

Original paper

Interaction between diazinon and nitrate pollutant through membrane technology

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ARTICLE INFO

Article history:

Received 7 October 2013

Received in revised form 12 January 2014

Accepted 28 Feb 2014

Keywords:

Contaminated water

Diazinon

Nitrate

Agricultural wastewater

Environment

Nanofiltration

ABSTRACT

The efficiency of diazinon (as insecticides) and nitrate (related to nitrogen fertilizer) removal from contaminated water is investigated through NF membrane technique. The effects of nitrate concentration (40-160 mg/l), diazinon concentration (10-1000 µg/l) and pH (5-9) on the efficiency of a commercial polyamide nanofilter membrane at a constant pressure of (800 KPa) are investigated. The response surface method (Box-Behnken design) is applied in design of experiment. As the diazinon concentration and pH are enhanced, the contaminant removal efficiency increases from 85 % to 90 %; while nitrate concentration has an opposite effect (removal efficiency reduces about 10 %). The regression models obtained for nitrate and diazinon rejection show good fitting to the experimental results (*r*-squared equal to 94 % and 98 %, respectively). The models are able to predict the evolution of diazinon and nitrate as a function of concentration and pH at a constant pressure.

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1. Introduction

Agriculture is an important industry in many parts of the world while the water pollutants wastewater can cause environmental contamination. This type of wastewater contains different pollutants such as: insecticides, pesticides, organic pollutants, chemical and animal fertilizers (Ongley 1996).

Nitrate as a carcinogenic compound is a key pollutant found in water runoff. According to World Health Organization standard, the maximum allowable concentration of nitrate in drinking water is 50 mg/L (World Health Organization 2003). Diazinon is one of the insecticides and pesticides used in agriculture. This compound is toxic and according to Canadian Standards, the maximum allowable concentration in drinking water is 20 µg/L (Moreno et al. 2005).

In recent years, great attention is paid to the use of nanofiltration (NF) process for simultaneous removal of organic and inorganic contaminants, water hardness, insecticides, heavy metals, nitrate, and micro-pollutants in one step (Kaya et al. 2010). NF is a membrane process occurring between ultrafiltration (UF) and reverse osmosis (RO). In this method, the separation mechanisms are based on the size of molecules, differences in diffusivity and solubility of feed components, and the electrical interaction between the surface of the membrane and ions present in the feed (Bellona and Drewes 2005).

In case of ionic mixtures, the electrostatic interactions with other anions may cause reduced nitrate rejection, particularly in presence of less permeable anions in solution according to Donnan exclusion. The nitrate removal efficiency can be changed in presence of chloride and sulphate (Santafé-Moros and Gozávez-Zafrilla 2010; Paugam et al. 2004). Tepus et al. (2009) investigated the comparison of nitrate and atrazine and dimethyleatrazine (as pesticides) removal from contaminated water using NF membrane. They used a commercial nanofilter membrane (DK- GE Osmonics Desal), and the results indicate that the presence of pesticides reduced the nitrate removal efficiency. A limited number of studies are performed to determine the effect of diazinon on the nitrate ion rejection by NF membranes. Due to the possibility of simultaneous presence of nitrate and diazinon in contaminated water within agricultural wastewater, the focuses of this study is to investigate the effect of diazinon and nitrate concentrations

and pH of solution on the simultaneous removal of the pollutants by applying a commercial NF. For this purpose, the response surface methodology is applied to optimize the response of the amounts of nitrate and diazinon removal.

2. Materials and methods

2.1. Chemicals

Potassium nitrate is supplied by Merck (Germany). Hydrochloric acid and sodium hydroxide are used to adjust the pH. Commercial emulsion of 60 % diazinon pesticide is supplied by Giah Sam Company (Iran). The nitrate and diazinon solutions are prepared using distilled water.

2.2. Experimental set-up

All experiments are performed in a NF pilot plant (Fig. 1), equipped with a spiral wound polyamide membrane (developed by Noshirvani University of Technology, Iran) operated in a continuous flow mode. The characteristics of the membrane are presented in Table 1. Two diaphragm pumps with a capacity of 1.6 liters per minute at a maximum outlet pressure of 8.5 bars are used in the setup.

