56 0.63 0.4622 X ₁ X ₁ NF-H 0.83 0.83 2.22 0.965 X ₁ X ₂ NF-H 0.55 0.4930 0.4041 X ₂ X ₂ NF-H 0.75 0.75 1.99 0.2173 X ₁ X ₂ NF-H 0.72 0.75 0.4930 0.55 Residual error NF-H 0.38 1.88 - - NF-K 1.46 7.28 - - - Model NF-K 3.1 1.03 1.54 0.4166 Pure Error NF-K 382.13 42.46 3.69	X1X2	1	NF-I	3.06	3.06	8.16	0.0356		
X,X31NF-I NF-K0.30.30.810.400X,X31NF-I NF-K0.00250.00250.00280.9997X,X31NF-I NF-K0.560.560.630.4612X,X11NF-I NF-K0.570.751.990.2173X,X31NF-I NF-K0.590.591.570.2652X,X31NF-I NF-K0.590.591.570.2652X,X31NF-I NF-K0.381.88X,X41NF-I NF-K0.381.88Lack of Fit3NF-I NF-K1.160.391.070.5159Lack of Fit3NF-I NF-K1.340.67Model9NF-I NF-K1.340.67Model9NF-I NF-K320.132.5538.41 NG-M0.0002X,-Cr ConcentrationNF-I NF-K320.132.620.0001-X,2NF-I NF-K1.40.11114.0171.680.0002X,2NF-I NF-K28.35628.3535.070.0001X,2NF-I NF-K25.3533.030.0022ConcentrationNF-I NF-K2.5352.5333.030.0022ConcentrationNF-I NF-K2.722.80.155X,X31 NF-K1.671.6671.6420.366X,X41 NF-K	X1X2	-	NF-K	9.3	9.3	10.48	0.023		
No.5 I NF-K 0.0025 0.0025 0.0026 0.9597 X,X 1 NF-K 0.56 0.56 0.63 0.4622 X,X 1 NF-K 0.56 0.56 0.63 0.4622 X,X 1 NF-K 0.61 6.61 7.44 0.0414 X,X 1 NF-F 0.75 0.75 1.99 0.2173 X,X3 1 NF-F 0.75 0.79 1.57 0.2652 X,X3 1 NF-K 3.79 3.79 4.26 0.939 Residual error NF-K 1.46 7.28 - - Lack of Fit 3 NF-K 3.1 0.39 1.07 0.5159 Lack of Fit 3 NF-K 382.13 42.46 3.69 0.0002 X1-Cr (M) NF-K 382.13 42.46 3.69 0.0002 X1-Cr NF 1.40.11 1.140.11 1.40 1.68	X ₁ X ₂	1	NF-I	0.3	0.3	0.81	0.4106		
XX31NF-I NF-K0.25 0.560.25 0.630.4516X,X11NF-I NF-K0.830.832.220.1965X,X21NF-I NF-K0.751.940.0414X,X31NF-I NF-K0.751.990.2173X,X31NF-I NF-K0.590.591.570.2652X,X31NF-I NF-K0.590.590.590.59Residual errorNF-I NF-K0.381.88Lack of Fit3NF-I NF-K1.160.391.070.5159Pure Error2NF-I NF-K0.67Model9NF-I NF-K1.340.67Model9NF-I NF-K382.134.24643.690.0003X1-Cr concentration1NF-I NF-K28.3525.33395.07-X2-PH1NF-I NF-K28.3525.33395.07X3-Nitrate concentration1NF-I NF-K28.3525.33395.07X,X31NF-I NF-K21.028270.28278.11X3-Nitrate Concentration1NF-I NF-K270.28270.28278.11X,X41NF-I NF-K270.28270.28278.11X,X51NF-I NF-K2722.244.320.001	X1X3	1	NF-K	0.0025	0.0025	0.0028	0.9597		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	V _a V _a	1	NF-I	0.25	0.25	0.67	0.4516		
XiX11NF-I0.830.832.220.1965XiX21NF-K6.616.617.440.0414XiX21NF-K0.490.490.550.4930XiX31NF-K0.590.591.570.2652XiX31NF-K0.393.794.260.0939Residual errorNF-K3.793.794.260.0939Residual errorNF-K1.467.28Lack of Fit3NF-K3.11.031.570.4166Pure Error2NF-K3.140.67Kitste removalNF-K3.140.67Kitste removalNF-K382.1342.4643.690.0002Xi-Cr(VI) NF-KNF-K832.1342.4643.690.0002Xi-Cr(VI) NF-KNF-K835.1585.1585.610.0002Xi-PireNF-K832.1342.4643.690.0002ConcentrationNF-K85.1585.1585.620.0002Xi-PireNF-K82.1342.4643.690.0002Xi-PireNF-K82.1342.4643.690.0002ConcentrationNF-K82.1342.4643.690.0002Xi-PireNF-K82.1342.4643.690.0002Xi-PireNF-K82.1342.4643.690.0002Xi-PireNF-K82.13	A2A3	T	NF-K	0.56	0.56	0.63	0.4622		
