Journal of Chemical Technology and Metallurgy, 53, 4, 2018, 657-663

REMOVAL OF PESTICIDES AND DESETHYLATRAZINE (DEA) BY NANOFILTRATION: EFFECTS OF ORGANIC AND INORGANIC SOLUTES ON SOLUTE REJECTION

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Received 21 March 2018
Accepted 08 May 2018

ABSTRACT

Water resource contamination by pesticides causes a real problem concerning drinking water production. This work is focused on the experimental study of humic acid (Natural Organic Matter, NOM) and nitrate salts ($Ca(NO_3)_2$ and $NaNO_3$) influence on pesticide elimination by nanofiltration. For this purpose, two flat sheet nanofiltration membranes, NF (FilmTec Corporation/Dow) and OPMN-K (Vladipor), are tested using at an ambient temperature using laboratory pilot equipment. The applied transmembrane pressure (TMP) varies between 10 bars and 25 bars, while the circulation velocity in the membrane cell remains fixed at 0.45 $m\ s^{-1}$. Three pesticides (simazine, atrazine and diuron) and one atrazine metabolite (DEA) are used in simple or multicomponent solutions of a different concentration. That of humic acid is maintained equal to 100 mg/L. It is found that OPMN-K membrane has a lower retention and a permeate flux compared to those of NF one. The results obtained indicate that the presence of organic (humic acid) or inorganic ($NaNO_3$, $Ca(CO_3)_2$) matter influences less strongly the retention of atrazine, simazine and DEA, while their influence on diuron retention is more pronounced.

Keywords: nanofiltration, drinking water treatment, pesticides, humic acid, NF, OPMN-K.

INTRODUCTION

The extensive use of nitrates and pesticides in agriculture generates contamination of surface and groundwater sources and hence affects harmfully the environmental systems [1]. At the same time, the limits imposed by the international authorities become more restrictive: according to the European Union (98/83/CE, 11/3/1998), the maximum pollution limit in respect to each pesticide is fixed at the value of 0.1 μg/L, while that referring to their total quantity amounts to 0.5 μg/L. Due to the pollution rise and increase of the restrictions concerning drinking water quality, new single or coupled water treatment processes emerge in water industry. Nanofiltration appears as an alternative separation method concerning some widely used processes like adsorption using activated carbon [2 - 6] and ozonation [7 - 9]. Adsorption is the most effective method for pesticides removal, but it is expensive due to the cost of active carbon regeneration. This cost is higher in case the treated water contains additional dissolved organic matters like humic acid, or slightly soluble hydrophobic substances of high molecular mass. The pesticides can adsorb on these water components through physi- or chemisorption forming negatively charged complexes. Organic matter, adsorbing on the carbon sites, blocks the latter, which results in adsorption capacity reduction [10]. The presence of humic acid (Natural Organic Matter, NOM) requires more regular active carbon regeneration. The most important disadvantage of ozonation seems to be the formation of products like peroxides, ozonides, organobromine and bromate causing a secondary contamination

Table 1. Molecular mass of pesticides and metabolite.

Pesticide	Molecular formula	Molecular mass [Da]
Atrazine	$C_8H_{14}ClN_5$	215.7
DEA	$C_6H_{10}ClN_5$	187.2
Diuron	$C_9H_{10}Cl_2N_2O$	233.1
Simazine	$C_7H_{12}ClN_5$	201.7

of water resources.

The nanofiltration appears to be a promising separation process for simultaneous treatment of organic and inorganic pollutants due to the high retention of both kinds of species (charged or neutral). The performance of this membrane process is due to two essential properties of nanofiltration membranes: the first one refers to their molecular cut-off (MWCO) between reverse osmosis and ultrafiltration membranes (from 200 Da to 2000 Da), while the second one is connected with the electrostatic repulsion between the charged solutes and the fixed charged sites of the membrane. According to these features, nanofiltration appears to be an effective water treatment process providing the removal of many molecular uncharged solutes like pesticides, hormones, toxins [11 - 14], many charged solutes like nitrates, sulphates, heavy metals[11, 15 - 17] and dissolved organic matter [18 - 21]. The nanofiltration may be used independently or combined with other separation processes like coagulation, microfiltration, adsorption [22 - 27].

