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Removal of malathion using ceramic nanofiltration/adsorption system

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ABSTRACT

Residual pesticides in industrial effluents of pesticide industry manifests a serious threat for sustainability of the biological wastewater treatment plants and also to nearby surface and ground water. This article is concerned with the separation of malathion using nanofiltration (NF), clay adsorption, and combination of both processes. Malathion removal using NF tubular ceramic membrane is ranged from 93.5 to 99.4% with malathion concentration range from 5.7 to 17.1 mg/l. Adsorption of malathion (0.4–2.9 mg/l) using Egyptian clays (kaolin and bentonites) reached about 0.65 mg/g. Sodium bentonite (Na–B) exhibited maximum adsorption capacity and removal as compared to kaolin (K) and calcium bentonite (Ca–B). The natural pH values of the different investigated clays in malathion solutions were 6.7, 7.3, and 9.5 for K, Ca–B, and Na–B, respectively. An integrated system of NF and clay adsorption permits effective control on the quality of NF permeates. Endeavors are currently underway to explore cost-effective treatment of NF concentrate.

Keywords: Pesticide; Malathion removal; Nanofiltration; Clay adsorption; Cost

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1. Introduction

Due to the increasing environmental and health concerns regarding the risk of hazardous pollutants in general and pesticides in particular, there is a need for development of a reliable and yet cost-effective technologies to suit the constrains of developing countries. Advanced oxidation process [1], membrane separation [2–4], adsorption [5], and other physico-chemical techniques [6] are typical model technologies for the removal of pesticides. Numerous investigators used nanofiltration (NF) membranes for the removal of different types of pesticides with removal efficiencies ranging from 82 to 99.8% [7–9]. Also, RO-based systems have been successfully applied for the removal of different types of pesticides with efficiencies ranging from 89 to 99% [10]. Photo-Fenton oxidation process decreased total pesticide concentration in an industrial effluent from 20.2 to 0.3 mg/l [11]. Further, the adsorption capacity of activated carbon (AC) approached 34–76 and 1.8–7.7 mg/g when applied for the treatment of Paraquat dichloride (1,000 mg/l) and (10–40 mg/l),

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respectively [12]. Powdered AC successfully eliminated isoproturon (1 mg/l) by about 99% [13]. Natural and synthetic clays are currently used for the removal of pesticides [14]. For instance, natural kaolin and bentonite manifested 15 and 32% for malathion removal using synthetic solutions containing malathion from 36.5 to 38 mg/l, respectively [15].

In this study, malathion (Ma) has been selected as a model for organo phosphorus pesticide since it has been extensively used in Egypt. Tubular ceramic NF membrane with cutoff approaching 1,000 Da has been used as a primary separator for the selected pesticide. Further, the removal of residual malathion from NF permeate has been tested using selected Egyptian clays on a separate adsorption stage.

2. Materials and methods

2.1. Materials

NF tubular ceramic membrane (Rhodia Orelis, France) has been used in this study. The physical and chemical specifications are depicted in Table 1. Egyptian kaolin (k) and bentonites (calcium (Ca–B) and sodium (Na–B) have been used as low-cost adsorbents. Kaolin was supplied from Abu Zeneima (Sinai) by Normeetec company for building materials, whereas bentonites have been supplied by the International company of mining and investment from Wadi Elnatron-Egypt. Typical reported chemical compositions of the selected clays are shown in Table 2 [16]. Analytical grade malathion (Ma) was obtained from (Fisher Scientific, IL, USA) [7] and commercial grade malathion (57%) from Kafr El–Zayat Co., Egypt.

2.2. Methods

The experimental NF system is schematically shown in Fig. 1. The system could be operated in batch or continuous mode under maximum operating pressure of 10 bars. Synthetic malathion solutions were delivered to the NF module under specified pressure, flow, and temperature (25 ± 2°C). Flux decline has been measured at different malathion concentrations (5.7–17.1 mg/l). Permeate samples were analyzed for malathion concentration analysis using Hewlett Packard gas chromatograph (GC model 6890) equipped with a flame photometric detector. pH was adjusted using dilute HCl/NaOH solutions. In adsorption experiments, stirring was kept at 250 rpm for 2 h using Jar test apparatus followed by centrifugation at 2,500 rpm for 10 min and the centrifugate was also analyzed. Adsorption variables included: clay type, dosage, pH, and malathion concentration. Adsorption capacity (Q_e) and removal percentage (% R) were calculated using the following equations:

$$Q_e = (C_i - C_e)^* V/m \tag{1}$$

Table 1
Physical and chemical specifications of NF membrane

Item	
Membrane material	$TiO_2-Al_2O_3$
Support	Ceramic
Configuration	Tubular, 19 flow channel
Membrane surface area (m^2)	0.245
Pore size	1 K Da
Operating pressure bar	up to 10 bar
Max. operating temperature	up to100°C
pH operating range	0–14
Dimension, (D × L)	25 mm ×1,178 mm

Table 2
Chemical compositions of selected clays [16]

Constituents (%)	K	Ca–B	Na–B
SiO_2	50.65	52.98	50.91
TiO_2	1.65	1.51	1.35
Al_2O_3	30.31	20	18.39
Fe_2O_3	4.61	10.02	10.09
L.O.I	11.37	9.94	10.26
Moisture content	0.60	7.60	2.1

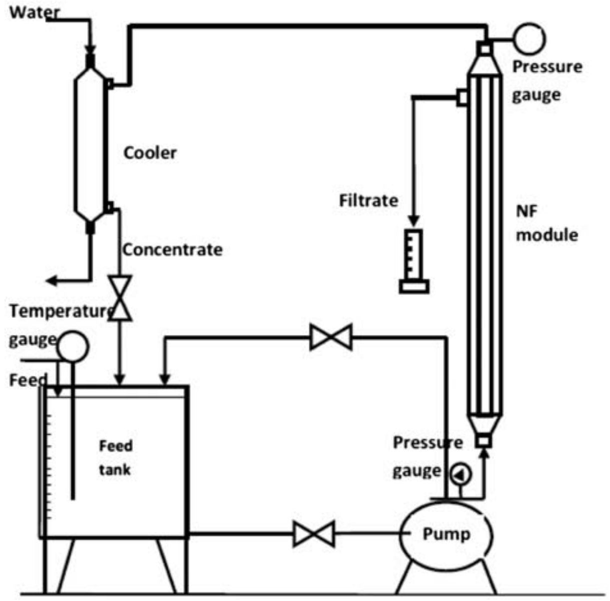

Fig. 1. Nanofiltration experimental set-up.

$$\%R = 100^{*}(C_i - C_e)/C_i \qquad (2)$$

where: Q_e: amount of adsorbed malathion per gram of clay (mg/g); %R: removal percentage; C_i and C_e: initial and effluent malathion concentrations (mg/l); V: volume of the solution (l); m: amount of clay used (g).

3. Results and discussions

3.1. NF separation

3.1.1. Water flux

Fig. 2 depicts the water flux data for the tested NF ceramic membrane at different operating pressures (TMP). Figs. 3 and 4 depict the linear flux decline relation and malathion rejection with malathion concentration range from 5.7 to 17.1 mg/l.

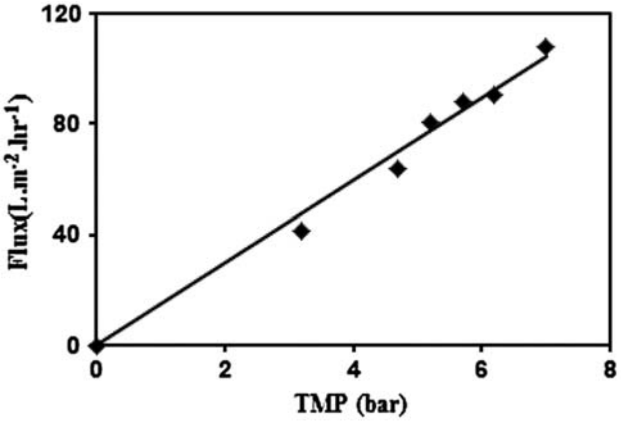

Fig. 2. Water flux data for NF ceramic membrane.