2.3. Methods

The factors and the selected levels are based on the actual levels in water resources (see Table 2). For all experiments, feed temperature and optimum pressure are set at 20±1 °C, and 800 kPa, respectively. The recovery rate is regulated at 75±2 percent. All the experimental results are obtained when the steady state is achieved. All measurements are performed according to standard methods relevant to water and wastewater (Arnold et al. 2003). The nitrate concentrations are measured by Jasco V-570 spectrophotometer according to standard method (4500B) (Arnold et al. 2003). The diazinon concentrations in contaminated water are measured by high performance liquid chromatography (HPLC- KNAUER model-Germany). The HPLC-column used is a C18 column, 15cm in length and 0.46 cm in internal diameter. The mobile phase was

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acetonitrile:water (70:30). The UV detector is operated at a wavelength of 220 nm. The diazinon and nitrate removal efficiency by nanofilter are determined as follow:

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

where, R represents the removal percentage of diazinon or nitrate and C_p and C_0 are the concentrations of the pollutant in the permeate and the feed water, respectively.

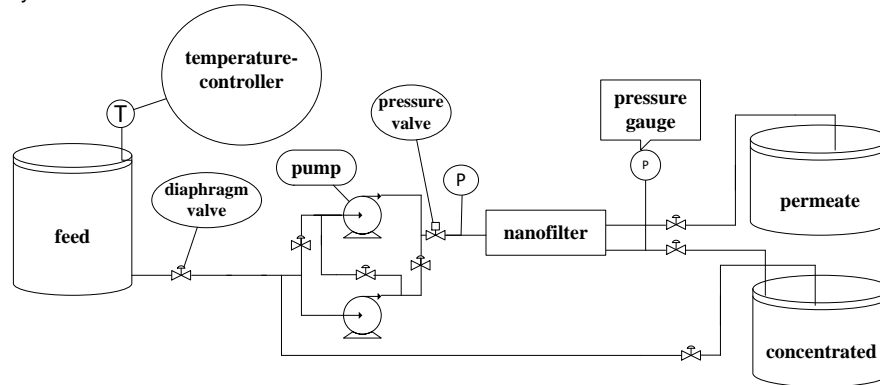


Fig. 1. Schematic view of the experimental setup.

Table 1. The specifications of the commercial polyamide nanofilter membrane.

Specification	Allowed range
Maximum operating pressure (bar)	20
Maximum operating temperature (°C)	50
pH range	3-12
Active surface (m ²)	0.35
Isoelectric point	4.6
Surface charge	Negative

Table 2. Factors and selected levels.

Factor	Level 1	Level 2	Level 3
Diazinon concentration (µg/L)	10±1	100±5	1000±10
Nitrate concentration (mg/L)	40±2	80±3	160±5
pH	5±0.1	7±0.1	9±0.1

2.4. Response surface methodology

Response surface methodology is an effective method for optimizing the responses (Myers and Montgomery 2002). In this method, the Box-Behnken design is used to optimize responses. This design includes three level factors, and a three-time implementation of the experiments in the central surface, in order to obtain the experimental error. A second order polynomial is presented by the design approach to fit the experimental data as (Myers and Montgomery 2002).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \tag{2}$$

where, X_1, X_2, X_3 represent the coded levels of the independent variables and b_0, b_i, b_{ij} ($i, j=1, 2, 3$) the coefficient estimates, and b_0 is the interception, b_i the linear terms, b_{ii} the quadric terms and b_{ij} is the interaction terms.

The statistical analyses of the results are obtained through Design-Expert released 8.0.1 software. The confidence level was selected at 95%. In this study, the objective is to maximize the pollutants removal efficiency.

3. Results and discussion

The levels of independent variables according to the Box-Behnken method and the nitrate rejection percent (Y_1) and the diazinon rejection percent (Y_2) responses for all experiments are presented in Table 3. In order to avoid systematic bias, the experiments are carried out on a random basis.

Table 3. Experimental design (conditions and responses) for nitrate and diazinon rejection.

