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Remediation of contaminated water from nitrate and diazinon by nanofiltration process

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ABSTRACT

Nitrate and diazinon pesticide is among the environmental challenges which enter water resources, mostly as a result of agricultural activities. In this study, the effects of diazinon concentration, nitrate concentration and pH on the efficiency of simultaneous removal of contaminants from polluted water were investigated, applying a commercial polyamide nanofilter. Each factor was considered in three levels where diazinon concentration, nitrate concentration and solution pH were in the range of 10–1,000 μg/L, 40–160 mg/L and 5–9, respectively. The experiments were conducted at constant pressure of 6 bar. The response surface method was adopted in the experimental design to obtain the impact of mentioned factors. It was found that increasing diazinon concentration and pH enhance the pesticide removal efficiency up to 94%, while increasing nitrate concentration increases the commercial nanofilter efficiency from 80 to 85%. The diazinon removal percentage at optimum condition was estimated to be about 93% at diazinon concentration of about 90 μg/L, nitrate concentration of about 80 mg/L and pH of 9.

Keywords: Agricultural wastewater; Diazinon; Nanofiltration; Nitrate; Water treatment

1. Introduction

Despite the fact that about two-thirds of the Earth's surface is covered by water, water crisis is one of the humans main concerns. According to United Nations predictions, about 48 countries will be suffering from water shortage by the year 2025 (about 32% of the world population) [1].

The annual consumption of fertilizer in the world was about 165 million tons in the year 2010, but it has been increased up to 185 million tons by the year 2012. About 7.4 tons of nitrogen fertilizer was consumed in Asia between years 2011–2012 [2].

According to Iranian national water standard, about 30–35 milliard cubic meter agricultural wastewater is produced every year, and as for irregular use of fertilizers, agricultural pesticides and herbicides in farms, underground and surface water sources are in the danger of contamination. One of the most widely used pesticides in this context is diazinon. The USEPA drinking water health advisory level for diazinon is 0.6 μg/L. The USEPA drinking water health advisory level is the concentration in drinking water that would result in no adverse human health effect for an adult lifetime exposure of 70 years [3].

The presented results by the Gilanian agricultural Jihad organization of Iran during the years 2008–2009

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indicate that about 376 tons of diazinon are used for weed eradication in this area. On the other hand, one of the indexes of surface and underground water sources contamination by nitrogen fertilizer is the presence of nitrate ion in water [4]. Nitrate can cause syndromic diseases in children under the age of six and formation of nitrozamin carcinogenic compound in adults [5]. According to the World Health Organization and Iranian national standard, the maximum allowable nitrate concentration in drinking water is 50 mg/L [6].

One of the modern, efficient and compatible-with-environment technologies in removing and elimination of pesticides from contaminated water is nanofiltration process. This process is a membrane process between ultrafiltration and reverse osmosis [7]. The NF separation mechanism is based on the molecular size, diffusivity difference, feed components solubility and electrical interaction between membrane surface and existing ions in the feed [8]. In recent years, applying nanofiltration in selective experiments; simultaneously reduction of organic and inorganic contaminants, water hardness elimination, disinfection and nitrate reduction; and removal of micro-pollutants are some of the reasons that this process has been considered as one of the best membrane processes in removing pesticides [9,10].

This study investigates the influence of the effective parameters on the performance of NF process for nitrate and diazinon pesticide reduction from contaminated water. The response surface methodology is adopted in order to design the experiments, so not only the number of experiments is reduced but also a more accurate analysis of results is achieved.

2. Materials and methods

2.1. Materials

KNO_3 (CAS No. 7757-79-1), HCl (%37) (CAS No. 7647-01-0), NaOH (CAS No. 1310-73-2) provided by Merck Company of Germany and commercial diazinon insecticide (%60 emulsion, CAS No. 333-41-5) supplied by Iranian Giah Sam Company, were used. Diazinon pesticide and potassium nitrate were dissolved in distilled water for preparation of the system feed.

2.2. The pilot setup

In this study, an experimental continuous nanofiltration system was used. Schematic view of this system is shown in Fig. 1. A Korean spiral wound polyamide membrane was used in the nanofilter module. The membrane specifications are presented in Table 1. The pumps used in this system are of diaphragmic-type. The pumps output flow and pressure are 0.8 liter per minute and 6 bar, respectively.

