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The role of pH in nanofiltration of atrazine and dimethoate from aqueous solution

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Abstract

This study examined the performance of nanofiltration membranes to retain atrazine and dimethoate in aqueous solution under different pH conditions. Four nanofiltration membranes, NF90, NF200, NF270 and DK are selected to be examined. The operating pressure, feed pesticide and stirring rate were kept constant at 6×10^5 Pa, 10 mg/L and 1000 rpm. It was found that increasing the solution's pH increased atrazine and dimethoate rejection but reduced the permeate flux performance for NF200, NF270 and DK. However, NF90 showed somewhat consistent performance in both rejection and permeate flux regardless of the solution's pH. NF90 maintained above 90% of atrazine rejection and approximately 80% of dimethoate rejection regardless of the changes in solution's pH. Thus, NF90 is deemed the more suitable nanofiltration membrane for atrazine and dimethoate retention from aqueous solution compared to NF200, NF270 and DK.

Keywords: Nanofiltration; Membrane technology; Pesticides; Dimethoate; Atrazine

1. Introduction

The effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. Pesticides that are sprayed in the air may eventually end up in soils or water. The atmosphere is an effective medium which can move airborne pesticides away from their application sites and redeposit them in far away locations [1]. On the other hand, pesticides applied directly to the soil may be washed off by rain into nearby bodies of surface water or percolate through the soil to lower soil layers and groundwater [2]. Pesticides uses and transfers have already extended to urbanized catchments [3]. However, it was noted that the movement of pesticide in and through the soil is primary a function of water solubility of the pesticides and of the adsorption capacities of the soil type [4].

No matter where the application of pesticides is, it will eventually end up becoming a possible threat to human's health via atmosphere and water. The presence of pesticides in water has been reported by previous researchers [5–9]. Low-level residues of pesticides in water generally may not present acute toxicity problems, but chronic effects will likely be of concern [10]. This is because pesticides could have chronic effects such as cancer [11–13], reproductive effects, fetal damage, delayed neurologic manifestations and possible immunologic disorders [12].

In view of this scenario, many studies on separation of pesticides using nanofiltration membranes have been done in recent years. Size exclusion by a nanofiltration membrane is recognized to be the main retention mechanism for pesticides. Other parameters such as hydrophobicity, dipole moment, polarity and charge of a molecule have also been found to influence the rejection performance [14–18]. On the other hand, according to Chen et al. [19], rejection of pesticides was dependent on operational flux and recovery as well. For a particular pesticide in the two operational fluxes and recoveries, the highest percent rejection occurred at high flux and low recovery, and the lowest percent rejection occurred at low flux and high recovery. Meanwhile, a study done by Zhang et al. [20] found that pore narrowing by ion adsorption and water matrix influenced rejections.

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Nomenclature

A	membrane area
C_f	concentration of feed
C_p	concentration of permeate
K_{ow}	octanol/water partition coefficient
L_p	membrane permeability
pK_a	acid disassociation constant
R	percentage of pesticide rejection
Δt	time difference
v_w	permeate flux
ΔV	cumulative volume difference

So far, not much attention has been given to the changes in nanofiltration performance during nanofiltration of pesticides in aqueous solution when there are changes in its pH. However, this factor must not be neglected as the role of pH is also important in determining the stability of membrane [21,22]. Therefore, the objective of this study is to investigate the performance of nanofiltration membranes to retain atrazine and dimethoate in aqueous solution under different pH conditions. The effect of initial solution's pH for pesticide rejection and permeate flux were obtained and examined. This study is a continuation from a previous study which focused on the effect feed concentration and operating pressure on the permeate flux and rejection of dimethoate and atrazine from aqueous solution [23].

2. Materials and methods

2.1. Pesticides

Dimethoate with 99.8% purity and atrazine with 97.4% purity were purchased from Riedel-de Haen (Germany). The molecular structures of both pesticides are presented in Table 1.

2.2. pH adjustment

The chemicals used to adjust the pH of the pesticide solutions for filtration experiments were hydrochloric acid, HCl 37% (w/w) and sodium hydroxide, NaOH (1 M). These chemicals were obtained from Merck.

2.3. Membranes

Three types of nanofiltration membranes provided by Dow/Filmtec (USA) and one type of nanofiltration membrane purchased from GE Water Technologies (USA) with molecular weight cut-off (MWCO) of around 200 Da were used in this experiment. The thin film polyamide membranes from Dow/Filmtech used were NF90, NF200 and NF270 while the thin film polyamide membrane from GE Water Technologies used was DK. Table 2 provides the specification of the membranes used as given by the manufacturers.