Run	Nitrate concentration in mg/L	Diazinon concentration in µg/L	pH	Nitrate Rejection Y_1 (%)	Diazinon Rejection Y_2 (%)
1	80±3 (0)	100±5 (0)	7±0.1 (0)	88.2	91.5
2	40±2 (-1)	100±5 (0)	5±0.1 (-1)	81.4	87.1
3	40±2 (-1)	100±5 (0)	9±0.1 (1)	93.5	94.7
4	40±2 (-1)	1000±10 (1)	7±0.1 (0)	90.2	93.5
5	40±2 (-1)	10±1 (-1)	7±0.1 (0)	81.1	81.4
6	160±5 (1)	100±5 (0)	5±0.1 (-1)	77.3	88.2
7	160±5 (1)	100±5 (0)	9±0.1 (1)	90.8	95.6
8	80±3 (0)	10±1 (-1)	9±0.1 (1)	85.6	91.2
9	80±3 (0)	100±5 (0)	7±0.1 (0)	85.9	92
10	80±3 (0)	1000±10 (1)	9±0.1 (1)	96.5	97
11	80±3 (0)	1000±10 (1)	5±0.1 (-1)	79.8	86.3
12	80±3 (0)	100±5 (0)	7±0.1 (0)	89.3	89.8
13	80±3 (0)	10±1 (-1)	5±0.1 (-1)	72.3	77.4
14	160±5 (1)	10±1 (-1)	7±0.1 (0)	78.6	82.3
15	160±5 (1)	1000±10 (1)	7±0.1 (0)	87.6	94.1

3.1. Analysis of experimental data

The analysis of variance is shown in Table 4. A factor is significant when its effect on response is inevitable and cannot be neglected. The effect of any factor is significant when its P -value is less than 0.05, which means that there is only 5% probability of error if a non-

significant factor is considered as a significant one. There is no evidence of 'lack-of-fit' since for diazinon and nitrate removal production P -values are 0.158 and 0.822 (≥ 0.05), respectively.

The greater F -value shows a greater effect of the factor on the response. For removal of diazinon from contaminated water, pH and diazinon concentration effects are significant while nitrate

concentration is not significant. The pH of Solution (X_1) followed by diazinon concentration of (X_2), and nitrate concentration of (X_3) have

the greatest effects on the nitrate removal from contaminated water. Besides, there are no interacting effects among the mentioned factors.

Table 4. Analysis of variance for nitrate (A) and diazinon (B) rejection

Source	d.f.	Seq SS	Adj MS	F	P
(A) Nitrate rejection					
Model	9	609.14	67.68	38.4	0.0004
X3-Nitrate concentration	1	17.7	17.7	10.04	0.0248
X2-Diazinon concentration	1	166.53	166.53	94.49	0.0002
X1-pH	1	386.42	386.42	219.25	<0.0001
X3X2	1	0.0025	0.0025	0.00142	0.9714
X3X1	1	0.49	0.49	0.28	0.6206
X2X1	1	2.89	2.89	1.64	0.2565
X3X3	1	1.39	1.39	0.79	0.4159
X2X2	1	29.21	29.21	16.57	0.0096
X1X1	1	7.63	7.63	4.33	0.0920
Residual error	5	8.81	1.76		
Lack of Fit	3	2.79	0.93	0.31	0.8216
Pure Error	2	6.02	3.01		
Total	14	617.95	1.39		
(B) Diazinon rejection					
Model	9	427.88	47.54	9.68	0.0111
X3-Nitrate concentration	1	8.53	8.53	0.31	0.6006
X2-Diazinon concentration	1	186.24	186.24	37.93	0.0016
X1-pH	1	195.03	195.03	39.72	0.0015
X3X2	1	0.022	0.022	0.00458	0.9487
X3X1	1	0.01	0.01	0.00204	0.9658
X2X1	1	2.4	2.4	0.49	0.5155
X3X3	1	0.021	0.021	0.00423	0.9507
X2X2	1	41.44	41.44	8.44	0.0336
X1X1	1	0.19	0.19	0.038	0.8530
Residual error	5	24.55	4.91		
Lack of Fit	3	21.89	7.30	5.49	0.1580
Pure Error	2	2.66	1.33		
Total	14	452.43			