2.3. Experimental procedure

The factors and their selected levels are presented in Table 2.

The factor levels are selected based on their real range in water sources and the authors' experience. The maximum diazinon concentration in one of the waste water treatment plant in Iran is reported as 852 μg/L. The nitrate concentration is about 140 mg/L in most surface water of the north of Iran [11]. For increasing pH and NaOH, and for decreasing pH, hydrochloric acid is used. The feed temperature was

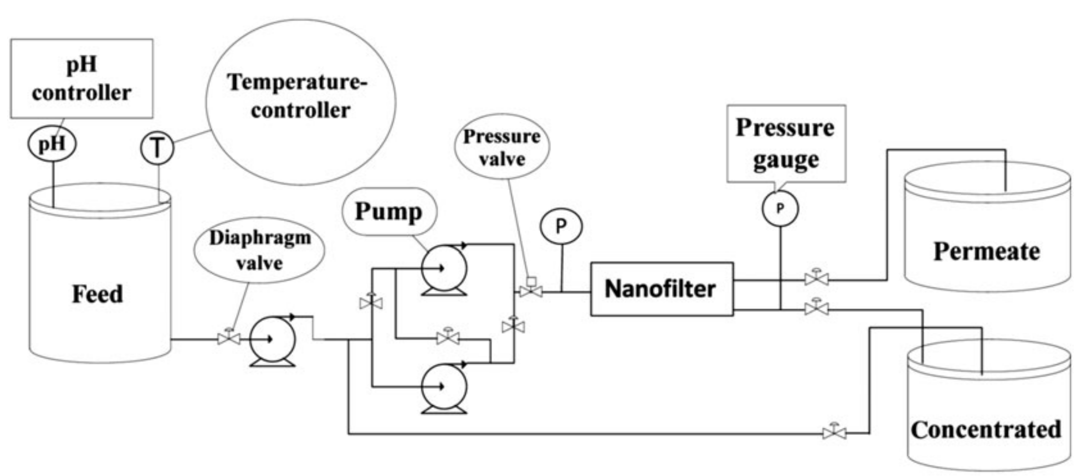

Fig. 1. Schematic view of the pilot system.

Table 1
Commercial polyamide TFC membrane specifications

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

Table 2
Levels and selected parameters

Levels	Diazinon concentration (μg/L)	Nitrate concentration (mg/L)	pH
1	1 ± 10	40 ± 2	5 ± 0.1
2	100 ± 5	80 ± 3	7 ± 0.1
3	1,000 ± 10	160 ± 5	9 ± 0.1

set at 20 ± 1˚C and the recovery percentage was about 75 ± 3%. All measurements were performed according to the water and wastewater standards [12].

In order to measure nitrate concentration, a spectrophotometric device V-570 provided by Japanese JACKSO company was used. The diazinon concentrations in contaminated water were analysed by high performance liquid chromatography (HPLC—KNAUER model—Germany). The HPLC-column used was a C18 column, 150 mm in length and 4.6 mm in internal diameter. The mobile phase was acetonitrile: water (70: 30) [13–15]. The UV detector was operated at a wavelength of 220 nm. In order to calculate the NF contaminant removal percentage, the following equation is used:

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

where R denotes the removal percentage, and C_p and C_0 are the contaminant concentration in the permeate and feed water, respectively.

2.4. Response surface methodology

Response surface methodology is an effective method for response optimization. In this method, Box–Behnken design is adopted to optimize the responses [16]. This design includes three, trihedral factors, and presents 15 experiment runs to conduct. The Design Expert software 8.0.1 was used for this design and the statistical analysis of the results. The confidence level was taken as 95%.

In order to avoid probable errors due to the systematic bias, the experiments were conducted randomly. In this study, the purpose is maximizing nitrate removal percentage that is considered as response.