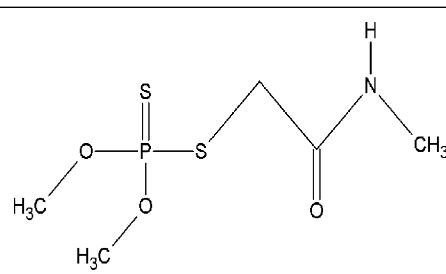
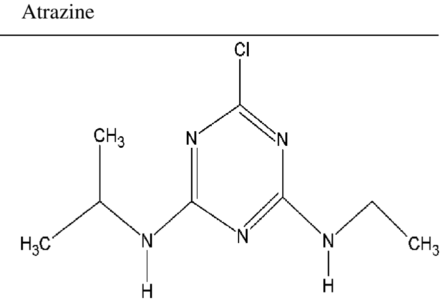
2.4. Membrane stirred cell

A 300 mL stirred cell (Sterlitech), model Sterlitech™ HP4750, USA, was used to conduct the dead-end filtration experiments. The effective membrane area is 1.46×10^{-3} m^2. The maximum operating pressure for this cell was 69×10^5 Pa.

2.5. Experimental set-up and procedure

Dead-end filtration experiments were carried out with the stirred cell (Sterlitech™ HP4750). The pesticide solution in the cell was stirred by a Teflon-coated magnetic bar. The cell was pressurized using compressed high purity nitrogen gas. The pressure in the permeate side was approximately atmospheric under all condition. The pesticides solution, prepared using deionized water, was adjusted to different initial pH by adding 1 M NaOH or 37% (w/w) HCl. The pH measurement was conducted using pH meter (Mettler Toledo Delta 320 pH Meter). The operating

Table 1
Properties of dimethoate and atrazine [2]

Pesticide	Dimethoate	Atrazine
Chemical structure		
Molecular weight (Da)	229.28	215.69
Solubility in water	25 g/L @ 21 °C	20 mg/L @ 20 °C
Acid disassociation constant, pK_a	2.0[a]	1.7[b]
Log K_{ow}	0.70	2.61[c]

[a] [30].
[b] [31].
[c] [32].

Table 2
Specification of membrane used

Membrane	NF90	NF200	NF270	DK
Manufacturer	Dow/Filmtec	Dow/Filmtec	Dow/Filmtec	Osmonics
Material	Polyamide	Polyamide	Polyamide	Polyamide
Contact angle[a] (°)	–	26 ± 2	28 ± 2	–
Surface charge (pH 7)	Negative[b]	Negative[b]	Negative[c]	Negative[d]
Pure water permeability[e] ($m^3/(m^2\,s\,Pa)$)	1.90×10^{-11}	1.17×10^{-11}	3.20×10^{-11}	7.84×10^{-12}
Maximum operating pressure (Pa)	41×10^5	41×10^5	41×10^5	40×10^5
Maximum operating temperature (°C)	45	45	45	38
pH range	3–10	3–10	3–10	3–10

[a] [33].
[b] [34].
[c] [35].
[d] [36]
[e] Our measurements.

pressure, feed pesticide and stirring rate were kept constant at 6×10^5 Pa, 10 mg/L and 1000 rpm while the initial solution's pH were varied at 4, 7 and 9.

The cell contained a nanofiltration membrane with an effective area of 1.46×10^{-3} m^2. The membrane was immersed for 24 h in deionized water before being used in any experimental work. Membrane permeability was determined by initially filtering it using deionized water at 12×10^5 Pa for approximately 8 h for compaction to avoid compression effect in the later stage of experiment. Then, stabilized water flux at different operating pressures was obtained and membrane permeability values (L_p) could be determined from the slope of flux against pressure graph.

For separation process, the same compaction process was carried out before the test cell was emptied and 1.8 L of feed solution was filled into the test cell and solution reservoir. The cell was then pressurized at the operating pressure indicated by a pressure regulator. Permeate from the bottom of the cell was collected and its weight was measured with an electronic balance of ±0.01 g accuracy. The cumulative weight were converted to cumulative volume and the permeate flux could be obtained. Permeate flux, υ_w (m^3/m^2 s), was obtained using Eq. (1):

$$\upsilon_w = \frac{\Delta V}{\Delta t A} \quad (1)$$

where ΔV is the cumulative volume difference (m^3), Δt is the time difference (s) and A is the membrane area (m^2), respectively.

Samples were collected at every 20 min for four times and the average values obtained from the samples were used as the results in this work. All experiments were conducted at room temperature (25 ± 2 °C). A schematic diagram of the experimental set up is shown in Fig. 1.

