Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 154 (2008) 633–638
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

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

A.L. Ahmad*, L.S. Tan, S.R. Abd. Shukor

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Prai Selatan, Pulau Pinang, Malaysia

Received 9 July 2007; received in revised form 23 October 2007; accepted 23 October 2007
Available online 4 December 2007

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.

* Corresponding author. Tel.: +60 4 5941012; fax: +60 4 5941013.
E-mail addresses: chlatif@eng.usm.my (A.L. Ahmad), tan.liansee@gmail.com (L.S. Tan), chsyamrizal@eng.usm.my (S.R. Abd. Shukor).

0304-3894/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2007.10.073

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.

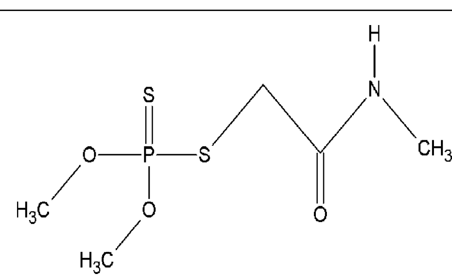
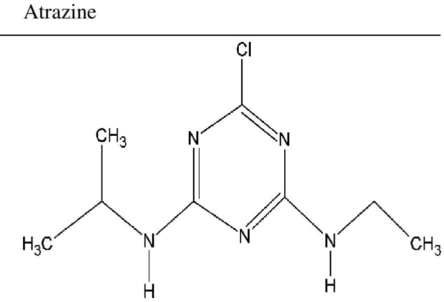
2.4. Membrane stirred cell

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].