

Investigation of effective parameters on the performance of NF membrane in simultaneous removal of Cr (VI) and Cu from contaminated water

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ABSTRACT: The present study investigates an NF process for removal of copper and hexavalent chromium, studying the effect of pH (5, 7, 9) as well as contaminants' concentration (50, 500, 5000 µg/L) at a constant pressure of 8 bar; with the recovery rate, regulated at 75±2%. To determine the main factors, affecting the system performance, and evaluate the interaction effects among the factors, the experiment is designed via RSM Method. The chrome shows a higher rejection, compared with Copper, all over the range of investigated factors. As Copper concentration grows, Cu removal efficiency drops while, the Cr (VI) removal efficiency ascends. Also by increasing chrome concentration, the Cu removal efficiency decreases, while Cr (VI) removal efficiency increases. Results show that with an increase in pH, the Cu removal drops and Cr removal is increased. The pH is the main parameter, influencing the removal rate. It has been found that the maximum removal efficiency is up to 99% and 73% for Cr (VI) and Cu, respectively. There is an adequate agreement between real data and that obtained from the models (R^2 was found to be 0.9889 and 0.9664, for Cu and Cr (VI) rejection, respectively).

Keywords: copper, environment, hexavalent chromium, nano filtration, water treatment.

INTRODUCTION

Following technological improvements and growth of different industries, wastewater from industrial processes are counted as a serious threat for the environment (Elcik et al., 2015; Ahmadpour & Jalilzadeh Yengejeh, 2016). In many areas in the world water bodies have been contaminated with heavy metal ions due to the discharge of industrial wastewater (Jadhav et al., 2016). Many industrial activities, including mining

drainage, smelting, metal finishing, operations of metal surface treatment, plating, electrolysis, electric device manufacturing, tannery operations, and fertilizer and chemical production industries are major sources of heavy metal contamination (Swarnalatha & Radhakrishnan, 2015; Kazemi et al., 2016). Heavy metal ions are responsible for many health problems in humans as well as in animals and plants (Lidén & Persson, 2016; Zeng et al., 2016).

Copper is a chemical element, indicated

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by the symbol Cu, whose atomic number is 29. Cu (II) ion, being toxic and carcinogenic, is one of the heavy metals with detrimental effects on living organisms (Tsai et al., 2016). Excessive ingestion can lead to health problems such as liver damage, kidney failure, acute poisoning, and gastrointestinal bleeding (Sargin & Arslan, 2016). Studies, aiming to remove Cu (II) ions effectively from contaminated water and wastewaters, are highly required. Given the health effect of copper, the World Health Organization (WHO) established a suitable and allowable limit of 1500 and 50 µg/L respectively, for presence of the metal in drinking water (WHO, 2004). Chromium (Cr), with atomic number 24, is located in group VI of the periodic table. It is widely used in many industrial processes such as mining the preservation of wood, textile dyeing, leather tanning, electroplating, metal finishing, timber treatment, and some other chemical industries, thus it contaminates the surface and ground waters (Elabbas et al., 2016; Jiang et al., 2016; Romero-Gonzalez et al., 2005). The level of chromium, allowed in drinking water was set at 0.05 mg/L by WHO (2004). Chromium exhibits variable oxidation states (from -2 to +6); however, its dominant oxidation states in natural waters are Cr (III) and Cr (VI) (Kaya et al., 2016; Goswami & Majumder, 2015; Erdem & Tumen, 2004).

There have been many techniques employed for heavy metal removal in wastewaters, such as membrane filtration, precipitation, chelation/complexation, ionexchange, oxidation/reduction, and adsorption (Shahram Forouz et al., 2016; Yousefi et al., 2016). Nowadays, there is a worldwide concern and effort for development of wastewater treatment technologies. However, membrane-based separation techniques have been widely employed in different countries to treat a wide variety of contaminated waters and wastewaters (Akbari et al., 2010). The application of membrane process in water

and wastewater treatment offers a number of advantages such as low energy requirement, no need of adding further chemicals, greater flexibility in designing systems with easy scale-up products of high quality and variable operating parameters, separation of the continuous mode, easily coupled with other processes and operations (hybrid processes), and environmentally friendliness (Zhang et al., 2013). The Nano Filtration (hereby NF) systems have been introduced as a suitable and efficient method. The effectiveness of NF membrane processes in water and wastewater treatment has now become one of the most reliable standard techniques to obtain good quality drinking water.

For a particular membrane and feed characteristics, the removal efficiency in a NF process is influenced by parameters such as ionic strength (Hafiane et al., 2000), pH (Hafiane et al., 2000; Taleb-Ahmed et al., 2002; Mahmoodi et al., 2014), pressure (Taleb-Ahmed et al., 2002; 2004), initial concentration (Muthukrishnan et al., 2008; Wang et al., 2007), cross flow rate (Anupam et al., 2011), etc. Earlier, Cr removal via membrane-based separation was attempted by several researchers (Taleb-Ahmed et al., 2002; Muthukrishnan & Guha, 2008; Malakootian et al., 2013; Barikbin et al., 2015). Also there are different researches that have been used for Cu rejection from contaminated water through NF process (Al-Rashdi et al., 2013; Bunani et al., 2013).