The mathematical model based on actual values for diazinon and nitrate removal percentages are expressed through Eqs. (3) and (4) as follows, respectively:

$$Y_1 = 91.1 + 0.438X_3 + 4.825X_2 + 4.938X_1 - 0.075X_2X_3 - 0.050X_1X_3 - 0.775X_1X_2 + 0.075X_3^2 - 3.350X_2^2 + 0.225X_1^2 \quad (3)$$

$$Y_2 = 87.8 - 1.488X_3 + 4.563X_2 + 6.950X_1 - 0.025X_2X_3 + 0.350X_1X_3 + 0.850X_1X_2 - 0.613X_3^2 - 2.813X_2^2 - 1.438X_1^2 \quad (4)$$

The regression parameter R^2 is applied to determine the agreement in comparison of the experimental responses to the ones estimated by Box-Behnken method. For diazinon and nitrate rejection, R^2 statistic parameter is 94.6 % and 98.6 %, respectively. Due to their proximity to unity, the proposed models are accurate and acceptable.

3.2. Diazinon removal

The contour plots for diazinon removal at varying pH/diazinon concentration values (a), pH/nitrate concentration values (b) and diazinon concentration/nitrate concentration values (c) are illustrated in Fig. 2, respectively. It should be noted that the third factor, in all these cases, is held constant at the center point, i.e. nitrate concentration of 80 mg/L, diazinon concentration of 100 µg/L and pH of solution 7, respectively. Furthermore, the graphs in Fig. 2 indicate that, in general, pH has a significant effect on diazinon rejection. With an increase in pH, the membrane surface swells causing a decrease in pore size; therefore, molecular transfer becomes difficult, that in turn increases the removal percentage. The results are in agreement with the other reported results (Ahmad et al. 2008).

As the diazinon concentration increases, its removal percentage increases. The reason is that the membrane pores are able to allow a limited number of pesticide molecules to cross and as the number of molecules per unit volume increases; their crossing becomes more

difficult. Due to the same implementation time for every experiment in different concentrations, the number of molecules that cannot cross membrane pores increases; therefore, the diazinon removal percentage by the membrane increases. The same similar trend mechanism is presented by other researchers (Tepus et al. 2009; Košutic et al. 2005).

The data indicated that with an increase in nitrate concentration, the diazinon removal efficiency increased slightly (Fig. 2b and 2c). The reason here is that when nitrate concentration increases, cation concentration increases as well; hence cation adsorption on membrane surface increases (since membrane surface charge is negative) and as a result, the repulsion between the membrane surface and the nitrate ion decreases and the nitrate ions are able to pass easily through the membrane pores. The effect of nitrate concentration and reduction of the removal efficiency of pollutants by nanofilter membrane are reported by other researchers (Richards et al. 2010; Santafe-Moros et al. 2007).

3.3. Nitrate removal

The contour plots for nitrate removal at varying pH/diazinon concentration values (a), pH/nitrate concentration values (b) and diazinon concentration/nitrate concentration values (c), can be observed in Fig. 3, respectively.

The results reveal that the removal percentage decreases with an increase in nitrate concentration. Since the electrical charge of the commercial nanofilter is negative at the operating conditions (isoelectric point of the membrane is 4.6), the removal efficiency of nitrate increases with an increase in pH, as illustrated in Figs. 3-b, c. The results indicate that an increase in pH from 5 to 9, the removal percentage of nitrate increases from about 75% to over 90%. Similar results are reported by Richards et al. (2010).

Here the results indicate that the removal efficiency increases as diazinon concentration increases. The diazinon molecule radius of 0.834 nm (Košutic et al. 2005) is greater than the nitrate ions radius

of 0.128 nm (Wang et al. 2005), thus, an increase in diazinon concentration increases the space barrier, which in turn increases the removal efficiency (Tepus et al. 2009; Plakas and karabelas 2012).