It is very important to understand and take into account the membrane-solute interactions (for a single solute solution) as well as the solute-solute interactions (for complex solutions) aiming a successful pollutants retention. This study is focused at testing two nanofiltration membranes for elimination of three pesticides (atrazine, simazine and diuron) and the most common chlorinated atrazine metabolite (desethylatrazine, DEA) in presence of natural organic matter (humic acid) and of nitrates ions ($NaNO_3$ and $Ca(NO_3)_2$). The experiments are carried out using two organic membranes: NF membrane (FilmTec Corporation/Dow) and OPMN-K membrane (Vladipor Society).

EXPERIMENTAL

Atrazine, simazine, diuron and desethylatrazine (DEA) (Table 1) of concentrations in the range from 5 µg L^{-1} to 100 µg L^{-1} were used as solutes in this study. The feed solution was prepared with deionized water (of conductivity less than 2 µS/cm). The concentration of humic acid (Aldrich) was equal to 100 mg L^{-1}. It was kept constant during all experiments.

Pesticide concentrations were obtained by a solid-phase extraction (SPE) coupled to high performance liquid chromatography (HPLC) using a chromatography column ZORBAX C18 (5µm, 46 mm, 250 mm). The mobile phase was a 40 % solution of acetonitrile (CAN) in osmotic water. UV detection was operated at $\lambda = 215$ nm for atrazine, simazine and DEA, while at $\lambda = 251$ nm for diuron. More details referring to SPE may be found elsewhere [12].

The membranes used in this study were flat sheet negatively charged organic membranes: NF was provided by FilmTec Corporation/Dow, while OPMN-K was provided by Vladipor (Table 2). Prior to their first utilization the membranes were immersed for 48 h in deionized water and compacted within 12 h at 25 bars aiming to reduce swelling and compaction effects in the course of the experiments.

The experimental set-up used for this study is presented schematically in Fig. 1. Feed was pumped

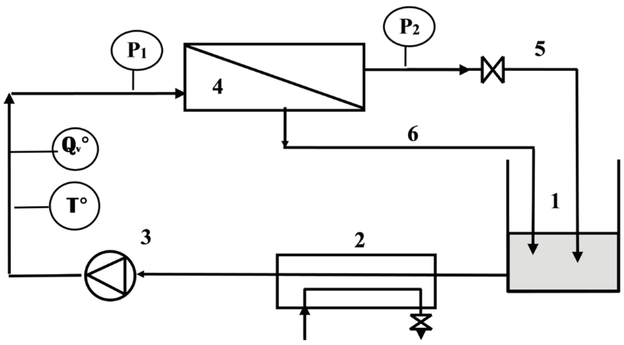


Fig. 1. Experimental set-up
1 - feed tank; 2 - heat exchanger; 3 - volumetric pump; 4 - membrane cell; 5 - retentate; 6 - permeate; Q_v - flow meter; P_1, P_2 - pressure gauges ; T° - temperature gauge.

Table 2. Specification of membranes.

Membrane	NF	OPMN-K
Manufacturer	FilmTec/Dow	Vladipor
Material	Polypiperazine amide	Polyamide
Operating pressure (bar)	15	16
Solute rejection (NaCl)	75 *	55
Water flux (at 15 bars)	67.5 L.m^{-2}.h^{-1}*	100 L.m^{-2}.h^{-1}
pH range	3-10	2-12
Nature of surface charge	Negative	Negative
MWCO (Da)	170*	330*
r_p (nm)	0.35	0.47