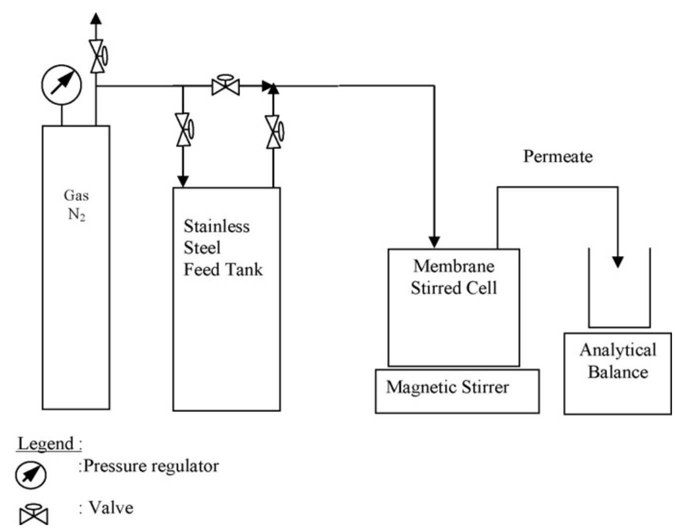


Fig. 1. Diagram of experimental set-up.

2.6. Analytical method

Concentration of atrazine and dimethoate in feed and permeate was analysed using high performance liquid chromatography (HPLC) by Perkin-Elmer (USA). The HPLC column used was Zorbax SB-CN (5 μ, 4.6 mm i.d. × 150 mm long, Agilent Technologies). The mobile phase was a mixture of 35% acetonitrile and 65% deionized water while the flow rate was set at 1.0 mL/min. The UV detector was operated at a wavelength of 200 nm. The peak for dimethoate was detected at around 3.5 min while the peak for atrazine was detected at around 5.3 min. Percentage of rejection was obtained with the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where R is the percentage of pesticide rejection, C_p is the concentration of permeate (mg/L) and C_f is the concentration of feed (mg/L)

3. Results and discussion

3.1. Rejection of atrazine and dimethoate

The effect of initial solution's pH on the atrazine and dimethoate rejection at fixed operating pressure, pesticide concentration and stirring rate are presented in Figs. 2 and 3. From the figures, it can be seen that the rejection performance for atrazine and dimethoate by NF200, NF270 and DK increased as the pH was increased while the rejection trend for NF90 was almost constant regardless of the pH condition. The

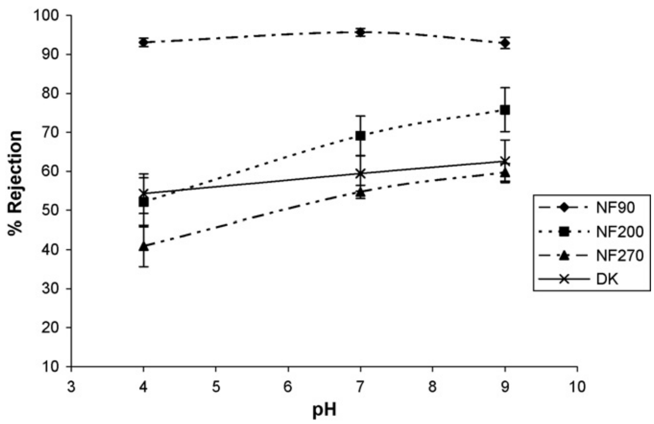


Fig. 2. Effect of initial solution's pH on rejection of atrazine.

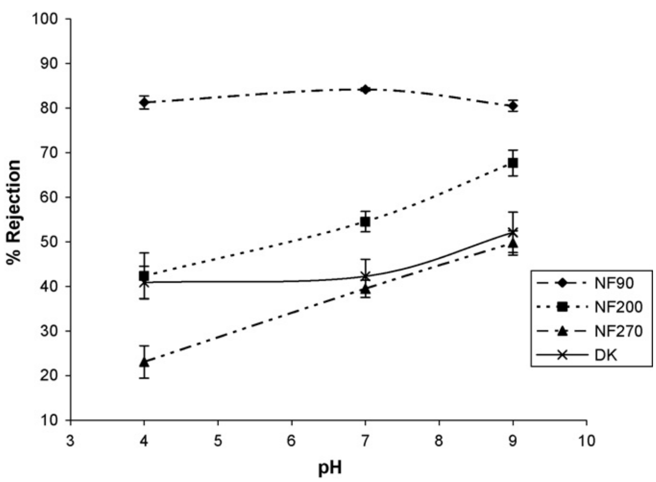


Fig. 3. Effect of initial solution's pH on rejection of dimethoate.

percentage of changes in rejection performance due to the alteration of initial solution's pH is also presented is Table 3 for clearer scrutiny. It is noted that atrazine was consistently better rejected than dimethoate although dimethoate has slightly higher molecular weight than atrazine. This behaviour had been discussed in our previous work whereby it was due to the higher hydrophobicity (log K_{ow}) and heterocyclic aromatic structure of atrazine [23].