The main goal of this study is to evaluate the efficiency of NF system in simultaneous removal of chrome and copper ions from contaminated water along with the effective factors of its performance. Another aim of this study is to investigate optimal operating condition for NF process for the maximum removal efficiency of Cr (VI) and Cu ions.

MATERIALS AND METHODS

The pH of these solutions was adjusted with hydrochloric acid (HCl) and sodium

hydroxide (NaOH) solutions. The temperature of the solution was kept constant at room temperature (25°C). Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were used to make the feed solution ready. All used chemical materials were supplied by Merck Company of Germany. The pilot consisted a feed tank, a pump, and a spiral module. The experimental setup is shown in Figure 1.

Using 60-65 L/hr NF pilot, accompanied by a semipermeable polyamide membrane (Babol Noshirvani University of Technology), the present study dealt with the trend in synthetic wastewater treatment after changing levels of factors, in pollutants mixture. Table 1 shows the main characteristics of membrane.

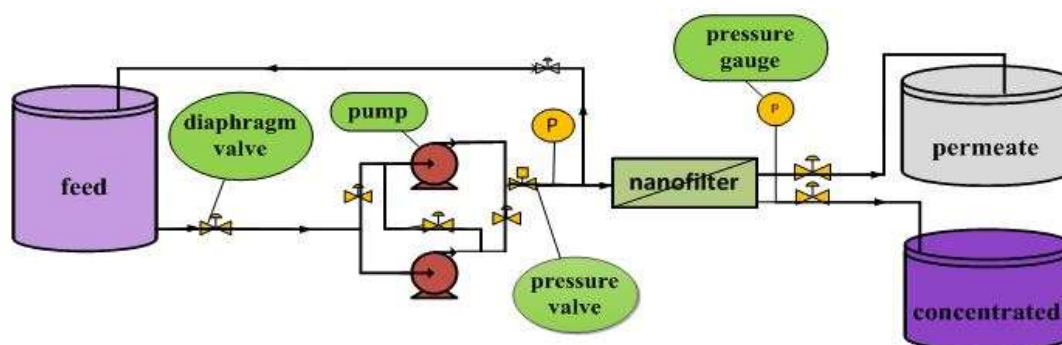


Fig. 1. Schematic display of the experimental setup, used in this study

Table 1. The specifications of the membrane

Specification	Allowed range
Maximum operating pressure (bar)	31
Maximum operating temperature (°C)	45
Continuous operating pH range	3-12
Active surface (m ²)	0.35
Isoelectric point	4.6
Surface charge	Negative

The feed tank, with a capacity of 70 L, was provided to store and supply effluent to the system as well as collect the recycled concentrate. A pump, capable of maintaining a pressure of 8.5 bar, was installed to transport feed liquid throughout the system. The feed solution was pumped to the membrane by the diaphragm-type pump. The maximum output flow of pump was 1.6 L/min and the filtration in the module occurred in cross-flow. The membrane was cleaned before each cycle by back-washing for half an hour.

Concentrations of Cu and Cr ions were determined by Philips PU 9100X Atomic Absorption Spectrometer (AAS). Samples of

these solutions were collected every 15 min during the analysis. The solutions' pH was measured too, using pH-Meter (model MP 220). Calibration curves of the tested ions were drawn with different concentrations. The instrument was calibrated regularly with its calibration verified before each sample set. All measurements were performed according to water and wastewater examination methods (Arnold, 2012). For all experiments, feed temperature and optimum pressure were set at $20 \pm 1^\circ\text{C}$, and 800 kPa, respectively and the recovery rate was regulated at $75 \pm 2\%$. Equation 1 for rejection is as follows:

$$R(\%) = \left(1 - \frac{C_p}{C_o}\right) \times 100 \quad (1)$$

where C_p is the concentration of the permeate, C_o the concentration of the feed, Q the filtration flow rate, Q_p the quantity of feed water; and Q_f the quantity of the permeate.

Selected factors and their corresponding experimental levels were determined based on previous experiences. The type of the experimental design, used for this investigation, was Box-Behnken for three levels and three factors (15 runs) with two replications in the center of the plan, considering chrome and arsenic rejection as a response. Results got analyzed with RSM model, in which the relation between the removal efficiency of the responses (Cr (VI) and Cu) and the variables (Cr and Cu concentration, pH and recovery rate) were analyzed at 95% confidence level. Table 2 shows the levels of the actual and coded factors.

A mathematical model in the form of a second order polynomial was formed to predict the response as a function of independent variables, involving their interactions. Generally the performance of the process is expressed by the following quadratic equation (Myers and Montgomery, 2002; Ahmadi et al., 2003):

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum b_{ij} x_i x_j \quad (2)$$

where Y is the predicted response; b_0 , the interception; b_i , the linear term; b_{ii} , the squared term; and b_{ij} , the interaction term, while x_i and x_j represent the actual independent variables.