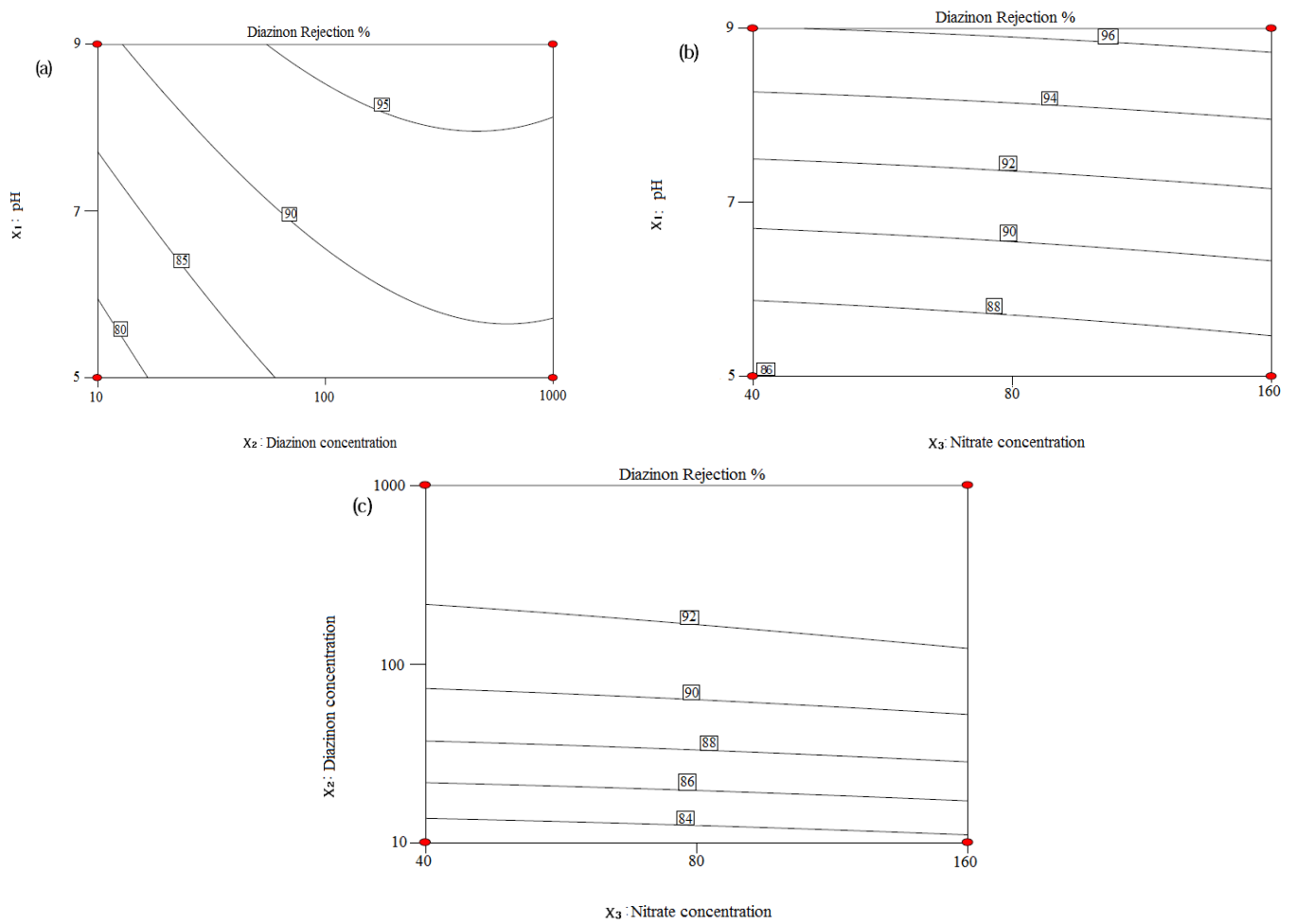
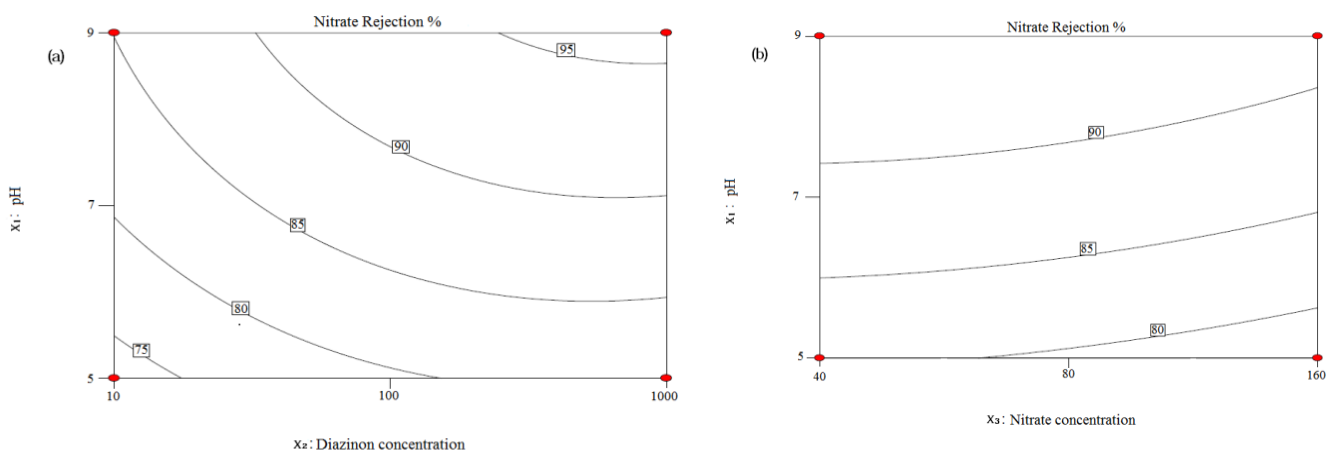