Meanwhile, Nghiem et al. [24] reported that the pore radius of NF90 is smaller than that of NF270 and the structures of these two membranes are slightly different although with the same polyamide thin-film composite. NF270 has a very thin semi-aromatic piperazine-based polyamide active layer while NF90 consists of a fully aromatic polyamide active layer [24]. This slight difference of membrane structures can be one of reasons that NF90 showed superior rejection characteristics compared to other nanofiltration membranes tested at the experimental conditions.

Table 3
Percentage of changes in rejection performance due to the alteration of initial solution's pH

Membrane	%Change in rejection			
	Atrazine		Dimethoate	
	pH 4	pH 9	pH 4	pH 9
NF90	2.71	2.85	3.43	4.33
NF200	24.55	9.68	22.35	24.11
NF270	25.12	9.22	41.59	26.04
DK	8.67	5.29	7.65	17.73

Puasa [25] reported that polyamide thin-film composite membranes have charge characteristics that influence the separation capabilities, which can be altered by the solution's pH and it was reported that the isoelectric point of polyamide membrane is generally between 4 and 5. The occurrence of an isoelectric point means that at lower pH than the isoelectric point, the membrane is positively charged and vice-versa. Hence, in the case of polymeric membranes , surface membrane charge is typically negative at high pH values, it increases as the pH decreases and switches to positive values at low pH's [26].

However, in contrary to the usual phenomenon which occurs for ionic species whereby at isoelectric point, the flux is usually at the highest while the rejection is at the lowest [27], the trend observed for the uncharged pesticides molecules is somewhat different. In the case of uncharged molecules, instead of being influenced by the changes in membrane surface charge, it is believed that it was the changes of the membrane structures and/or formation of high molar mass complexes which significantly affected the performance of solute rejection and permeate flux [28]. Nevertheless, the possibility of formation of high molar mass complexes at high pH is sidelined in this research since the rejection of atrazine and dimethoate only increased at high pH for NF200, NF270 and DK while NF90 showed a slight decrease of rejection at high pH.

Hence, it is deduced that the trend of atrazine and dimethoate rejection obtained for NF200, NF270 and DK in this experiment was due to the changes of the membrane structures caused by the solution's pH. The results obtained were in agreement with observation done by Freger et al. [29] whereby the rejection of lactate decreased with the decrease of pH. In another work by Freger et al. [22], it was concluded that at low pH, acidic hydrolysis disrupted the chemical bonds in the membrane polymer matrix. This condition reduced the degree of crosslinking (i.e., rigidity) of the polymer matrix which eventually caused the decrease of rejection. At the same time, acidic hydrolysis also caused the increase of the hydrophilic sites at the membrane [22]. The increase of hydrophilic sites would cause the increase of permeate flux. On the other hand, the increase of atrazine and dimethoate rejection at high pH observed for NF200, NF270 and DK could be caused by the hydration swelling of the membrane skin layer [29]. This could result in shrinking of membrane pore size, and thus, reduced the permeation of solute through the pores of the membrane. Meanwhile, it is believed that NF90 was rather chemical-resistant as it showed somewhat consistent performance regardless of the solution's pH. There was only a drop of about 3% of rejection performance for NF90 compared to the obvious increase or reduction of rejection performance shown by the rest of the nanofiltration membranes tested.

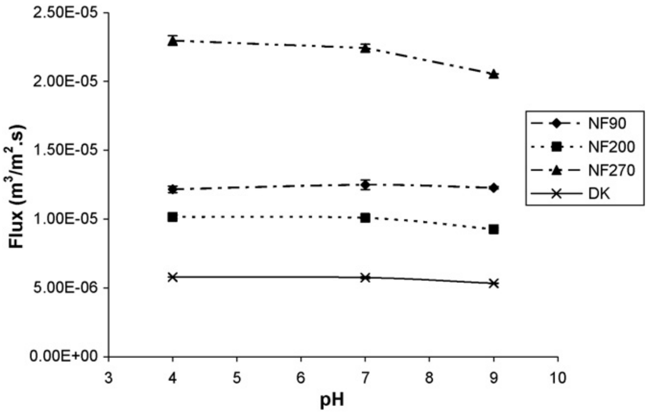


Fig. 4. Effect of initial solution's pH on permeate flux during rejection of atrazine.