AlA1INF-K6.616.617.440.0414XxX21NF-K0.750.751.990.2173XsX31NF-K0.490.490.550.4330XsX31NF-K3.793.794.2600.0939Residual errorNF-K1.467.28Lack of Fit3NF-K1.160.391.570.5159Lack of Fit3NF-K1.160.391.570.5159Pure Error2NF-K1.160.391.540.4166Pure Error2NF-K1.340.67Model9NF-K836.0892.958.410.0002X1-Cr(VI)NF-K382.1342.4643.690.0003X1-CrNF-K835.1585.1587.620.0002X2-pH1NF-K85.1585.1585.000.0022X2-pH1NF-K82.33628.3533.030.0022X1-Nitrate1NF-K84.184.18.650.0322X1-X11NF-K8.765.763.620.1154X1-X2NF-K0.0370.0370.0230.884.9X1-X31NF-K2.722.722.80.155X1-X4NF-K0.0370.0370.0220.6574X2-Nitrate1NF-K0.0370.0370.0230.884.9X1-X3NF-K	V V	1	NF-I	0.83	0.83	2.22	0.1965		
XiX21NF-1 NF-K0.75 0.491.99 0.4900.2173 0.4930XiX31NF-K NF-K0.590.550.4930Residual error-NF-K NF-K3.793.794.260.0939Residual error-NF-K0.381.88Lack of Fit3NF-I NF-K1.160.391.070.5159Pure Error2NF-I NF-K1.340.67Model9NF-I NF-K1.340.67Model9NF-I NF-K3.21.342.4643.690.0003Xi-Cr concentrationNF-I NF-K836.0892.958.410.0002Xi-Cr concentrationNF-I NF-K835.1585.1585.000.0022Xi-Cr concentrationNF-I NF-K270.28270.28278.11-0.0001Xi-Xa xi-NirieNF-I NF-K5.25352.5335.07-0.0001Xi-XaNF-I NF-K270.28270.28278.11-0.0022Xi-Xa1NF-I NF-K5.765.763.620.0322Xi-Xa1NF-I NF-K5.763.620.0134Xi-Xa1NF-I NF-K0.273.620.154Xi-Xa1NF-I NF-K2.722.722.80.0921Xi-Xa1NF-I NF-K0.0370.0370.0220.022Xi-Xa1NF-I NF-K0.03	X ₁ X ₁	1	NF-K	6.61	6.61	7.44	0.0414		
χ_{X_2} 1 NF-K 0.49 0.49 0.55 0.4930 χ_3X_3 1 NF-K 0.59 0.59 1.57 0.2652 χ_3X_3 NF-I 0.38 1.88 - - Residual error NF-K 1.46 7.28 - - Lack of Fit 3 NF-I 1.16 0.39 1.54 0.4166 Pure Error 2 NF-I 0.72 0.36 - - (B) Nitrate removal NF-K 382.13 42.46 43.69 0.0002 X ₁ -Cr (V) NF-K 382.13 42.46 43.69 0.0002 X ₁ -Cr NF-I 114.01 114.01 71.68 0.0002 X ₂ -pH 1 NF-K 382.13 42.46 43.69 0.0002 X ₂ -pH 1 NF-K 85.15 85.15 87.62 0.0002 X ₂ -pH 1 NF-K 270.28 278.11 <0.0001			NF-I	0.75	0.75	1.99	0.2173		
$\chi_3\chi_3$ 1NF-10.590.590.500.003Residual errorNF-K3.793.794.260.0939Residual errorNF-K1.467.28Lack of Fit3NF-I1.160.391.070.5159Pure Error2NF-I0.720.36(b) Nitrate removal2NF-I0.720.36(b) Nitrate removal3NF-I1.340.67(c) Nitrate removal9NF-K382.1342.4643.690.0003X:-Cr(V) NF-K1NF-I836.0892.958.410.0004concentration1NF-K882.1342.4643.690.0003X:-Cr(V) NF-K1NF-I628.35628.3595.070.0001X:-Cr(V) NF-KNF-K85.1587.620.00020.0002X:-Cr(V) NF-KNF-K85.1587.620.0001X:-CrNF-K85.1585.1587.620.0001X:-CrNF-K85.1585.1587.620.0002X:-CrNF-K85.1585.1587.620.0001X:-CrNF-K85.1585.1587.620.0001X:-CrNF-K85.1585.1587.620.0001X:-CrNF-K84.18.418.650.0322ConcentrationNF-K8.418.418.65 <t< td=""><td>X_2X_2</td><td>1</td><td>NF-K</td><td>0.49</td><td>0.49</td><td>0.55</td><td>0 4930</td></t<>	X_2X_2	1	NF-K	0.49	0.49	0.55	0 4930		
