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Dimethoate and atrazine retention from aqueous solution by nanofiltration membranes

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Abstract

In order to produce sufficient food supply for the ever-increasing human population, pesticides usage is indispensable in the agriculture sector to control crop losses. However, the effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. This eventually leads to contamination of drinking water source especially for rivers located near active agriculture practices. This paper studied the application of nanofiltration membrane in the removal of dimethoate and atrazine in aqueous solution. Dimethoate was selected as the subject of study since it is being listed as one of the pesticides in guidelines for drinking water by World Health Organization. Nevertheless, data on effectiveness of dimethoate rejection using membranes has not been found so far. Meanwhile, atrazine is classified as one of the most commonly used pesticides in Malaysia. Separation was done using a small batch-type membrane separation cell with integrated magnetic stirrer while concentration of dimethoate and atrazine in aqueous solution was analyzed using high performance liquid chromatography (HPLC). Four nanofiltration membranes NF90, NF200, NF270 and DK were tested for their respective performance to separate dimethoate and atrazine. Of all four membranes, NF90 showed the best performance in retention of dimethoate and atrazine in water.

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

1. Introduction

Malaysia is an active player in agriculture practice, planting oil palm, paddy, fruit, vegetables and many other products for local consumption and some for export purposes. Pesticides are also part and parcel of agriculture sector as a mean of pest control for sustainability of the industry. Annually, sales figure of approximately RM 300 million is recorded by Malaysian CropLife and Public Health Association [1]. The huge amount of pesticides used is emerging as contaminants in water. This is not surprising because pesticides sprayed on crops can be drifted by wind into nearby water source while pesticides applied directly to the soil can be washed off by rain into nearby surface water bodies or percolate through the soil to lower soil layers and groundwater [2].

In this study, the pollutants selected were dimethoate and atrazine. Dimethoate is a type of organophosphorus insecticide that has been identified as one of the chemicals from agriculture activities for which guideline value has been established by World Health Organization in the guidelines for drinking water [3]. In fact, its presence in water is not a surprise since it is highly soluble in water and adsorbs very weakly to soil particles, thus, subjecting it to considerable leaching [2]. Although this would normally cause minute concentration of pesticides presence in water, its chronic effect to the livings has been of more concern. Doull [4] reported that dimethoate could cause oncogenicity, mutagenicity, fetotoxicity and reproductive effects. Meanwhile, the other pollutant studied is atrazine as it is among the most commonly used pesticides in Malaysia especially for its usage as herbicide in plantations. Although atrazine is considered to be a low toxic herbicide, extensive amount of its usage has ranked it among the most common pesticides found in surface water and groundwater [5]. This situation has warranted urgent global attention to abate their presence in drinking water. Recent reports have revealed that high doses of atrazine induce abnormalities and deformities in non-target organisms. Furthermore, the syn-

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Nomenclature

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

ergy effect of dimethoate–atrazine is more lethal than the effect of the individual pesticide since the toxicity of dimethoate was enhanced significantly when they are in binary combination [6].

Traditionally, removal of pesticides for the production of drinking water was done by activated carbon filtration. It was effective, but expensive and required frequent regeneration [7]. Over the past few years, nanofiltration membranes have been studied as potentially useful means of pesticide removal considering the fact that the molecular weights (MWt) of most pesticides are more than 200 Da [2,5].

Nanofiltration has been successfully applied in drinking water treatment plant in Mery-sur-Oise, France [8], Leiduin [9] and Heemskerk [10] in Holland as well as Saffron Walden in England [11]. However, there is still a long list of pesticides in guidelines for drinking water by World Health Organization [3] but lack of data for their effective separation using membrane, including dimethoate. Therefore, there are still room for the investigation of the feasibility of using membrane technology to remove dimethoate from water, with addition to observation for binary mixture of dimethoate–atrazine.

Thus, the objective of this study is to examine the performance of nanofiltration membranes to retain dimethoate and atrazine in aqueous solution. Four nanofiltration membranes were subjected to stirred dead-end filtration. The effect of feed concentration and operating pressure on the permeate flux and feed-based rejection of dimethoate and atrazine were investigated.

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. Membranes

Three types of nanofiltration membranes provided by Dow/Filmtec (USA) and another type of nanofiltration membrane purchased from Osmonics (USA) 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 Osmonics used was DK. Polyamide membranes were used in this study because they were able to achieve good pesticides retention [12,13]. Table 2 provides the specification of the membranes used as given by the manufacturers.