3.2. *Permeate flux performance*

The effect of initial solution's pH on the permeate flux during rejection of atrazine and dimethoate at fixed operating pressure, feed pesticide concentration and stirring rate are presented in Figs. 4 and 5, respectively. As the acid hydrolysis at low pH or swelling of membrane skin layer at high pH, as explained in the previous section, is believed to be responsible for the increase or decrease in pesticide rejection for NF200, NF270 and DK, it is expected that the permeate flux would be as much affected by solution's pH as the pesticide rejection performance due to the acid hydrolysis and hydration swelling. The effect of initial solution's pH on permeate flux of pure water is shown in Fig. 6. Similar trend of permeate flux was observed with the presence of pesticide at different pH which further supported the deduction that the variation of trend observed was due to the changes of the membrane structures.

However, it seemed that except for NF270, the effect of solution's pH seemed not to be as much on permeate flux if compared to the degree of changes seen in the rejection performance. Thus, it is believed that the difference in permeate flux was not that obvious because the changes at the polymer was little, but it was sufficient to efficiently retain or allow more solutes through the membrane. Again, NF90 showed that it was somewhat resistant

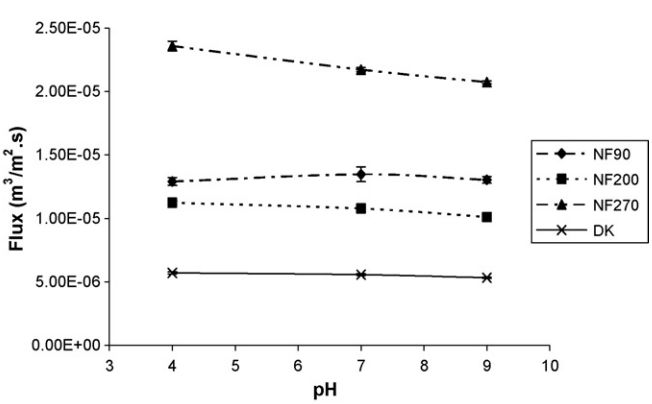


Fig. 5. Effect of initial solution's pH on permeate flux during rejection of dimethoate.

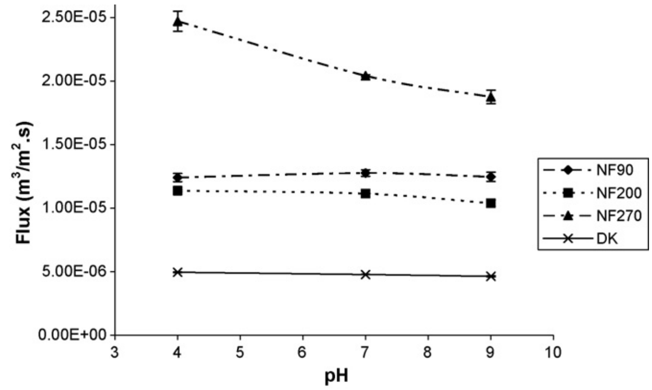


Fig. 6. Effect of initial solution's pH on permeate flux of pure water.

to the changes of solution's pH as it showed almost constant flux performance regardless of the pH condition.

4. Conclusion

In this study, the feasibility of nanofiltration membranes for the rejection of pesticides in aqueous solution was evaluated with the perspective of understanding the performance of nanofiltration membranes in different pH conditions. Four nanofiltration membranes, NF90, NF200, NF270 and DK, with molecular weight cut-off of around 200 were subjected to stirred dead-end filtration and the effect of initial pH's solution on the permeate flux and feed-based rejection of atrazine and dimethoate was investigated. It was found that increasing the solution's pH increased atrazine and dimethoate rejection but at the same time, reduced the permeate flux performance for NF200, NF270 and DK. However, effect of solution's pH had rather small significance on the performance of NF90.

From the results, it can be concluded that the NF90 had the highest rejection of all the membranes tested. It managed to maintain above 90% of atrazine rejection and approximately 80% of dimethoate rejection regardless of the changes in solution's pH. Besides, it was rather chemical-resistant as it showed somewhat consistent performance in both rejection and permeate flux regardless of the solution's pH. This finding strengthens the conclusion from our study [23] that NF90 is deemed the more suitable nanofiltration membrane for atrazine and dimethoate retention from aqueous solution compared to NF200, NF270 and DK.

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