The experimental design matrix, contour plots, ANOVA studies, and normal plot of the residuals were generated using the Design Expert 8.0.6 software.

RESULTS AND DISCUSSION

Table 3 shows the removal percentage values for each run of the Box-Behnken experimental design. The maximum removal efficiency was found to be up to 99% and 73% for Cr (VI) and Cu, respectively. In this condition the values of Cr and Cu concentration in the outlet from the NF unit were 5 µg/L and 133 µg/L, respectively, being within the ranges, considered appropriate and allowable by World Health Organization.

Each factor's significance as well as its interaction was determined using p -value. It should be pointed out here that as F -value ascends, its effect on the response grows. Table 4 and 5 represent the ANOVA table for removal efficiency of Cr (VI) and Cu, respectively, which demonstrate factors' significance and their interactions at various levels. As it can be seen in Table 4 and 5 for Cr (VI) and Cu removal, the initial concentration, pH, and the interaction between initial concentration of chrome and pH were importance variables in NF process, with very small P values ($P < 0.05$). The pH is the main parameter to affect the removal rate. According to the results, pH contributed to the response for Cr (VI) and Cu removal. The impacts of the interaction between chrome concentration and pH ($A*B$) Band on the response can be adjusted by the latter. Fig. 2 illustrates the transformation of chrome ions with pH.

Table 2. Factor levels and coded values used in the experimental design

Factors	(-1)	(0)	(1)
Cr concentration (µg/L)	50	500	5000
Cu concentration (µg/L)	50	500	5000
pH	5	7	9

Table 3. The Box-behnken experimental design and results for the simultaneous removal of Cr (VI) and Cu

No.	Cr concentrationn (µg/L)	pH	Cu concentration (µg/L)	Cr (VI) removal (%)	Cu removal (%)
1	50 (-1)	9 (1)	500 (0)	98.1	64
2	500 (0)	5 (-1)	5000 (1)	89.3	69.1
3	5000 (1)	7 (0)	5000 (1)	96.5	58.9
4	500 (0)	5 (-1)	50 (-1)	89.2	73.5
5	50 (-1)	5 (-1)	500 (0)	85.2	72.6
6	5000 (1)	7 (0)	50 (-1)	93.2	62.3
7	500 (0)	7 (0)	500 (0)	93.6	64.9
8	500 (0)	7 (0)	500 (0)	94.7	63.6
9	500 (0)	9 (1)	5000 (1)	98.9	58.7
10	500 (0)	7 (0)	500 (0)	94.3	64.2
11	500 (0)	9 (1)	50 (-1)	95.8	59.8
12	50 (-1)	7 (0)	50 (-1)	90.8	67.9
13	5000 (1)	9 (1)	500 (0)	99.9	56
14	50 (-1)	7 (0)	5000 (1)	94.5	68.6
15	5000 (1)	5 (-1)	500 (0)	93.7	69.8

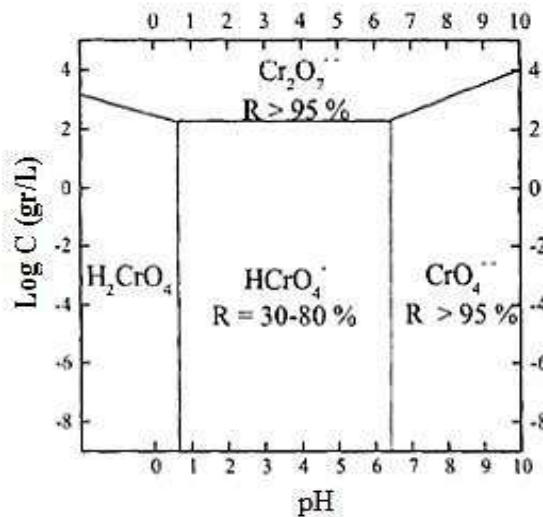


Fig. 2. The transformation of chrome ions with pH (Taleb-Ahmed et al., 2002)

The chrome ions change from HCrO_4^- to CrO_4^{2-} structure and transform as pH alters from 2 to 11. Therefore their electrical charge and ionic radius change can affect the removal efficiencies.