3. Results and discussion

The measured Diazinon removal efficiency from contaminated water, based on the Box–Behnken

Table 3
Box–Behnken method results

Experiment no.	Nitrate concentration (mg/L)	pH	Diazinon concentration (μg/L)	Diazinon removal percentage
1	80 ± 3	7 ± 0.1	100 ± 5	89.9
2	40 ± 2	5 ± 0.1	100 ± 5	85.3
3	40 ± 2	9 ± 0.1	100 ± 5	91.4
4	40 ± 2	7 ± 0.1	1,000 ± 10	90.8
5	40 ± 2	7 ± 0.1	10 ± 1	80.9
6	160 ± 5	5 ± 0.1	100 ± 5	88
7	160 ± 5	9 ± 0.1	100 ± 5	92.2
8	80 ± 3	9 ± 0.1	10 ± 1	88.7
9	80 ± 3	7 ± 0.1	100 ± 5	91.1
10	80 ± 3	9 ± 0.1	1,000 ± 10	95
11	80 ± 3	5 ± 0.1	1,000 ± 10	86
12	80 ± 3	7 ± 0.1	100 ± 5	88.6
13	80 ± 3	5 ± 0.1	10 ± 1	73.1
14	160 ± 5	7 ± 0.1	10 ± 1	81.4
15	160 ± 5	7 ± 0.1	1,000 ± 10	91.5

Table 4
Analysis of variance for diazinon removal rate

Model terms	Mean square	Sum of squares	df	F-value	P-value	Status
Model	45.30	407.72	9	7.7	0.0185	Significant
A: Nitrate concentration	2.76	2.76	1	0.47	0.5238	Not significant
B: Dizinon concentration	192.08	192.8	1	32.63	0.0023	Significant
C: pH	152.25	152.25	1	25.87	0.0038	Significant
B × A	0.01	0.01	1	0.0017	0.9687	Not significant
C × A	0.9	0.9	1	0.15	0.7115	Not significant
C × B	10.89	10.89	1	1.85	0.2319	Not significant
A × A	0.034	0.034	1	0.0058	0.9424	Not significant
B × B	48.41	48.41	1	8.22	0.0351	Significant
C × C	1.1	1.1	1	0.19	0.6835	Not significant
Lack of fit	8.77	26.3	3	5.61	0.1551	Not significant
Pure Error	1.56	3.13	2	–	–	–

method, is represented in Table 3. The analysis of results variance is represented in Table 4.

The mathematical model based on actual values for diazinon removal percentages is expressed through Eq. (2) as follows:

$$Y = 89.87 + 4.36X_3 + 4.9X_2 + 0.59X_1 - 1.65X_2X_3 - 0.48X_1X_3 + 0.05X_1X_2 - 0.55X_3^2 - 3.62X_2^2 - 0.096X_1^2 \quad (2)$$

where Y, X_1, X_2 and X_3 denote diazinon removal efficiency, nitrate concentration, diazinon concentration and pH, respectively.

In order to recognize the agreement of the experimental response value and the calculated value by the Box–Behnken method, the regression factor R^2 is used. The results indicate that the regression value is about 0.93. Therefore, due to the proximity of the regression value to one, the response surface methodology is an accurate and acceptable method.

Meanwhile, as the *F*-value increases, its effect on the response increases. Diazinon concentration and pH have maximum effects on the diazinon removal efficiency from contaminated water, respectively. But, nitrate concentration does not have so much effect on the diazinon removal percentage. Also, there is no interaction among the mentioned factors as well.

The response surface diagrams for the removal percentage of diazinon as a function of diazinon concentration, nitrate concentration and pH are shown in Fig. 2.

The results of Fig. 2(b) and (c) indicate that with an increase in nitrate concentration, the removal percentage increases slightly. In fact by increasing the nitrate concentration, the cation concentration is increased, which leads to an increase in cation absorption on the membrane surface. Because of this, the repulsion force between nitrate ions and the membrane surface is reduced so that nitrate ions can cross membrane pores more easily. This phenomenon makes some of the membrane pores to be blocked, and the diazinon removal efficiency is increased consequently (due to the fact that diazinon molecules are only separated according to the molecular size).

With an increase in pH, the membrane thin polyamide layer swells, and its pores shrink consequently. It is revealed from the Fig. 2(a) and (b) that with an increase in pH, the removal efficiency of diazinon is increased. The obtained results show that increasing pH from 5 to 9 increases the nitrate removal efficiency from 75 to 90%.

