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Retention of pesticides and metabolites by nanofiltration by effects of size and dipole moment

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HIGHLIGHTS

- Pesticide and metabolite elimination by nanofiltration was studied.
- Membrane performance vs transmembrane pressures and feed concentration were evaluated.
- Solute size influence (Stokes radius, molecular weight, length, width) is discussed.
- Influence of solute dipole moment on rejection is discussed.

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ABSTRACT

This study is focused on the possibility of pesticide and DEA elimination by nanofiltration using NF and OPMN-K membranes. Experiments are carried out on laboratory equipment in batch circulation and applied pressures vary between 10 and 25 bars. Three common pesticides (simazine, atrazine, diuron) and a chlorinated metabolite of atrazine: diethylatrazine is used as solutes, either alone or in complex solutions.
For all experiments, NF shows better performance compared to OPMN-K. The most retained pesticide is atrazine and the least retained is diuron due to its higher dipole moment (high carbonyl group contribution) coupled to linear form which may also induce a decrease in its steric retention. In the case of pesticide/DEA mixtures, DEA rejection is better (up to 44%) for all pressures due to the formation of macromolecular complexes. It is also noticed that molecular weight and size, expressed by Stokes radius, are not the only parameters influencing rejection: shape of the molecule (molecular length and width) has a strong influence on rejection. The observed rejection increases when length and width increase.
The nanofiltration technology seems to be a good way to treat the problem of pesticide pollution in one step process.

1. Introduction

The water pollution by pesticides is frequent for many countries. The concentrations of these pollutions in water resources are increasing gradually, exceeding the European Union drinking water specifications (98/83/CE, 11/3/1998). It is estimated that less than 0.3% of the quantity of pesticides applied by the farmers is in direct contact with the insects and the parasites. The huge amount is divided into three parts: the most important part (can reach 80–90%) evaporates and passes in the air [4]; the second part contaminates surface water directly and the third part contaminates the soil, percolates to the lower layers and contaminates the groundwater (M.A. [12]).

Simazine and atrazine are herbicides of the triazine class and diuron is a substituted urea herbicide. DEA is the most common from three chlorinated metabolites of atrazine generated in soil, water and animal tissue and its concentration in water presents about 70% from the total concentration of metabolites.

Simazine ($C_7H_{12}ClN_5$) is adsorbed especially in particulate form and rarely in gaseous form (gas/particle ratio may be in the range of 20%/80%) [22]. It is used to control broad-leaved weeds and annual grasses and it remains active in the soil for 2–7 months after application. Atrazine ($C_8H_{14}ClN_5$) use was denied by the EU, due to its contamination of drinking water and subsequent problems for humans [1]. However, it continues to be one of the most widely used herbicides in the world. It is considered to be persistent due to its moderate water solubility (33 mg/L) and small soil sorption partition coefficient (Kd = 3.7 L/kg) [21]. In soil, atrazine is transformed into several products including desethylatrazine

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(DEA), deisopropylatrazine (DIA), diaminochlorotriazine (DACT) and hydroxyatrazine (HA). The principal atrazine metabolite is desethylatrazine (DEA). The DEA ($C_6H_{10}ClN_5$) is a powder with a low solubility in water (27 $mg \cdot L^{-1}$) and it is also considered to be persistent. The last pesticide used in this study is diuron ($C_9H_{10}Cl_2N_2O$). Diuron is used to control a wide variety of annual and perennial grassy weeds. It is considered as persistent (one month to one year). Diuron can be found in many environments such as soil, sediments and water in the solid phase rather than in the gaseous or liquid phase [10,17].

The traditional method for pesticide removal is activated carbon filtration [11]. Although this method is effective, it is expensive due to the activated carbon regeneration.

Over the past two decades, membrane processes and particularly nanofiltration have been studied as a potential way of pesticide removal. Moreover, the nanofiltration allows reducing the water hardness, and the retention of nitrate, pesticides and micro-organisms, without chemical addition. The choice of the membrane separation process is due to the characteristics of membranes used. Nanofiltration membranes are microporous with pore diameter near nanometer and usually charged. The very high selectivity of the process is usually explained in terms of size effect, charge effect (due to electrostatic interactions between ions and membrane charged sites), and differences in diffusivity and solute solubility [16,18,20]. In many studies, it is demonstrated that molecular weight, size and geometry of solutes are very important parameters influencing the pesticide rejection [5,13,14,19,23,24]. A number of parameters such as hydrophobicity, polarity, pH and water matrix also influence the rejection performance of the membrane [2,3,13,15,24,25].