The model is given by Equation (3), and represents Cr (VI) and Cu rejection (Y_1 , Y_2) as a function of Cr concentration (X_1), pH (X_2), Cu concentration (X_3), and

$$Y_1 = 94.2 - 1.775 X_1 + 4.47 X_2 + 1.275 X_3 - 1.8 X_1 X_2 - 0.1 X_1 X_3 + 0.75 X_2 X_3 + 0.3 X_1^2 - 0.15 X_2^2 - 0.75 X_3^2$$

$$Y_2 = 64.23 - 3.38 X_1 - 5.68 X_2 - 1.025 X_3 - 1.25 X_1 X_2 - 1.25 X_1 X_3 + 0.825 X_2 X_3 + 0.383 X_1^2 + 1.23 X_2^2 - 0.1916 X_3^2$$

In the regression equation above, positive and negative signs before each term indicate synergistic and antagonistic

recovery rate (X_4). Values of all coefficients of Equation (3) were calculated, using a multiple regression analysis technique included in the RSM from the experimental data with the help of Design Expert 8.0.6 software to obtain the regression equation for Cr (VI) and Cu removal as shown below:

effects, respectively. In order to determine the model's adequacy, the lack-of-fit test, the graphic analysis of the residuals, and

the regression parameter R^2 were used. ANOVA values, shown in Table 4 and 5, indicate that the lack-of-fit of the model was not statistically significant (p-value=0.1212 and 0.2822).

The value of R^2 determinant was found to be 0.9889 and 0.9664 for Cr (VI) and Cu rejection, respectively. Due to the proximity of R^2 to one, the proposed models were acceptable and the observed variation on the response (Y_1 and Y_2) were explained by the model. The graphic analysis of the residuals showed that they

experienced approximately a normal distribution and were independent, without any pattern or rare tendency. Thus the fitted model was adequate to describe the behavior and prediction of Cr (VI) and Cu simultaneous removal based on the investigated factors.

Figures 3 and 4 show the normal probability plotted versus residual (in percent). This plot was used in order to identify and make sure that the normal distribution was error-free. Hence, the plotted patterns must not be in an S-shaped curve.

Table 4. Analysis of the variances for Cr (VI) removal rate

Model terms	Sum of the error squares(SS)	Mean square error(MS)	Degree of freedom	F-ratio	P-value	Status
Model	216.27	24.03	9	15.99	0.0035	Significant
A: Cr concentration	25.2	25.2	1	16.77	0.0094	Significant
B: pH	160.2	160.2	1	106.59	0.0001	Significant
C: Cu concentration	13	13	1	8.65	0.0322	Significant
A *B	12.96	12.96	1	8.62	0.0324	Significant
A *C	0.04	0.04	1	0.027	0.8768	Not significant
B * C	2.25	2.25	1	1.5	0.2756	Not significant
A *A	0.33	0.33	1	0.22	0.658	Not significant
B* B	0.083	0.083	1	0.055	0.8235	Not significant
C* C	2.08	2.08	1	1.38	0.2927	Not significant
Lack of fit	6.89	2.3	3	7.41	0.1212	Not significant
Pure Error	0.62	0.31	2	-	-	-

Table 5. Analysis of variance for Cu removal rate

Model terms	Sum of the error squares(SS)	Mean square error(MS)	Degree of freedom	F-ratio	P-value	Status
Model	381.8	42.42	9	49.68	0.0002	Significant
A: Cr concentration	91.8	91.8	1	107.52	0.0001	Significant
B: pH	258.78	258.78	1	303.08	< 0.0001	Significant
C: Cu concentration	8.41	8.41	1	9.84	0.0257	Significant
A *B	9.61	9.61	1	11.26	0.0202	Significant
A *C	4.2	4.2	1	4.92	0.0773	Not significant
B * C	2.72	2.72	1	3.19	0.1342	Not significant
A *A	0.54	0.54	1	0.64	0.4615	Not significant
B* B	5.62	5.62	1	6.58	0.0504	Not significant
C* C	0.14	0.14	1	0.16	0.7067	Not significant
Lack of fit	4.27	1.29	3	0.16	0.2822	Not significant
Pure Error	0.85	0.42	2	-	-	-