XaXa 1 NF - K 0.35 0.35 1.37 0.205 Residual error NF-K 3.79 3.79 4.26 0.0939 Residual error NF-K 1.46 7.28 - - Lack of Fit 3 NF-K 3.1 1.03 1.54 0.4166 Pure Error 2 NF-K 1.34 0.67 - - (B) Nitrate removal NF-K 1.34 0.67 - - Model 9 NF-K 382.13 42.46 43.69 0.0002 xi-Cr (VI) 1 NF-K 85.15 87.62 0.0002 xi-Cr (VI) 1 NF-K 85.15 87.62 0.0002 xi-Ph 1 NF-K 85.15 87.62 0.0002 xi-Sr NF-K 82.35 628.35 395.07 <0.001			NF-I	0.59	0.59	1 57	0.2652		
Residual error NF-I 0.38 1.83 - - Residual error NF-K 1.46 7.28 - - Lack of Fit 3 NF-K 1.16 0.39 1.07 0.5159 Lack of Fit 3 NF-K 3.1 1.03 1.54 0.4166 Pure Error 2 NF-K 3.1 0.36 - - Model 9 NF-K 3.34 0.67 - - Model 9 NF-K 836.08 92.9 58.41 0.0002 X ₁ -Cr (VI) 1 NF-K 832.13 42.46 3.69 0.0003 X ₁ -Cr (VI) 1 NF-K 85.15 87.62 0.0001 X ₂ -pH 1 NF-K 270.28 270.28 278.11 <0.0001	X ₃ X ₃	1		2 70	2 70	1.57	0.2052		
Residual error NF-K 1.46 7.28 - - Lack of Fit 3 NF-K 1.16 0.39 1.07 0.5159 Pure Error 2 NF-K 3.1 1.03 1.54 0.4166 Pure Error 2 NF-K 3.1 0.67 - - (B) Nitrate removal NF-K 1.34 0.67 - - Model 9 NF-I 836.08 92.9 58.41 0.0002 X1-Cr (V) 1 NF-K 382.13 42.46 43.69 0.0003 X1-Cr (V) 1 NF-K 85.15 85.15 87.62 0.0002 X2-pH 1 NF-K 82.35 52.53 33.03 0.0022 concentration 1 NF-K 8.41 8.41 8.65 0.3222 X1X2 1 NF-K 8.76 5.76 6.96 0.0461 X1X3 1 NF-K 8.21 <				0.20	1 00	4.20	0.0939		
Lack of Fit3NF-A NF-K1.46 NF-K 7.26 0.391.07 1.07 0.5159 0.4166Pure Error2NF-I NF-K0.72 NF-K0.36 0.67(b) Nitrate removal0.67(b) Nitrate removalModel9NF-I NF-K382.13 382.1342.46 42.4643.69 43.690.0002X:-Cr concentrationNF-K NF-K885.15 28.3587.62 20.00020.0002X_2-pH1 NF-KNF-K 270.28270.28 270.28278.11 20.0001<0001	Residual error			0.50	1.00	-	-		
Lack of Fit 3 NF-K 3.1 1.00 1.07 0.5159 Pure Error 2 NF-K 3.1 1.03 1.54 0.4166 Pure Error 2 NF-K 3.1 0.67 - - (B) Nitrate removal .				1.40	7.28	-	-		
Pure Error 2 NF-k 3.1 1.03 1.54 0.4166 Pure Error 2 NF-k 1.34 0.67 - - (B) Nitrate removal NF-k 386.08 92.9 58.41 0.0002 Xi-Cr (V) 1 NF-k 382.13 42.46 43.69 0.0003 Xi-Cr (V) 1 NF-k 382.13 42.46 3.69 0.0002 Xi-Cr (V) 1 NF-k 385.15 85.15 85.15 0.0002 Xi-pH 1 NF-k 270.28 270.28 278.11 <0.0001	Lack of Fit	3	NF-I	1.16	0.39	1.07	0.5159		
Pure Error 2 NF-I 0.72 0.36 - - (B) Nitrate removal NF-K 1.34 0.67 - - (B) Nitrate removal %F-K 382.13 0.67 58.41 0.0002 X1-Cr (VI) NF-K 382.13 42.46 36.99 0.0003 X1-Cr (VI) NF-K 85.15 85.15 87.62 0.0001 Concentration NF-K 85.15 628.35 028.35 028.35 0001 X2-pH 1 NF-K 270.28 270.28 270.28 278.11 0.0002 X3-Nitrate 1 NF-K 8.41 8.41 8.65 0.0322 Concentration 1 NF-K 0.22 0.13 0.7358 X1X2 1 NF-K 0.22 0.23 0.849 X1X3 1 NF-K 0.22 0.22 0.22 0.22 0.22 X1X3 1 NF-K 0.037 0.037<			NF-K	3.1	1.03	1.54	0.4166		