Fig. 2. Contour plots of the removal percentage of diazinon; (a): the effect of pH and diazinon concentration on the removal efficiency at constant nitrate concentration of 80 mg/L; (b): the effect of pH and nitrate concentration on the removal efficiency at constant diazinon concentration of 100 µg/L; (c): the effect of diazinon and nitrate concentrations on the removal efficiency of diazinon at pH=7.



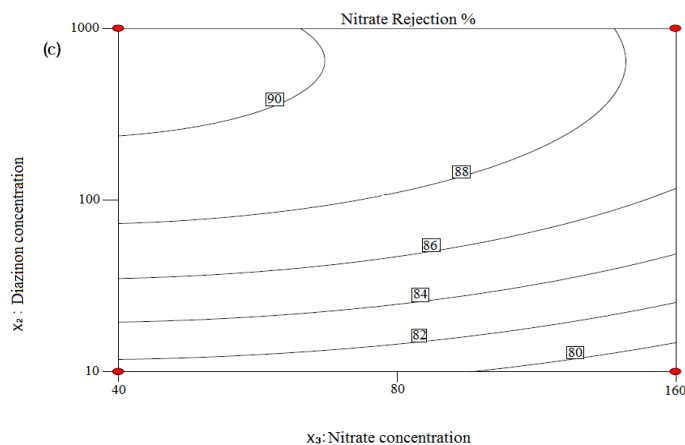


Fig. 3. Contour plots of the removal percentage of nitrate; (a): the effect of pH and diazinon concentration on the removal efficiency at constant nitrate concentration of 80 mg/L; (b): the effect of pH and nitrate concentration on the removal efficiency at constant diazinon concentration of 100 μ g/L; (c): the effect of diazinon and nitrate concentrations on the removal efficiency of nitrate at pH=7.

4. Conclusions

The nanofiltration process using a commercial spiral polyamide nanofilter is efficient for simultaneous removal of nitrate and diazinon from contaminated agricultural wastewater. The physical and chemical

properties of water and the characteristics of membrane have great impacts on the nanofiltration system performance. Higher levels of diazinon and nitrate concentrations can be rejected as diazinon concentration increases at maximum pH of 9, with adjustment of the nitrate concentration close to 45 mg/L.

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