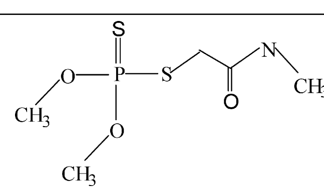
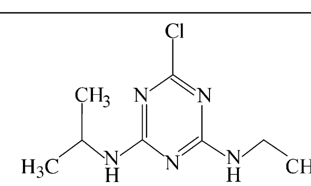
2.3. Membrane stirred cell

A 300-mL stirred cell (Sterlitech), model Sterlitech™ HP4750, USA, was used to conduct the dead-end filtration experiments. The membrane diameter was chosen to be 0.049 m with effective membrane area of 1.46×10^{-3} m^2. The maximum operating pressure for this cell was $69 \times 10^{+5}$ Pa.

2.4. Experimental setup 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 transmembrane pressures used during experiments were 6 and $12 \times 10^{+5}$ Pa. The concentration of pesticide was set to be at 2 and 20 mg/L. This concentration was higher than the usual concentration found in the case of run-off due to consideration of the membrane in case of accidental spill of pesticides in water source. The stirring speed was set constant at 1000 rpm.

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 at 21 °C	20 mg/L at 20 °C
Log octanol/water partition coefficient, K_{ow}	0.70	2.61[a]

[a] [16].

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	–
Pure water permeability[b] ($m^3/(m^2\,s\,Pa)$)	1.90×10^{-11}	1.17×10^{-11}	3.20×10^{-11}	7.84×10^{-12}
Maximum operating pressure (Pa)	$41 \times 10^{+5}$	$41 \times 10^{+5}$	$41 \times 10^{+5}$	$40 \times 10^{+5}$
Maximum operating temperature (°C)	45	45	45	38
pH range	3–10	3–10	3–10	3–10

[a] [5].
[b] Our measurements.

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 $12 \times 10^{+5}$ 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, v_w (m^3/m^2 s), was obtained using Eq. (1):

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

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

All experiments were conducted at room temperature (25 ± 2 °C). A schematic diagram of the experimental setup is shown in Fig. 1.

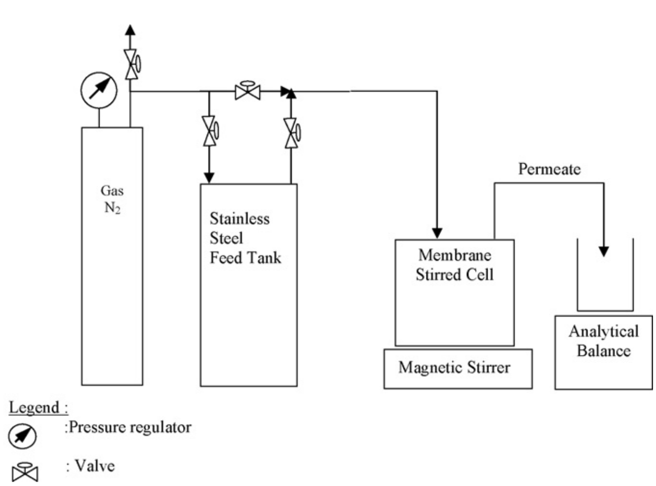


Fig. 1. Schematic diagram of experimental setup.

2.5. Analytical method

Concentration of dimethoate and atrazine in feed and permeate was analysed using high performance liquid chromatography (HPLC) by Perkin Elmer (USA). The HPLC column used was Zorbax SB-CN (5μ, 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. Retention of dimethoate and atrazine

The retention performance of dimethoate and atrazine by NF90, NF200, NF270 and DK at different pressure and concentration is presented in Figs. 2 and 3, respectively. From these figures, it is obvious that the retention of both dimethoate and atrazine tend to be better when the pressure was increased from 6 to $12 \times 10^{+5}$ Pa. It could be seen that NF90 produced the best retention performance for the operating pressure and feed concentration tested, at approximately 85% for dimethoate and more than 95% retention for atrazine. The performance of DK was the second highest of all four membranes tested while NF200 showed slightly lower retention than DK when both were operated at the same pressure and feed concentration. NF270 showed the lowest rejection performance out of the four membranes tested, especially for dimethoate retention. Higher retention was observed at higher pressure due to the increased water flux. The concentration of permeate became diluted with the increased water flux as the solute molecule was rejected by molecular sieving effect.