Kindel NF-K 1.34 0.67 - - (B) Nitrate removal Model 9 NF-K 836.08 92.9 58.41 0.0002 X1-Cr (VI) 1 NF-K 382.13 42.46 43.69 0.0003 X1-Cr (VI) 1 NF-H 114.01 114.01 71.68 0.0002 X2-PH 1 NF-K 85.15 85.15 87.62 0.0001 X3-Nitrate NF-K 270.28 270.28 278.11 <0.0022 Concentration NF-K 8.41 8.41 8.65 0.0322 X1X2 1 NF-K 8.41 8.65 0.0322 X1X3 1 NF-K 8.41 8.65 0.0322 X1X3 1 NF-K 6.76 6.76 6.96 0.0461 X1X3 1 NF-K 0.22 0.22 0.13 0.7358 X1X3 1 NF-K 0.37 0.037 0.023 0.8849 X1X3 1 NF-K 0.22 0.22	Pure Error	2	NF-I	0.72	0.36	-	-		
(B) Nitrate remove View Since Since </td <td></td> <td>_</td> <td>NF-K</td> <td>1.34</td> <td>0.67</td> <td>-</td> <td>-</td>		_	NF-K	1.34	0.67	-	-		
(B) Nitrate removal NiF-ic 3836.08 92.9 58.41 0.0003 Xi-Cr (VI) NF-K 382.13 42.46 43.69 0.0003 Xi-Cr (VI) NF-K 382.13 42.46 43.69 0.0003 concentration NF-K 85.15 85.15 87.62 0.0002 Xi-pH 1 NF-K 85.15 87.62 0.0001 Xi-PH 1 NF-K 85.15 87.62 0.0001 Xi-Nitrate NF-K 270.28 270.81 270.28 0.002 concentration NF-K 8.41 8.41 8.65 0.0322 XiX2 NF-K 8.41 8.41 8.65 0.0322 XiX3 NF-I 11.9 11.9 7.48 0.0410 XiX3 NF-I 0.2 0.2 0.13 0.7358 XiX3 NF-I NF-I 0.2 0.22 0.22 0.22 XiX3 NF-I S.76 5.76 3.62 0.1154 XiX1 NF-K 0.22 0.2									
Model ${ } { } { } { } { } { } { } { } { } { }$	(B) Nitrate removal								
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Model	9	NF-I	836.08	92.9	58.41	0.0002		
$\begin{array}{cccc} X_1 - Cr & (Vi) \\ concentration & I & NF-I & 114.01 & 114.01 & 71.68 & 0.0004 \\ concentration & NF-K & 85.15 & 85.15 & 87.62 & 0.0002 \\ \hline X_2 - pH & I & NF-I & 628.35 & 628.35 & 395.07 & <0.0001 \\ \hline X_3 - Nitrate & I & NF-I & 52.53 & 270.28 & 270.28 & 278.11 & 0.0021 \\ \hline X_3 - Nitrate & I & NF-I & 52.53 & 52.53 & 33.03 & 0.0022 \\ concentration & I & NF-K & 8.41 & 8.41 & 8.65 & 0.0322 \\ \hline X_1 X_2 & I & NF-I & 11.9 & 11.9 & 7.48 & 0.0410 \\ \hline NF-K & 6.76 & 6.76 & 6.96 & 0.0461 \\ \hline X_1 X_3 & I & NF-I & 0.2 & 0.2 & 0.13 & 0.7358 \\ \hline X_1 X_3 & I & NF-I & 0.2 & 0.2 & 0.13 & 0.0921 \\ \hline X_2 X_3 & I & NF-I & 5.76 & 5.76 & 3.62 & 0.1154 \\ \hline X_1 X_1 & NF-K & 2.72 & 2.72 & 2.8 & 0.155 \\ \hline X_1 X_1 & NF-I & 0.037 & 0.037 & 0.023 & 0.8849 \\ \hline X_1 X_1 & NF-I & 0.037 & 0.037 & 0.023 & 0.8849 \\ \hline X_2 X_2 & I & NF-I & 0.037 & 0.037 & 0.023 & 0.8849 \\ \hline X_3 X_3 & I & NF-I & 0.026 & 0.22 & 0.22 & 0.6574 \\ \hline X_3 X_3 & I & NF-I & 5.10 & 5.10 & 3.21 & 0.1334 \\ \hline X_3 X_3 & I & NF-I & 5.10 & 5.10 & 3.21 & 0.1334 \\ \hline X_3 X_3 & I & NF-I & 0.27 & 1.37 & - & - \\ \hline Residual error & NF-K & 0.97 & 4.86 & - & - \\ \hline Lack of Fit & 3 & NF-I & 3.97 & 1.32 & 0.67 & 0.6469 \\ \hline Pure Error & 2 & NF-I & 3.98 & 1.99 & - & - \\ \hline NF-K & 0.99 & 0.49 & - & - \\ \hline NF-K & 0.99 & 0.49 & - & - \\ \hline \end{array}$	Wouch	5	NF-K	382.13	42.46	43.69	0.0003		