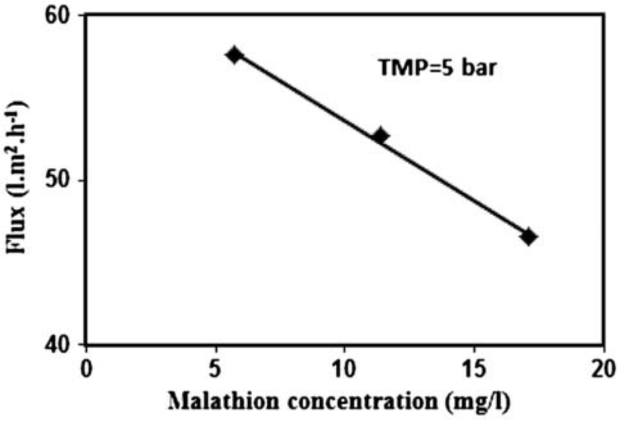

Fig. 3. Effect of malathion concentration on flux.

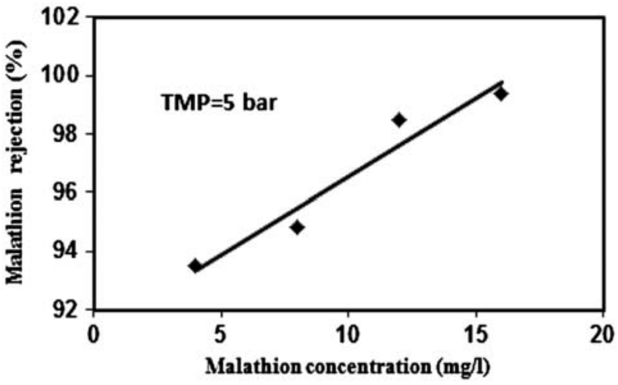

Fig. 4. Effect of malathion concentration on rejection.

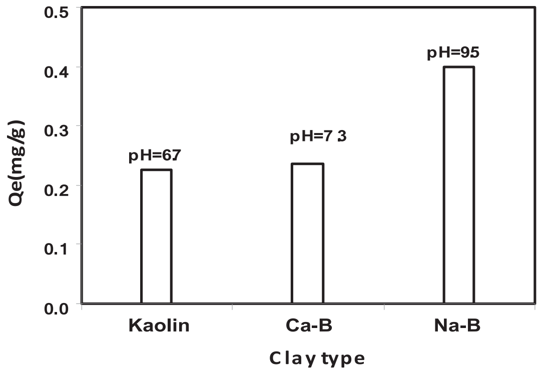

Fig. 5. Adsorption capacity of malathion using selected Egyptian clays. (Ma = 1 mg/l and clay dosage = 2 g/l).

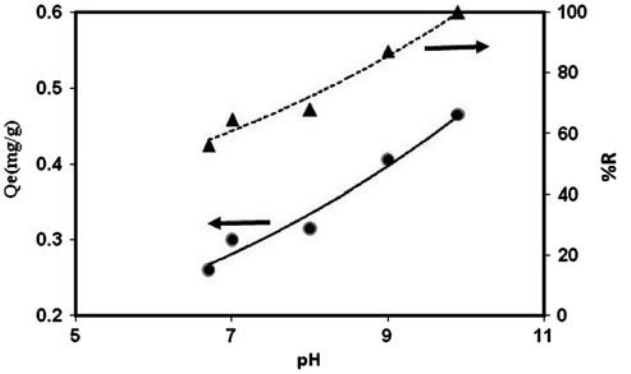

Fig. 6. Effect of pH on Q_e and percentage removal using Na–B, (Ma = 1 mg/l and dosage = 2 g/l).

3.2. Adsorption of malathion using Egyptian kaolin and bentonites

Adsorption of malathion by different types of clays is shown in Fig. 5. Na–B showed higher adsorption capacity as compared to kaolin and Ca–B. The observed solution pH after clay addition was 6.7, 7.3 and 9.5 for kaolin, Ca–B and Na–B, respectively.