The results of Fig. 2(a) and (c) indicate that by an increase in diazinon concentration, the removal efficiency is increased. In fact, the diazinon molecules have a large molecular radius about 0.834 nm, that would lead to an increase in space prevention; therefore, as its concentration increases, the diazinon removal efficiency is significantly increased [17,18]. Moreover, the presence of potassium cations on the membrane surface as an adsorbed layer causes significant space prevention; hence, the diazinon molecules cannot cross through the membrane pores easily.

The maximum efficiency of 93% is estimated in the concentration levels about 48 mg/L of nitrate, pH of 9 and diazinon concentration about 90 μg/L, which has a reasonably good agreement with the experimental results.

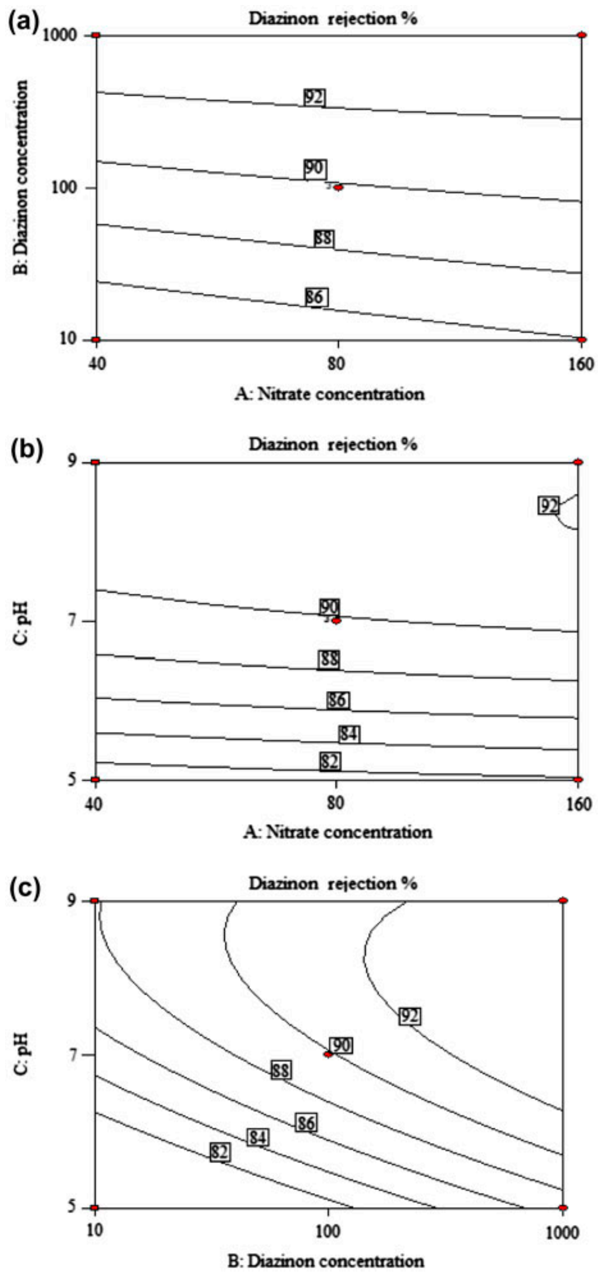

Fig. 2. Contour plots of the diazinon removal efficiency: (a): the effect of diazinon and nitrate concentrations on the removal efficiency of diazinon at constant pH; (b): the effect of pH and nitrate concentration on the removal efficiency at constant diazinon concentration; and (c): the effect of pH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

4. Conclusion

The simultaneous removal of diazinon pesticide and nitrate ions from contaminated water sources by applying NF process was studied. It was found that the diazinon concentration and pH have significant influences on the system performance while the nitrate concentration and interaction effects among the studied factors do not have effective contributions. An increase in diazinon concentration increases the removal percentage up to 90%. By increasing pH, the diazinon removal efficiency is increased. The Box–Behnken design can be adopted to develop a mathematical model for predicting the diazinon removal through NF process. The value of R^2 about 0.93 for the presented mathematical model indicates the high correlation between measured and the predicted values.

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