concentration 1 NF-K 85.15 85.15 87.62 0.0002 χ_2 -pH 1 NF-I 628.35 395.07 <0.0011	X1-Cr (VI)	1	NF-I	114.01	114.01	71.68	0.0004		
χ_2 -pH 1 NF-I 628.35 628.35 395.07 <0.001 X ₃ -Nitrate concentration 1 NF-K 270.28 270.28 278.11 <0.0021	concentration	T	NF-K	85.15	85.15	87.62	0.0002		
X2pri I NF-K 270.28 270.28 278.11 <0.0001 X3-Nitrate concentration 1 NF-I 52.53 33.03 0.0022 $\chi_1 \chi_2$ 1 NF-K 8.41 8.41 8.65 0.0322 $\chi_1 \chi_2$ 1 NF-I 11.9 11.9 7.48 0.0410 $\chi_1 \chi_2$ 1 NF-I 0.2 0.2 0.13 0.7358 $\chi_1 \chi_3$ 1 NF-I 0.2 0.2 0.32 0.0921 $\chi_2 \chi_3$ 1 NF-I 0.2 0.2 0.13 0.7358 $\chi_2 \chi_3$ 1 NF-I 0.27 2.72 2.8 0.155 $\chi_1 \chi_1$ 1 NF-I 0.037 0.023 0.8849 $\chi_1 \chi_3$ 1 NF-I 0.022 0.22 0.22 0.574 $\chi_2 \chi_2$ 1 NF-I 16.67 16.67 0.48 0.0866 $\chi_3 \chi_3$ 1 NF-I 0.026 0.026	V nH	1	NF-I	628.35	628.35	395.07	<0.0001		
$\begin{array}{cccccc} X_3 - Nitrate \\ concentration \\ ref $	х₂-рп	T	NF-K	270.28	270.28	278.11	<0.0001		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	X₃-Nitrate		NF-I	52.53	52.53	33.03	0.0022		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	concentration	1	NF-K	8.41	8.41	8.65	0.0322		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			NF-I	11.9	11.9	7.48	0.0410		
X1X31NF-I NF-K0.20.120.130.7358X2X31NF-K4.24.24.320.0921X2X31NF-I5.765.763.620.1154X1X11NF-K2.722.722.80.155X1X11NF-K0.0370.0370.0230.8849X2X21NF-K0.220.220.220.6574X3X31NF-K4.44.44.530.0866X3X31NF-K0.0260.0260.0260.8773Residual errorNF-I0.271.37Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.992NF-I3.981.99	X ₁ X ₂	1	NF-K	6.76	6.76	6.96	0.0461		
X_1X_3 1NF N0.120.120.120.120.100 X_2X_3 1NF-K4.24.24.320.0921 X_2X_3 1NF-I5.765.763.620.1154 X_1X_1 1NF-K2.722.722.80.155 X_1X_1 1NF-I0.0370.0370.0230.8849 X_2X_2 1NF-I0.0220.220.220.6574 X_2X_2 1NF-K4.44.44.530.0866 X_3X_3 1NF-I5.105.103.210.1334 X_3X_3 1NF-I0.0260.0260.0260.8773Residual errorNF-I0.271.37Lack of Fit3NF-I3.971.320.6770.6469Pure Error2NF-I3.981.99Pure Error2NF-I3.981.99			NF-I	0.2	0.2	0.13	0 7358		
X_2X_3 1NF-I5.765.763.620.1154 X_1X_1 1NF-K2.722.722.80.155 X_1X_1 1NF-I0.0370.0370.0230.8849 X_2X_2 1NF-I0.220.220.220.6574 X_2X_2 1NF-I16.6716.6710.480.023 X_3X_3 1NF-I5.105.103.210.1334 X_3X_3 1NF-I0.0260.0260.0260.8773Residual errorNF-I0.271.37 $NF-K$ 0.974.86Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.992NF-I0.990.49	X_1X_3	1	NF-K	4.2	4.2	4 32	0.0921		