* *our experimental data*

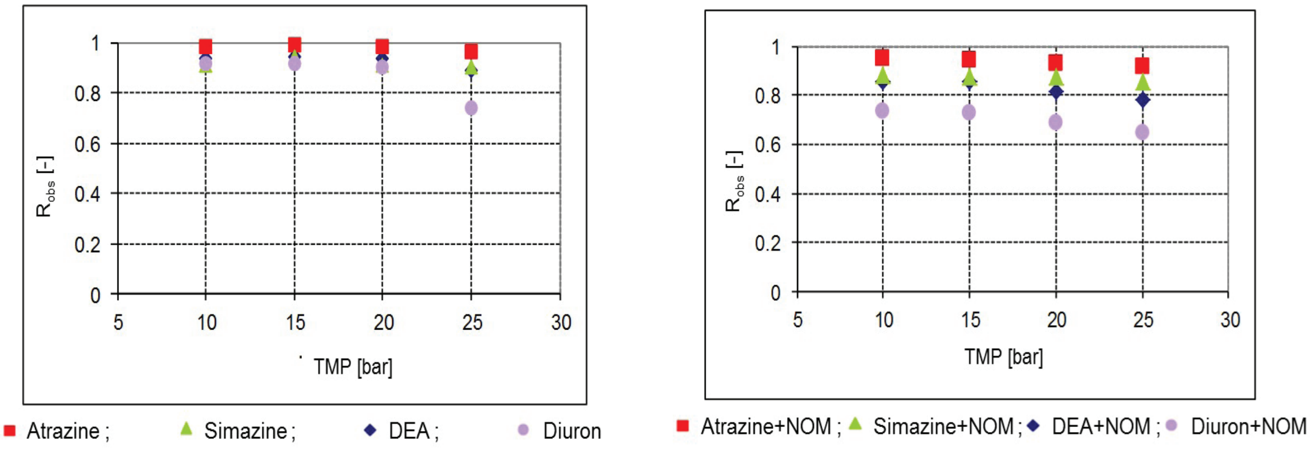
(3) from a stainless steel tank (1) and directed to the membrane cell containing a flat sheet membrane (with a filtration area of 86.10^{-4} m^2). The permeate (6) was collected and weighted prior its returning to the tank. The feed mass flow was measured using a flow meter (Q_v). A pressure valve was used to adjust the pressure. The latter value was measured upstream (P_1) and downstream (P_2) the cell. The temperature was maintained constant using a heat exchanger (2).

All experiments were carried out at 20 ± 1°C in a batch circulation mode. The applied transmembrane pressure (TMP) varied between 10 bars and 25 bars, while the circulation velocity in the cell remained fixed at 0.45 m s^{-1}. The latter value corresponded to a flow rate of 5 L min^{-1} and Re = 3300.

The observed rejection was calculated using the equation:

$$R_{obs} = \left(1 - \frac{C_p}{C_0}\right) \tag{1}$$

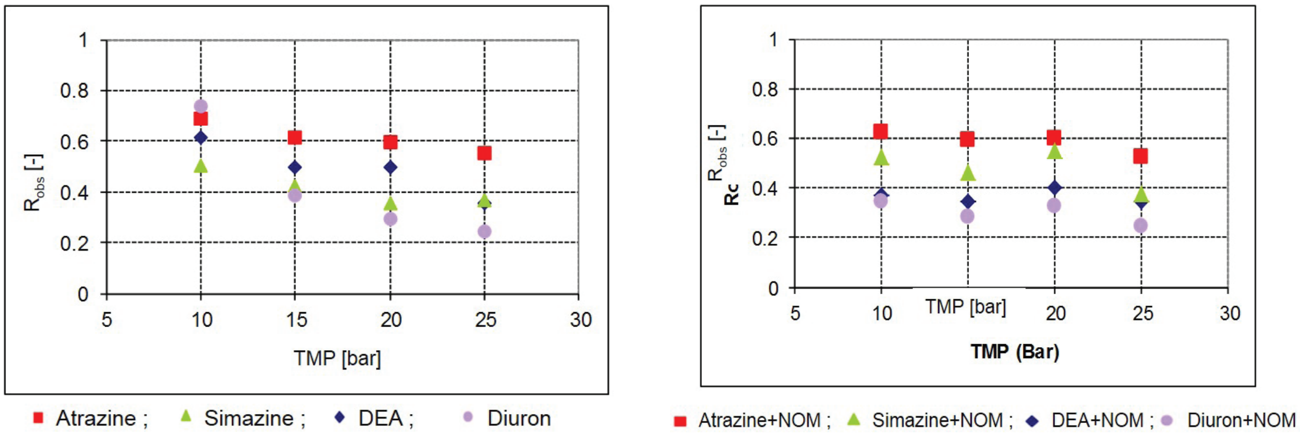
where C_0 was the feed concentration (ppm), while C_P was the permeate concentration (ppm).