Meanwhile, the concentration effect was less significant on rejection of dimethoate and atrazine as compared to the effect of pressure as there was only slight increment of rejection per-

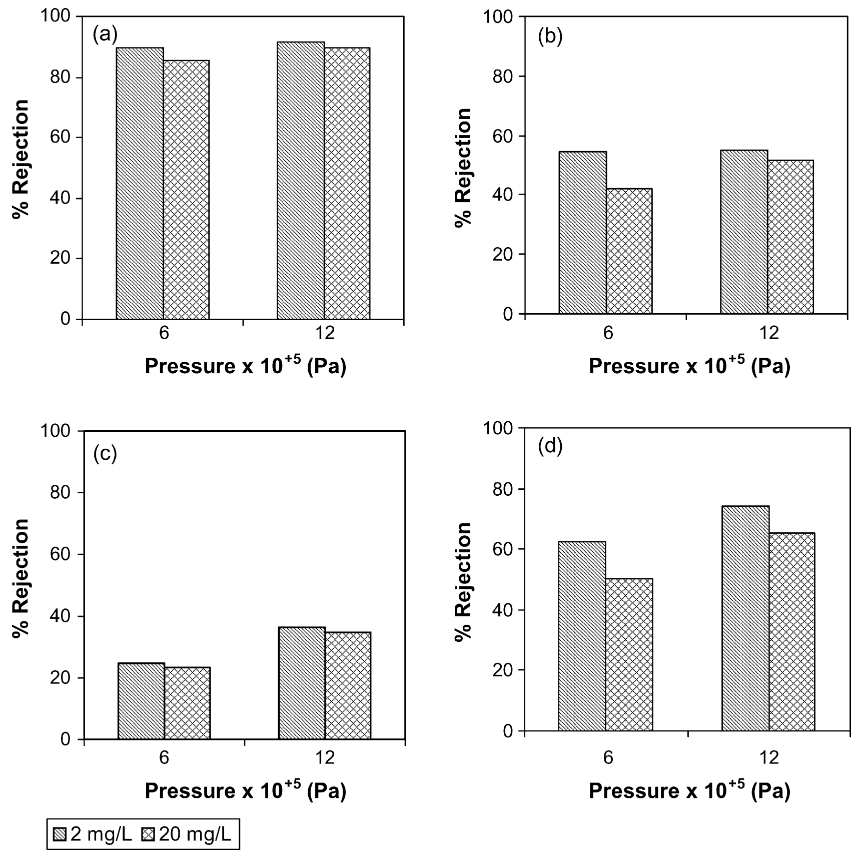


Fig. 2. Rejection of dimethoate by NF90 (a), NF200 (b), NF270 (c), and DK (d).