X_2X_3 1NF-K2.722.722.80.1134 X_1X_1 1NF-K2.722.722.80.155 X_1X_1 1NF-I0.0370.0370.0230.8849 X_2X_2 1NF-K0.220.220.220.6574 X_2X_2 1NF-I16.6716.6710.480.023 X_3X_3 1NF-I5.105.103.210.1334 X_3X_3 1NF-I0.0260.0260.0260.8773Residual errorNF-I0.271.37Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.99Pure Error2NF-I3.981.99			NF-I	5.76	5.76	3.62	0.0521		
X1X11NF-I NF-K0.0370.0370.0230.8849X2X21NF-K0.220.220.220.6574X3X31NF-I NF-K16.6716.6710.480.023X3X31NF-I NF-K5.105.103.210.1334Residual errorNF-I NF-K0.0260.0260.0260.8773Lack of Fit3NF-I NF-K3.971.320.670.6469Pure Error2NF-I NF-K3.981.99	X_2X_3	1		5.70 2.72	2 72	2.02 2.02	0.1154		
X_1X_1 1NF-I0.0370.0370.0230.0849 X_2X_2 1NF-K0.220.220.220.6574 X_2X_2 1NF-I16.6710.480.023 X_3X_3 1NF-K4.44.44.530.0866 X_3X_3 1NF-I5.105.103.210.1334Residual errorNF-I0.0260.0260.0260.8773Residual errorNF-I0.271.37Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.99Pure Error2NF-I3.981.99				0.027	0.027	2.0	0.133		
X2X21NF-I16.6716.6710.480.023X3X31NF-K4.44.44.530.0866X3X31NF-I5.105.103.210.1334Residual errorNF-I0.0260.0260.0260.8773Residual errorNF-K0.974.86Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.99	X_1X_1	1		0.037	0.037	0.025	0.0049		
X_2X_2 1NF-I16.6716.6710.480.023 X_3X_3 1NF-K4.44.44.530.0866 X_3X_3 1NF-I5.105.103.210.1334Residual errorNF-I0.0260.0260.0260.8773Residual errorNF-K0.974.86Lack of Fit3NF-I3.971.320.670.6469Pure Error2NF-I3.981.99Pure Error2NF-I0.990.49				0.22	0.22	0.22	0.0574		
NF-K4.44.44.530.0866 X_3X_3 1NF-I5.105.103.210.1334NF-K0.0260.0260.0260.0260.8773Residual errorNF-I0.271.37NF-K0.974.86Lack of Fit3NF-I3.971.320.67Pure Error2NF-I3.981.99	X_2X_2	1	NF-I	16.67	16.67	10.48	0.023		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			NF-K	4.4	4.4	4.53	0.0866		
NF-K 0.026 0.026 0.026 0.8773 Residual error NF-I 0.27 1.37 - - NF-K 0.97 4.86 - - - Lack of Fit 3 NF-I 3.97 1.32 0.677 0.6469 Pure Error 2 NF-I 3.98 1.99 - -	X3X3	1	NF-I	5.10	5.10	3.21	0.1334		
Residual error NF-I 0.27 1.37 - - NF-K 0.97 4.86 - - - Lack of Fit 3 NF-I 3.97 1.32 0.67 0.6469 Pure Error 2 NF-I 3.98 1.99 - -		-	NF-K	0.026	0.026	0.026	0.8773		
NB-K 0.97 4.86 - - Lack of Fit 3 NF-I 3.97 1.32 0.67 0.6469 Pure Error 2 NF-I 3.98 1.99 - -	Residual error		NF-I	0.27	1.37	-	-		
Lack of Fit 3 NF-I 3.97 1.32 0.67 0.6469 NF-K 3.87 1.29 0.97 0.2885 Pure Error 2 NF-K 3.98 1.99 - -	Residual error		NF-K	0.97	4.86	-	-		
Pure Error NF-K 3.87 1.29 0.97 0.2885 Pure Error 2 NF-I 3.98 1.99 - -	Lack of Fit	2	NF-I	3.97	1.32	0.67	0.6469		
Pure Error 2 NF-I 3.98 1.99	LOCK UT FIL	5	NF-K	3.87	1.29	0.97	0.2885		
	Duro Error	n	NF-I	3.98	1.99	-	-		
		2	NF-K	0.99	0.49	-	-		