a) pesticide and DEA retention in the absence of NOM [14]

b) pesticide and DEA retention in the presence of NOM

Fig. 2. Humic acid influence on pesticides and DEA retention versus applied transmembrane pressure (membrane NF).



a) pesticide and DEA retention in the absence of NOM [14]

b) pesticide and DEA retention in the presence of NOM

Fig. 3. Humic acid influence on pesticides and DEA retention versus applied transmembrane pressure (membrane OPMN-K).

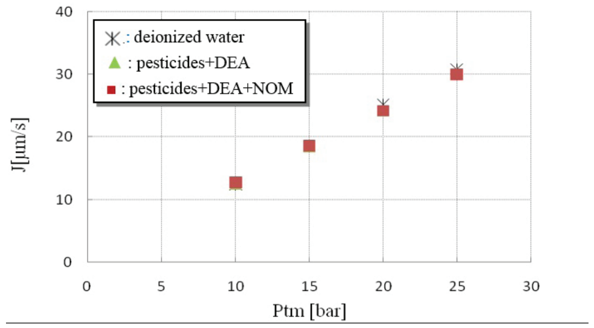


Fig. 4. Permeate flux versus transmembrane pressure for water, pesticide + metabolite mixture and pesticide + metabolite + NOM mixture (membrane NF).

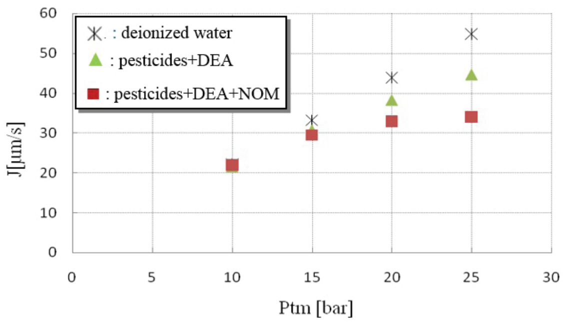


Fig. 5. Permeate flux versus transmembrane pressure for water, pesticide + metabolite mixture and pesticide + metabolite + NOM mixture (membrane OPMN-K).

RESULTS AND DISCUSSION

Organic matter influence

The influence of the natural organic matter (NOM) on pesticide retention is studied experimentally by addition of humic acid to the feed solution (a single solute solution and a pesticide mixture). The acid concentration is kept constant equal to 100 mg L^{-1}. The feed solution is mixed in the course of 48 h. This is done to ensure good homogenization and provide sufficient contact time between the pesticides and humic acid providing complexes formation.

The humic acid effect on the solute retention using NF membrane is shown in Fig. 2. The results obtained provide to conclude that the presence of humic acid has not influence on atrazine and simazine rejections. As far as DEA is concerned, its retention decreases with about 10 % when compared to that obtained in absence of NOM. The diuron retention is the more affected and decreases with between 19 % and 21 %. These values are close to the results reported by Boussael et al. [18] using a Desal DK membrane of properties close to those of NF membrane. It is supposed that NOM, adsorbed on the membrane, induce a negative charge and diuron permeates more easily through the membrane due to its higher dipole moment.