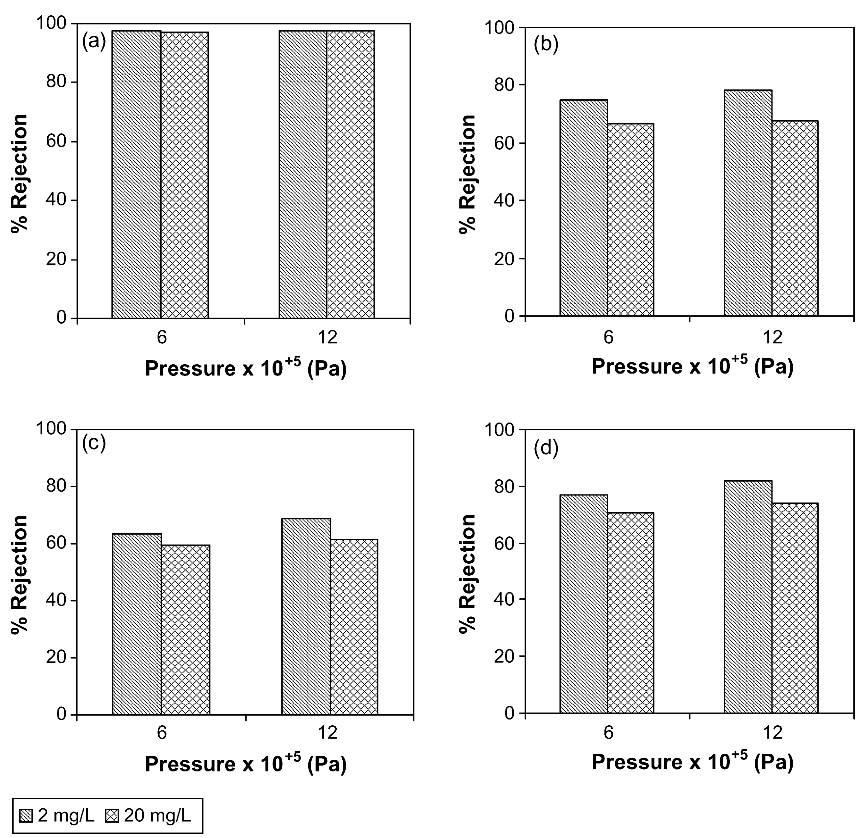


Fig. 3. Rejection of atrazine by NF90 (a), NF200 (b), NF270 (c), and DK (d).

formance although the concentration was increased 10 times as compared to two times increment of pressure. This finding is in agreement with work done by Causserand et al. [13] and Zhang et al. [14]. This shows that in practical terms, the membranes have almost the same efficiency level for dimethoate rejection even though the feed concentration varies as much as 10 times from time to time. However, atrazine retention performance of NF200 and NF270 of around 80% was obtained by Plakas et al. [5] when the concentration of atrazine was between 0.150 and 0.300 mg/L. This suggests that while effect of concentration did not pose much impact if compared to effect of pressure, it was still a valid gradient for transport of solute through membrane. NF90 was found to be a more robust membrane in view of atrazine retention since its retention was almost equal even at such high concentration of 2–20 mg/L.

Overall, all four membranes tested showed better retention for atrazine than dimethoate although dimethoate has slightly higher molecular weight than atrazine. Several reports [15–18] suggested that although molecular sieving effect must not be neglected, hydrophobicity of the solutes played a very important role in determining the retention performance by membrane. The higher the value of log K_{ow}, the better the rejection would be. This behaviour was shown in this study since atrazine has higher hydrophobicity than dimethoate. Moreover, dimethoate has aliphatic molecular structure compared to the heterocyclic aromatic structure of atrazine. Kiso et al. [16] reported that non-phenylic pesticides were rejected at a relatively lower degree than phenylic pesticides.

3.2. Permeate flux performance

Figs. 4 and 5 show the flux performance of the membranes for dimethoate and atrazine retention, respectively. Based on these figures, it was obvious that the increase in pressure had significant effect on permeate flux for both dimethoate and atrazine retention tests. All membranes tested experienced approximately double increment of permeate flux when the operating pressure was doubled from 6 to $12 \times 10^{+5}$ Pa. This shows that permeate flux increment corresponded linearly to the pressure applied to the solution. Meanwhile, concentration of feed had very little effect on the permeate flux as compared to operating pressure. It showed no significant trend although it caused slightly lower permeate flux when it was increased for certain membrane especially at $P = 12 \times 10^{+5}$ Pa run. Thus, effect of concentration can be excluded from consideration when it comes to flux performance.