3.2. Effect of pH on Cr (VI) and nitrate removal

The results indicated that by increasing the pH, the removal efficiency of Cr (VI) and nitrate by both of the membranes was enhanced (Figure 3 a and b). However, the pH had a greater influence on the removal efficiency of Cr (VI) than that of the nitrate. At a nitrate concentration of 80 mg/L and when the pH was increased from 5 to 9, the removal efficiency of Cr (VI) showed a 9 % and 10 % rise for NF-K and NF-I, respectively, and the removal efficiency of nitrate increased about 14 % and 19 % for the NF-K and NF-I, respectively. This can be explained by the fact that the Cr

(VI) ions were in the form of dichromate at around a pH of 5, while chromate and dichromate ions were formed at pH values higher than 7 [23-24]. Hence, by increasing the pH from 5 to 9, the Cr (VI) ions transformed from monovalent into the divalent form which increased the removal efficiency. Additionally, since the selected pH range was above the membrane isoelectric point, any increase in the pH level multiplied the membrane negative charge. Therefore, the repulsion force between the anions and the negatively charged membrane surface intensified and consequently, raised the removal efficiency of both the Cr (VI) and nitrate.



Fig. 3. Contour plot comparison of Iranian and Korean membranes a) Cr (VI) removal contour plot at a constant concentration of 0.5 mg/L; b) Nitrate removal contour plot at a constant concentration of 80 mg/L.

3.3. Effect of initial nitrate concentration on Cr (VI) and nitrate removal

Considering Figure 4a and b, it is evident that the more the nitrate concentration increased, the more the removal efficiency dropped. However, the trend was reversed for the removal efficiency of Cr (VI). At a pH=7 and a Cr (VI) concentration of 0.5 mg/L, as the nitrate concentration increased from 40 mg/L to 160 mg/L, the removal efficiency of Cr (VI) was enhanced up to 4 % and 2 % for the NF-K and NF-I, respectively. On the other hand, this enhancement in

the removal efficiency of the nitrate varied between 1.5 % and 0.5 % for the NF-K and NF-I, respectively. In fact, when the nitrate concentration increased, the cation (K⁺) concentration was raised too. These cations were absorbed on the membrane surface and since the membrane itself had the negative charge, a shield formed on it. Thus, the newly formed cation layer on the membrane surface weakened the repulsion force between the negatively charged membrane and the anions which further facilitated the interaction of Cr (VI) and nitrate anions with the membrane surface. Because both the ion size and the

electrical charge of Cr (VI) were larger compared to nitrate ions, they could hardly pass the membrane pores and as a result, the removal efficiency of Cr (VI) increased. Similar results have also been obtained by several authors [15,25,26]. On the other hand, the nitrate ions could cross the pores of the membrane more easily due to their smaller size and caused a drop in the removal efficiency of nitrate.