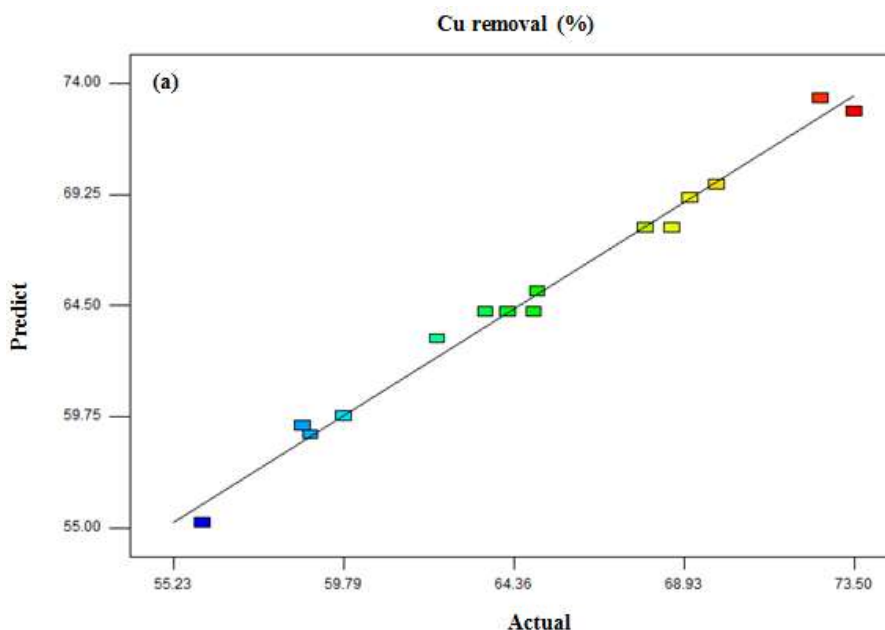


Fig. 3. The actual versus predict plot (a): Cu removal

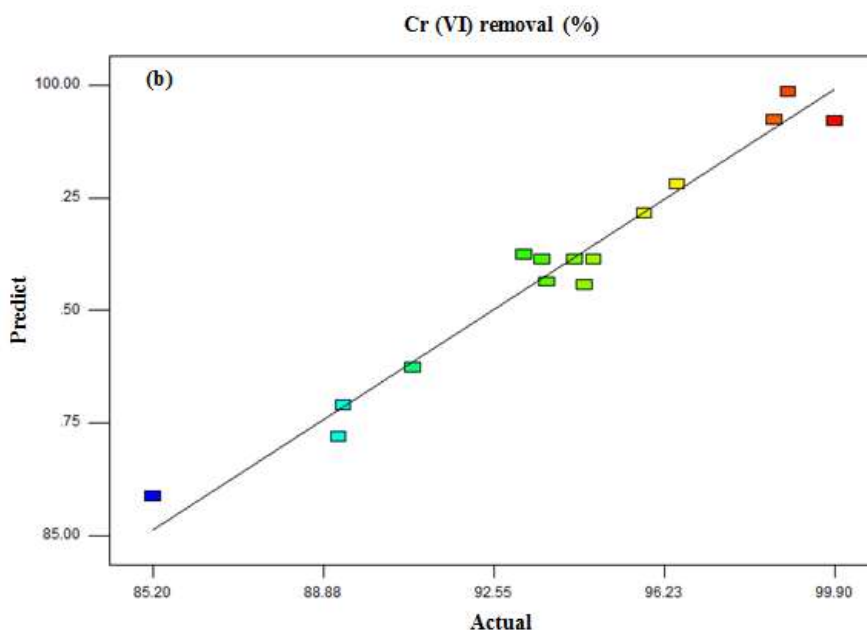


Fig. 4. The actual versus predict plot (b): Cr (VI) removal

As it can be observed in Figures 3 and 4 the curves were not S-shaped and the tendency tended to be a straight line, indicating that the model was acceptable.

Findings showed that Cr (VI) removal efficiency was enhanced as the concentration of Chrome rose, while copper removal efficiency declined. The maximum removal efficiency for multiple

metal mixtures elimination (copper and chrome) was 73.5% and 99.9%, respectively. When the chrome concentration increased, its cation concentration (K^+) followed the same example, in turn resulting in the formation of a cation layer on the membrane surface as well as the repulsion force between negatively-charged membrane surfaces and

the reduced anions, hence both chrome and copper anions were enabled to move closer to the membrane surface. Since the copper ionic radius is smaller than chrome ions and is positively-charged, they could cross through membrane pores more easily, and the copper removal efficiency was

decreased consequently. In order to maintain the electrical balance between two sides of the membrane, the chrome removal efficiency should be increased. Figures 5 and 6 illustrate the removal of chrome with feed concentration.