Concerning OPMN-K membrane, the presence of NOM causes a slight decrease of retention for all solutes except atrazine (Fig. 3). A more important variation is observed for DEA, for which the rate of retention decreases significantly, between 20 % and 40 %.

The results obtained show that NF membrane is more efficient than OPMN-K one. This observation can be explained by the lower MWCO of NF ($MWCO_{NF}$ = 170 Da). This value is about two times smaller than that of

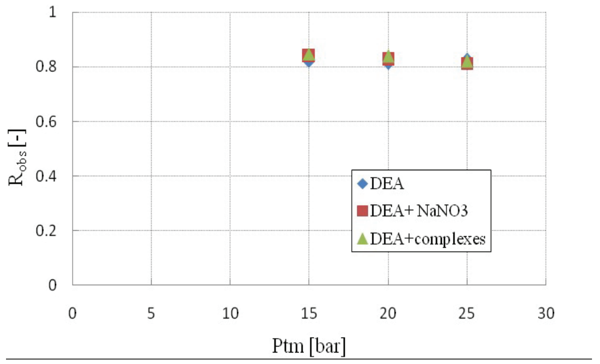


Fig. 6. DEA retention versus transmembrane pressure for three solutions: DEA simple solution, DEA+ $NaNO_3$ and DEA+ $Ca(NO_3)_2$+ $NaNO_3$ (membrane NF).

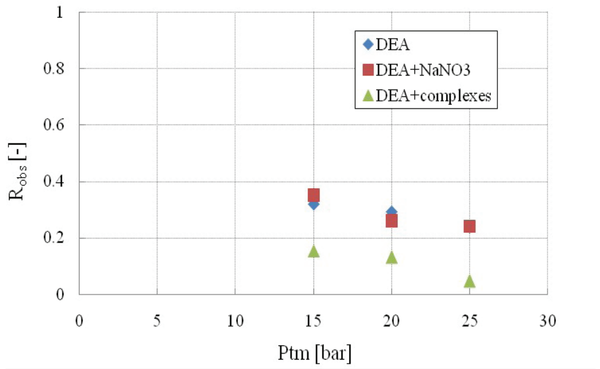


Fig. 7. DEA retention versus transmembrane pressure for three solutions: DEA simple solution, DEA+ $NaNO_3$ and DEA+ $Ca(NO_3)_2$+ $NaNO_3$ (membrane OPMN-K).

MWCO of OPMN-K ($MWCO_{OPMN-K}$ = 330 Da). This leads to a smaller pore radius of NF membrane ($r_{p,NF}$ = 0.35 nm) compared to that of OPMN-K one ($r_{p,OPMN-K}$ = 0.47 nm). Atrazine is the most retained pesticide for both membranes, while diuron is the least retained one: the average rejection observed amounts to 45 % for OPMN-K membrane and 87 % for NF membrane. The higher dipole moment and the linear form, which leads to a lower steric retention, can explain the lower diuron retention.

The permeate fluxes obtained for both membranes are compared for three cases: pure water flux, pesticide+DEA solution and pesticides+DEA+NOM solution. The results obtained are illustrated in Fig. 4 and Fig. 5. One can see that fluxes obtained in case of NF remain unchanged (Fig. 4) unlike those obtained using OPMN-K (Fig. 5).

One can see that the permeate flux in case of OPMN-K (Fig. 5) increases with pressure for pesticide+DEA and pesticide+metabolite+NOM solutions, but the dependence varies. The flow increase goes through two steps: the permeate flow increases linearly with pressure at low values coinciding with that observed with pure water and pesticides-NOM flow; at a pressure of 15 bar, the permeate flux of the pesticides-metabolite mixture increases less significantly, while at 25 bar it decreases significantly: about 18 % compared to that of the water flow. The flux of the more complex solution (humic acid+pesticides+DEA) is the same at low pressure values (less than 10 bar), then begins to decrease slightly when compared to that of the water flux (10 bar < TMP < 20 bar), and finally, at 20 bar, it stays constant.