Decreasing pH of Na–B from 10 to 7 was associated with the decrease in Q_e and percentage removal as shown in Fig. 6 which suggests a possible effect of pH on the adsorption capacity. Furthermore, comparing the adsorption of kaolin and Na–B at controlled pH (7–8) using different clay dosages (1–5 g/l), revealed the advantages of Na–B within the investigated range. It was observed also that 2 g/l dosage is sufficient to achieve practical removal of malathion within the prevailing experimental conditions as shown in Fig. 7. The adsorption capacity increases from 0.18 to 1.2 mg/g with increasing malathion concentration from 0.4 to 2.9 mg/l as shown in Fig. 8. This concentration range corresponds to NF permeate concentration for treating malathion feed range from 5.7 to 17.1 mg/l. This emphasizes the advantage of operating NF systems at high malathion concentration. In this way, maximum efficiency could be obtained by Na–B adsorbent within pH range from 9 to 10. Increasing malathion concentration, obviously improves Q_e with corresponding decrease in percentage removal at the same clay dosage as shown in Fig. 4. This result is opposite to the effect of pH in Fig. 6 where, both Q_e and percentage removal manifest almost linear increase with pH at low fixed malathion concentration.

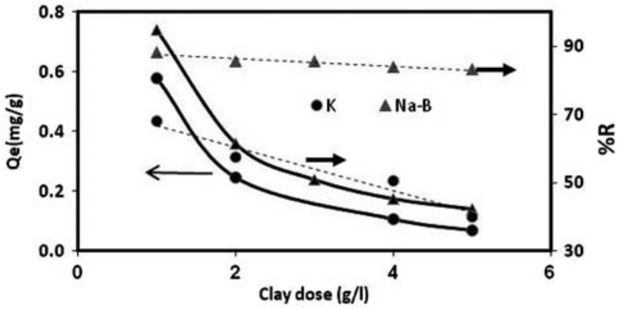

Fig. 7. Dependence of Q_e and percentage removal on clay dosages, (Ma = 1 mg/l and pH = 7–8).

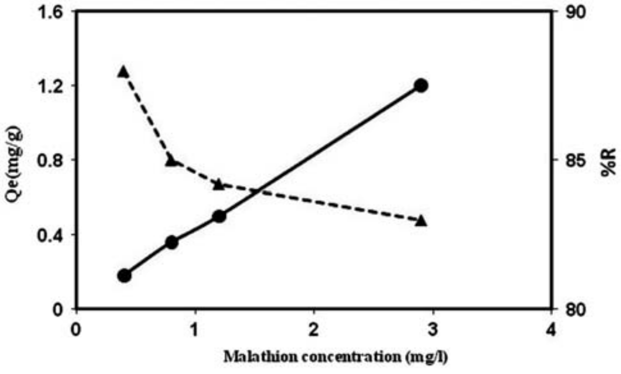

Fig. 8. Effect of malathion concentration on Q_e and percentage removal, (Na-B dosage = 2 g/l and pH= 7).

In general, the results of this wok manifested the promising features of both NF and clay adsorption for the removal of malathion as a model pesticide. The selected NF membrane is a commercial tubular ceramic with 1,000 Da cutoff. Further enhancement could be obtained using membranes with lower cutoff (e.g. 200 Da).

Kaolin and bentonites are low-cost adsorbents and can be obtained easily from commercial market. Na–B proved to be promising adsorbent at its natural pH > 9.

3.3. Process design considerations

The results of this work avail numerous opportunities that will be explored in our laboratory to address the treatment of NF concentrate and residual pesticides in the permeate. Process design considerations in potential investigations include the following priorities:

Using low cutoff NF membrane (e.g. 200 Da) with maximum possible flux to obtain relatively minimum volume of rich NF concentrate.

Exploring the effect of a second-stage adsorbent based on activated carbon to remove residual pesticide concentration after clay stage.

4. Conclusions and recommendations

Malathion has been selected as a model pesticide to study the promising NF/adsorption system for the decontamination of pesticide industry effluents. NF ceramic tubular membrane (1,000 Da cutoff) and low-cost clay adsorbents have been used in this study. Both separation stages manifested promising features for dealing with malathion containing effluent. Process design consideration indicates the need to capitalize on these results for further optimization of system performance. Two important issues need further investigations; exploring lower cut-off NF membranes (e.g. 200 Da) will permit improved rejection and better quality permeates. Moreover, adoption of a second-stage adsorption based on activated carbon is perceived to be a necessary modification for almost complete decontamination of NF permeates.

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