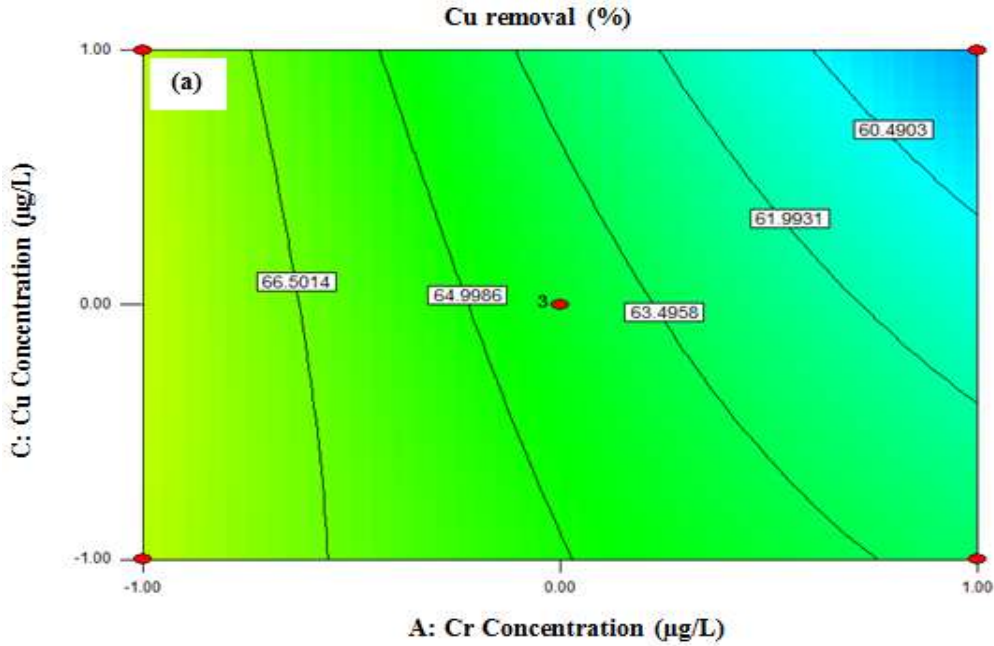


Fig. 5. The contour plots for the Cr and Cu concentration (a): Cu rejection

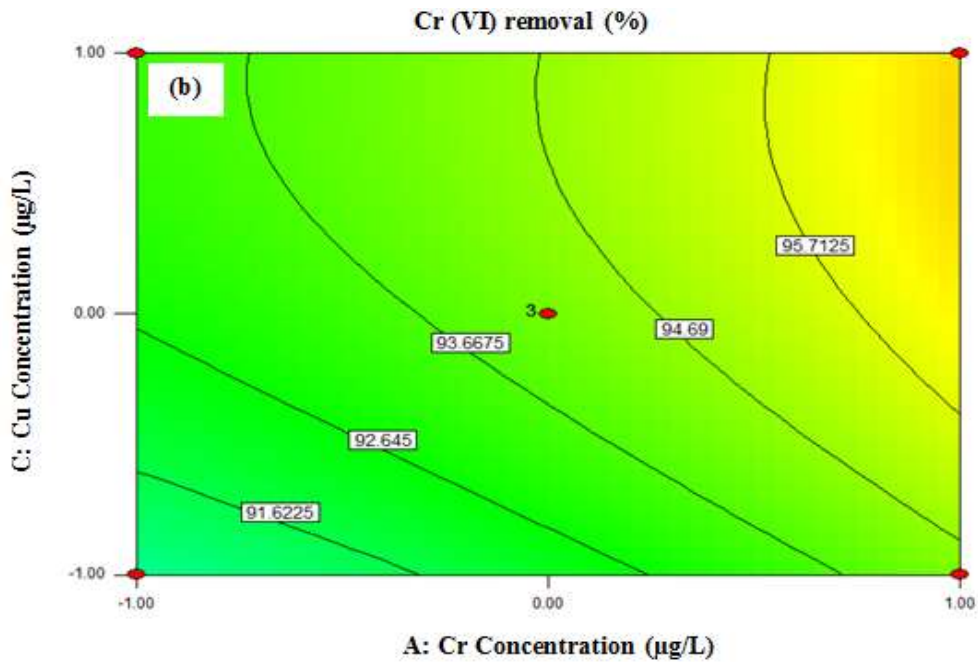


Fig. 6. The contour plots for the Cr and Cu concentration (b): Cr (VI) rejection

Same similar trend mechanism for Cr concentration's influence on the Cr removal has been presented by other researchers (Barikbin et al., 2015; Hafiane et al., 2007; Malakootian et al., 2013).

According to Figures 7 and 8, an increase in copper concentration raised Cr (VI) and lowered Cu removal efficiencies, as the copper ion is positively charged and ionic radius of copper is larger than the chrome.