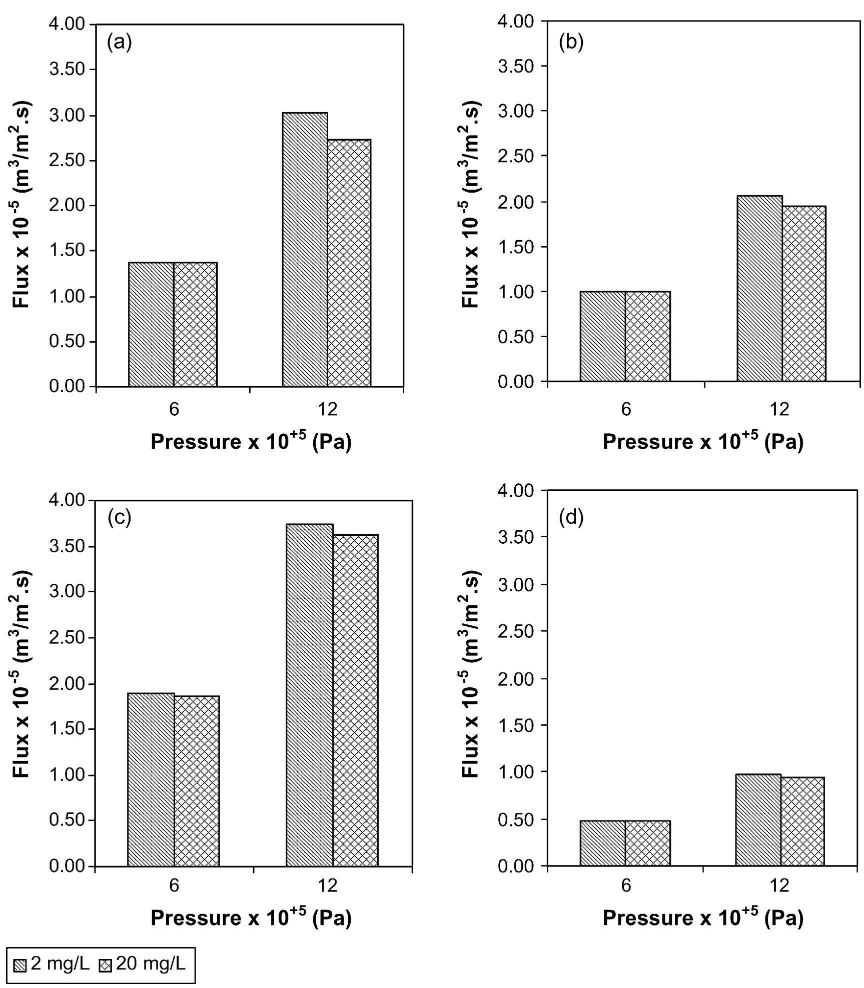


Fig. 4. Flux performance on dimethoate by NF90 (a), NF200 (b), NF270 (c), and DK (d).

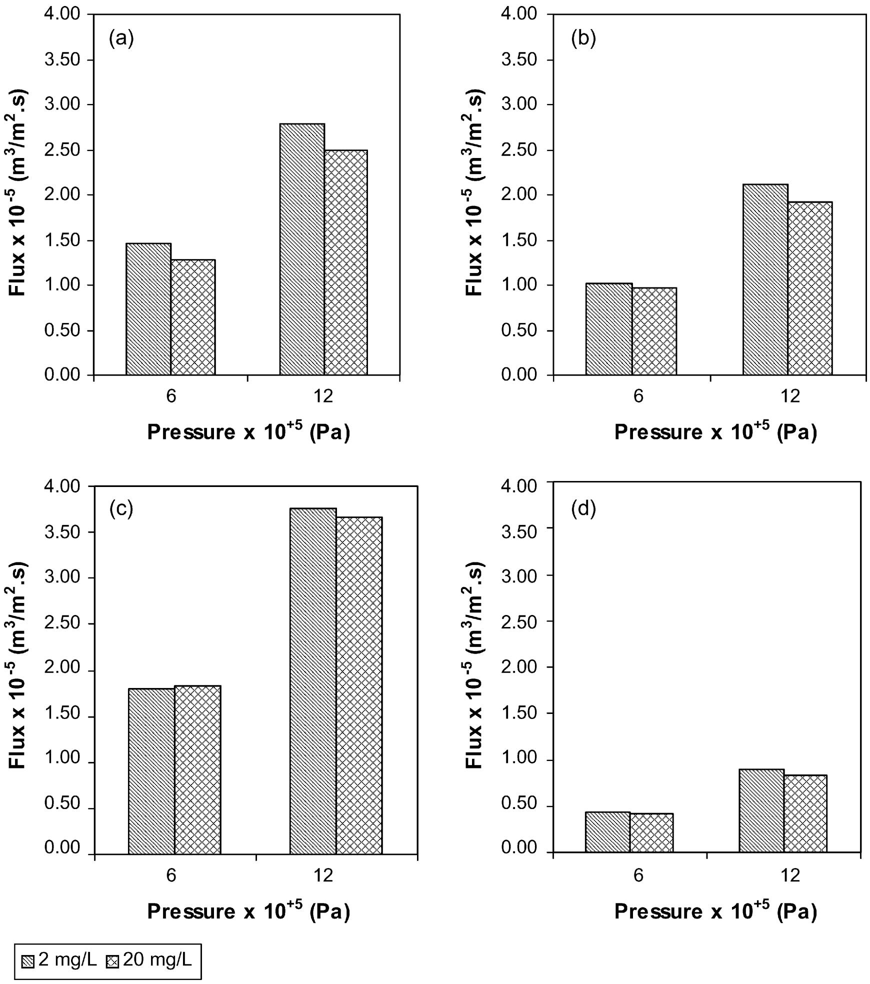


Fig. 5. Flux performance on atrazine by NF90 (a), NF200 (b), NF270 (c), and DK (d).