However, in this condition, the reduction rate of the

efficiency depended on the pH of the feed solution. For instance, at a pH of about 5, the Cr (VI) ions were in the divalent form and were larger in size in comparison to the nitrates. Therefore, the removal efficiency of nitrate decreased while the removal efficiency of chromium increased. On the contrary, at pH values higher than 7, the Cr (VI) ions were in the divalent form and caused a shift in the removal efficiency of Cr (VI).



Fig. 4. Contour plot comparison of Iranian and Korean membranes a) Cr (VI) removal contour plot at pH=7; b) Nitrate removal contour plot at constant concentration of 0.5 mg/L.

3.4. Effect of initial Cr (VI) concentration on chromium and nitrate removal

According to Figure 3b and 4a, as the Cr (VI) concentration increased, the removal efficiency of Cr (VI) was enhanced. In contrast, the nitrate was removed less efficiently. At constant pH of 7 and a nitrate concentration of 80 mg/L, when the Cr (VI) concentration increased from 0 to 5 mg/L, the removal efficiency of Cr(VI) for the NF-K and NF-I rose about 3.5% and 2.5%, respectively. However, the removal efficiency of nitrate for the NF-K and NF-I was reduced up to 6% and 7%, respectively. The explanation is similar to the facts mentioned before. Indeed, by increasing the concentration of Cr (VI), the concentration of cations (K⁺) increased too, which further resulted in the formation of a cation layer on the membrane surface and weakness of the repulsion force between the negatively charged membrane surface and the anions. Therefore, the dichromate and nitrate anions could get closer to the membrane surface. At a pH of around 5, since the size of the nitrate ions were smaller than the Cr (VI) ions, they could cross the membrane pores more easily; consequently, the removal efficiency of nitrate decreased while the Cr (VI) was removed more efficiently. At pH values higher than 7, since Cr (VI) ions were in divalent form and had a larger ionic radius and electrical charge compared to nitrates, their removal efficiency increased. In this condition, in order to maintain the electrical balance between the two sides of the

membrane, more nitrate ions crossed the membrane pores and the nitrate removal efficiency was further increased. Similar results were observed in several other works [15,25,26, 27].

3.5. Interaction of Cr (VI) and nitrate in actual water samples

The results of nanofiltration on actual water samples at an optimum pressure of 0.6 and 0.8 Mpa for NF-K and NF-I, respectively, are presented in Table 3. However, the water characteristics are specified in Table 2. According to Table 3, the NF-K could remove Cr (VI) and nitrate by 95 % and 76.4 %, respectively, while the NF-I was more successful and yielded about 97.3 % and 86 % for them, respectively. This could be explained by the fact that the NF-I had smaller pores or more exclusion effect and could remove anions with higher rates. The effect of other contributing factors on the actual water samples were the same as indicated for the synthetic water.

4. Conclusions

In this study, the removal efficiency of hexavalent chromium and nitrate ions by means of two different commercial spiral wound polyamide nanofilters was investigated for both synthetic and actual water specimens. The results are summarized as follows:

1- Both of the commercial polyamide spiral wound nanofilters can effectively remove Cr (VI) and nitrate from the contaminated water.

2- The interaction between the ions and charge of membranes influenced the pollutant removal efficiency. However, the NF-I showed a slightly better efficiency compared to the NF-K due to its smaller pore size or more exclusion effect.

3- The removal efficiency of nitrate and Cr (VI) depended greatly on pH, their initial concentration, and the interaction between the concentration of Cr (VI) and the pH. 4- The removal efficiency was obtained in the range of 86.2 to 98.8% for Cr (VI) and 65.4 to 90.4% for nitrate. The results showed that the presence of chromium ions in the solution reduced the amount of nitrate removal from water.

5- The Box–Behnken design was employed to develop a mathematical model for predicting the removal efficiency of Cr (VI) and nitrate by the nanofiltration process.

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