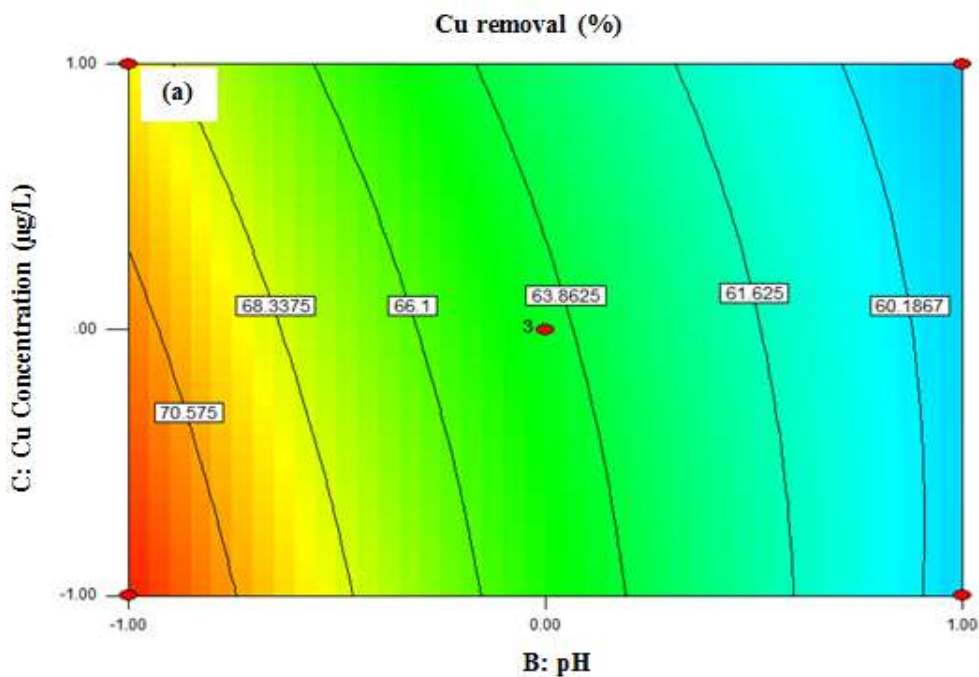


Fig. 7. The contour plots for pH and Cu concentration (a): Cu rejection

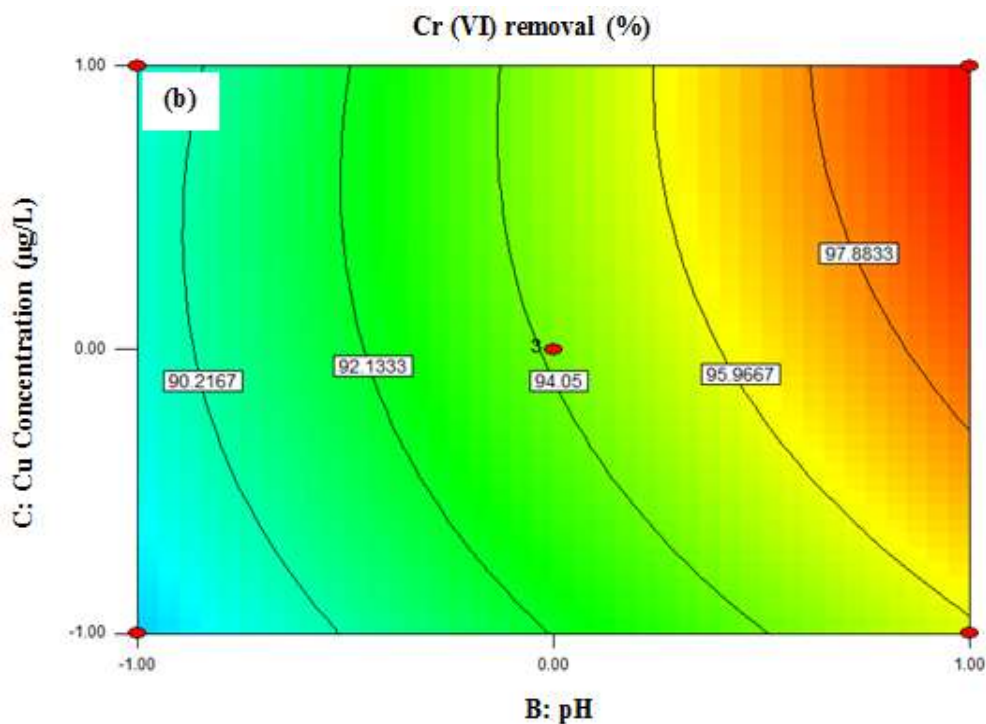


Fig. 8. The contour plots for pH and Cu concentration (b): Cr (VI) rejection

Therefore, by increasing copper concentration, the repulsion force between the membrane and the copper ascends. Since a limited number of molecules are able to pass through the pores, while competing with chrome to cross the membrane, more copper ions manage to pass through the membrane, thus its removal efficiency was decreased. The effect of Cu concentration and the removal

efficiency of Cu by NF membrane have been reported by other researchers too (Malakootian et al., 2013; Al-Rashdi et al., 2013).

Figures 9 and 10 show the impact of pH on the rejection of Cr (VI) and Cu. Chrome rejection by the membrane rose as the pH was increased. It was observed that the rejection of copper ion declined as the solution's pH level was increased.