NF270 produced the highest permeate flux for all conditions tested. This was especially obvious at operating pressure of $12 \times 10^{+5}$ Pa. NF90 showed the second highest permeate flux out of the four membranes with approximately 40% lower compared to permeate flux by NF270. Meanwhile, NF200 showed considerably low flux rate compared to NF270 while DK produced the lowest permeate flux performance as it has approximately 300% lower flux compared to NF270. Based on the published data, NF270 had average pore size of 0.71 nm, NF90 had average pore size 0.55 nm while NF200 had average pore size of 0.38 nm [19,20]. Hence, the results obtained in this study corresponded to the average pore size reported in the literature.

However, this also showed that while 0.55 nm average pore size for NF90 was sufficient to retain dimethoate and atrazine with high percentage of rejection, solute-membrane interaction factor was also important [15,18,21] as DK and NF200 could not sustain as much rejection as NF90 although DK had similar average pore size with NF90 [22] while NF200 had smaller average pore size. The interaction between membrane material for DK and pesticides tested was believed to contribute to the crossing of solutes through the membrane because it had lower percentage of retention of pesticides compared to NF90. This validated the claim by the manufacturer that NF90 is suitable for pesticides and herbicides removal [23].

3.3. *Retention performance of NF90 for atrazine–dimethoate*

Since NF90 showed good rejection for both atrazine and dimethoate individually, rejection of atrazine–dimethoate was tested at pressure of $6 \times 10^{+5}$ Pa and stirring rate of 1000 rpm to examine if the membrane would have the same good performance when the two pesticides co-exist. The ratio of atrazine:dimethoate was set at 20:80, 50:50 and 80:20 for a total of 10 mg/L pesticides. Fig. 6 shows that NF90 still maintained its good performance of retention for both atrazine and dimethoate in the presence of binary mixture of pesticides, although there was slightly lower retention observed compared to the single solute condition. This observation was in line with observation by Plakas et al. [5] which suggested that simultaneous filtration of more than one pesticide resulted in a kind of competitive adsorption on the membrane surface and, thus, created a greater passage to the permeate side. These results were also in agreement with the report by Kiso et al. [16] which found that herbicides displaying higher rejection in single solute solutions

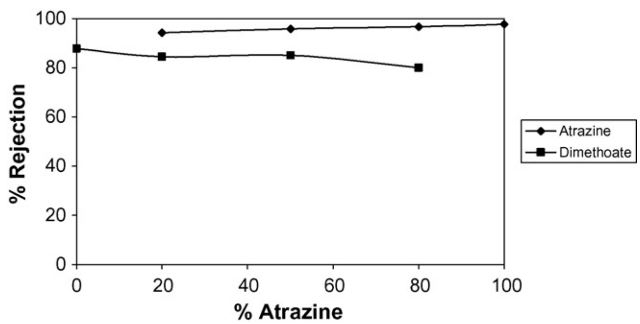


Fig. 6. Rejection performance of atrazine–dimethoate for NF90.

may permeate more in mixed solute systems. However, results obtained in this study showed that while there was slight reduction of pesticides retention, the performance of NF90 was still commendable even though it was in mixed solute system.

4. Conclusion

The performance of nanofiltration membrane to retain dimethoate and atrazine in aqueous solution was examined in this study. Four nanofiltration membranes, NF90, NF200, NF270 and DK, which have molecular weight cut-off of around 200 were subjected to stirred dead-end filtration and the effect of feed concentration and operating pressure on the permeate flux and feed-based rejection of dimethoate was investigated. It was found that increasing the transmembrane pressure posed positive effect on dimethoate and atrazine rejection and permeate flux. However, effect of feed concentration had little significance on the performance of the membranes tested.

NF90 showed the best retention performance while NF270 showed the highest permeate flux out of the four membranes tested. However, good retention quality should be the primary property in choosing the appropriate nanofiltration membrane for application in pesticides treatment from water. Therefore, despite its high permeate flux, NF270 is not suitable especially for dimethoate retention as it showed the poorest retention quality. NF90 is deemed the more suitable nanofiltration membrane for dimethoate and atrazine retention from aqueous solution since, it showed the highest retention of dimethoate and atrazine coupled with considerably good permeate flux. Furthermore, although there was slight reduction of retention performance for NF90 in binary atrazine–dimethoate solution, it still managed to maintain its robust retention performance.

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