The deviation of the curves observed at high pressure values in the both cases is probably due to the adsorption of the humic acid-pesticide complex on the membrane surface and the appearance of a concentration polarization phenomenon. The latter is described by Placas and Karabelas [11] in case of neutral pesticides nanofiltration in presence of low hydrophobic natural organic matter and metal ions at a low concentration. There, the solute is poorly rejected due to enhanced concentration polarization. This observation is confirmed by the flux value showed below and one can see that it is more pronounced for OPMN-K membrane (due to its larger pores). In our opinion, the concentration polarization observed in using this membrane is coupled to the pore clogging due to NOM-solute complex adsorption at pores surface reducing thus their pore radius.

Inorganic matter influence

The choice of DEA for this part of the study is determined by its lower molecular mass as well as its presence in soil/ground water. Two nitrate salts are added consecutively to the initial solution of DEA in deionised water (C_{DEA} = 100 µg L^{-1}): $NaNO_3$ (70 ppm) is introduced initially to be followed by $Ca(NO_3)_2$ addition at 70 ppm. These solutions are nanofiltrated and the results are presented in Fig. 6 (NF membrane) and in Fig. 7 (OPMN-K membrane). It is seen from the Fig. 6 that the addition of $NaNO_3$ does not change DEA retention observed by using

NF membrane. The same figure highlights also the fact that the introduction of divalent counter-ions (Ca^{2+}) to the above solution ($Ca\ (NO_3)_2$) does not affect DEA retention.

One can notice that DEA rejection in case of using OPMN-K does not change with the addition of $NaNO_3$, while the addition of $Ca\ (NO_3)_2$ causes a real drop of the retention (Fig. 7). This important increase of DEA rejection is probably due to membrane neutralization induced by Ca^{2+} ion, whose charge is greater than that of Na^+. According to the observation of some authors [28] the decrease of neutral solutes retention can be also attributed to decrease of their hydrodynamic radius.

CONCLUSIONS

Results presented in this study concerning filtration of pesticides and DEA show that the nanofiltration on NF and OPMN-K membranes has a good ability to eliminate pesticides and DEA. Retention of these organic neutral substances is due to steric effect and which is why the pesticides are more retained by NF membrane having a smaller MWCO compared to OPMN-K one. The latter provides a significant permeate flux and a lower solute retention compared to those of NF. The increase of the applied transmembrane pressure causes a slight increase of the solute retention in the case of NF membrane, while the rejection of solutes decreases more significantly for OPMN-K membrane due to its greater pore radius. Diuron presents an exception as it is the least retained substance by both membranes despite its high molecular mass. The low retention of diuron compared to that of the other solutes studied is due to its higher dipole moment (a great carbonyl group contribution) and to the linear form of this molecule. The phenomenon considered is accentuated in presence of humic acid.

The presence of organic and inorganic ($Ca(NO_3)_2$ and $NaNO_3$) matter in the treated solutions influences less strongly the retention of atrazine, simazine and DEA in case of both membranes application. However, atrazine metabolite retention decreases with about 10 % when compared to that observed in case of a simple DEA solution using an identical membrane (NF). The diuron retention decreases with 19 % to 21 %. In case of OPMN-K membrane, the pesticide retention is not affected by humic acid (NOM) addition, while DEA retention decreases significantly. Due to the formed complexes, the humic acid effect on pesticide retention depends on the solute structure and the membrane MWCO.

$NaNO_3$ addition does not affect DEA rejection for both membranes. The addition of $Ca(NO_3)_2$ to the feed containing initially $NaNO_3$ decreases the retention observed for OPMN-K membrane but does not affect that found on using NF one. The addition of inorganic matter causes a better expressed modification of the wide-pore membrane (OPMN-K) rejection. This influence is probably due to the membrane neutralization by the counter ion and consequently to its electrostatic repulsion decrease.

Acknowledgements

The authors would like to thank Dow/FilmTec and Vladipor companies for membranes supply.

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