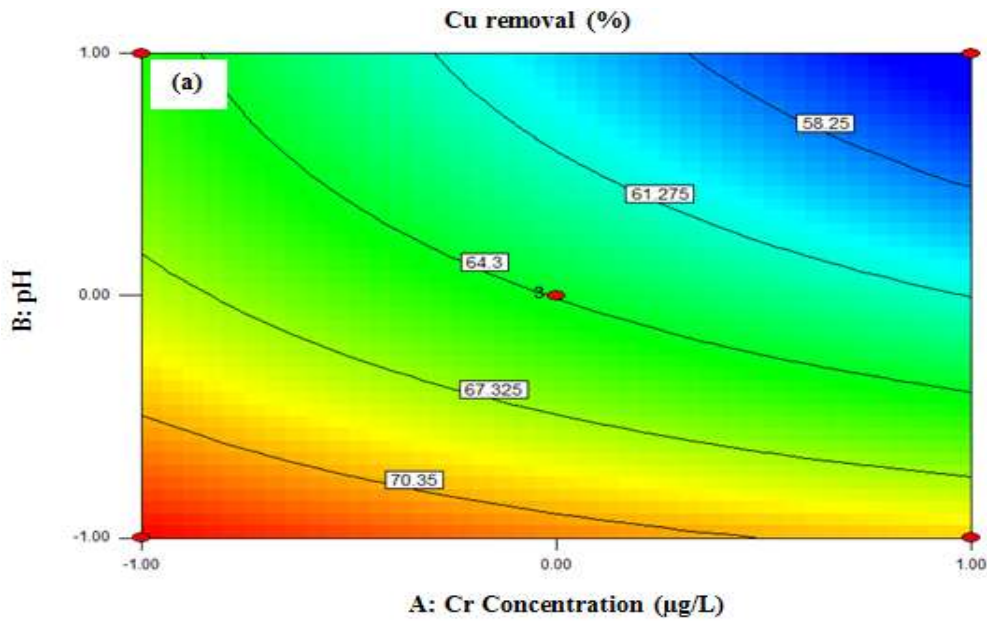


Fig. 9. The contour plots for pH and Cr concentration (a): Cu rejection

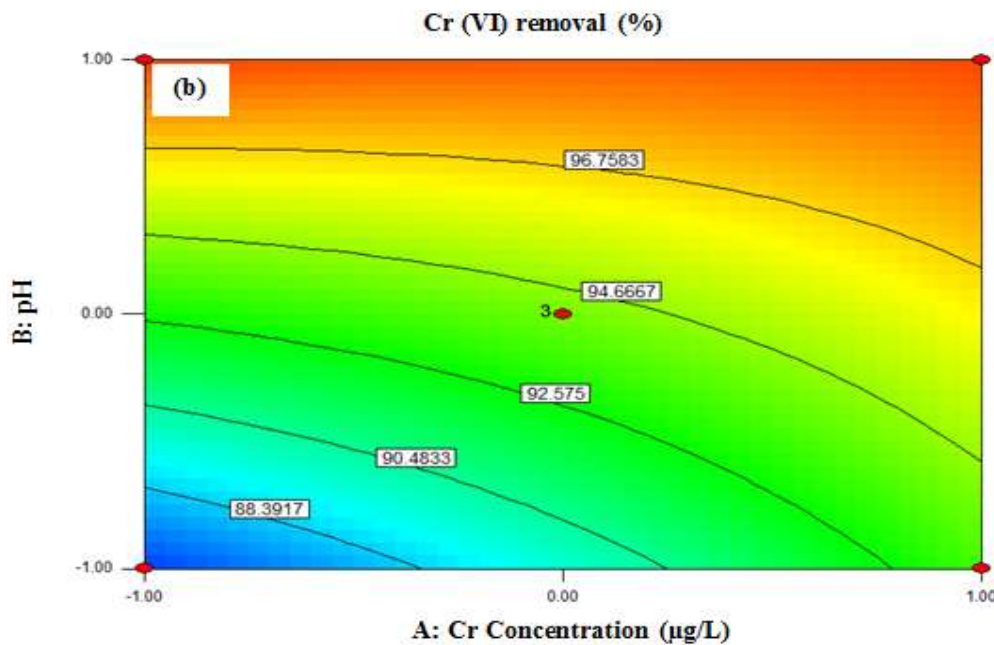


Fig. 10. The contour plots for pH and Cr concentration (b): Cr (VI) rejection

The Iso-Electric Point (IEP), at which the membrane charge is equal to zero, is located around 4.6. In this study the ranges of pH were higher than the point of zero charge or IEP. The IEP of membrane indicated that the surface of membrane was negatively charged in the pH range, selected for the investigation, and the effective charge density dropped at lower pHs. When the solution's pH rose, the membrane's negative charge got stronger; therefore, the electrostatic charge repulsion of chrome ions as well as attraction of copper ions with membrane surface was increased.

Consequently, the chrome removal efficiencies ascended, while those of copper removal descended. Due to the transformation of chrome and arsenic ions into divalent ions (CrO_4^{2-}), the Cr (VI) rejection had a much higher rate, compared to monovalent ions (HCrO_4^-) at higher pH values. Similar trends of rejection at pH values above the IEP for NF membrane have been reported by Malakootian et al. (2013) and Al-Rashdi et al. (2013).

CONCLUSION

Based on the experimental data and ANOVA table, initial concentration, pH, and interaction between initial concentration of chrome and pH had a significant influence on simultaneous removal of Cr (VI) and Cu ions from contaminated water, with the pH having the highest effect on the rejection. Results show that by increasing pH, the removal rate of chrome ions was increased and the copper removal was decreased. With an increase in copper concentration, Cr (VI) removal efficiency rose, while the Cu removal efficiency dropped to 56%. Similarly, raising chrome concentration led to increased Cr (VI) removal efficiency, while the Cu removal efficiency declined. Arsenic showed a higher rejection, when compared with chrome, within the range of all investigated factors. Results indicate that there is an adequate agreement between experimental data and those, obtained from the models. The maximum

removal efficiencies, predicted at optimum conditions by Design Expert software, were approximately 99.9% and 73.5% for Cr (VI) and Cu rejection, respectively.

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