Due to the membrane characteristics and considering the fact that the molecular weight of simazine, atrazine, diuron and DEA are important, one can predict, that the performance of nanofiltration membranes to retain those pesticides must be highly significant.

The objective of this work is to study the performance of two industrial nanofiltration membranes to retain atrazine, simazine, desethylatrazine and diuron. Nanofiltration membranes (OPMN-K from Vladipor society and NF from Filmtec Corporation of Dow Chemical Company) are used in a flat sheet cell with tangential flow. The effect of feed composition (simple solutions of each solute and mixture of two or four solutes) and operating pressure on the permeate flux and pesticide rejection is investigated for both membranes.

2. Materials and methods

2.1. Pesticides and pesticide metabolite (DEA)

For experiments, the pesticides used are atrazine, simazine and diuron. The used atrazine metabolite is desethylatrazine (DEA). The molecular structure of solutes is presented in Table 1, where D_s is molecular diffusivity.

The Stokes radius r_s [8] is calculated by:

$$\log r_s = -1.4854 + 0.461 . \log M \quad (1)$$

where r_s is Stokes radius [nm] and M: molecular weight [$g \cdot mol^{-1}$].

Each solution is prepared with osmotic water (conductivity less than 2 μS/cm). The solute concentration in the feed phase is 100 $\mu g \cdot L^{-1}$. In the mixtures used, the concentration of each pesticide is also 100 $\mu g \cdot L^{-1}$.

2.2. Analytical method

Solute concentrations are analyzed using solid-phase extraction (SPE) coupled to high performance liquid chromatography (HPLC). For sample preconcentration, SPE is chosen, which does not require sophisticated equipment and provides a high efficiency.

The HPLC column used is ZORBAX C18 (5 μm, 46 mm, 250 mm). The mobile phase is a mixture acetonitrile (CAN)/deionized water (40/60). The UV detection is operated at a wavelength of 215 nm for atrazine, simazine, DEA and at 251 nm for diuron.

The sample pre-concentration by SPE is carried out with BondElut C18 cartridges (500 mg, 3 mL). The cartridges are previously conditioned by three successive elutions: 3 mL of CH_2Cl_2/MeOH (80/20), 3 mL of MeOH and 2×3 mL of deionized water. Then, 100 mL of the liquid sample is passed through the cartridge. The sample flow rate is controlled at approximately 5 $mL \cdot min^{-1}$. Before eluting solutes, the cartridge is dried by passing air for 5 min. Pesticides are eluted successively with 1 mL of methanol (MeOH) and 3 mL of CH_2Cl_2/MeOH (80/20). Finally, obtained solution is dried by passing nitrogen and 1 mL of MeOH/deionized water (50/50) is added to the sample.

2.3. Nanofiltration membranes

The membranes used in this study are flat sheet, organic, negatively charged, nanofiltration membranes NF (provided by FilmTec Corporation/Dow) and OPMN-K (provided by Vladipor Society). Their characteristics are summarized in Table 2.

To reduce swelling and compaction effects during experimentations, membranes were immersed during 48 h in deionized water and were compacted during 12 h at 25 bars.

2.4. Experimental setup and procedure

The experimental setup used in this study is detailed elsewhere [6]. All experiments have been carried out at 20±1 °C in batch mode: both permeate and retentate solutions have been carried back to the feed tank. The applied transmembrane pressure (TMP) has varied between 10 and 25 bars and the circulation velocity in the flat membrane cell has fixed to 0.45 $m \cdot s^{-1}$ (Re = 3300) corresponding to a flow rate of 5 $L \cdot min^{-1}$.

Observed solute rejection is obtained using the following equation:

$$R_{obs} = \left(1 - \frac{C_p}{C_0}\right) \times 100 \quad (2)$$

C_0 feed concentration [ppm]
C_P permeate concentration [ppm]

3. Results and discussion

3.1. Membrane characterization

Firstly, the membranes are characterized with pure water at four transmembrane pressures (10, 15, 20 and 25 bars) in order to calculate the water permeability of the membrane at steady state conditions. For these experiences, deionized water is used at constant temperature T = 20±1 °C. For both membranes, the results show a flow proportional to the applied pressure. The water permeability is determined by linear regression. The permeability is K_{water} = 0.0045 $m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for NF membrane and K_{water} = 0.0079 $m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for OPMN-K membrane (Fig. 1).

Organic, molecular solutes like saccharose, glucose and glycerol have been used to get average pore sizes of NF and OPMN-K membranes (Table 3). Experiments are carried out at four transmembrane pressures: 10, 15, 20 and 25 bars.

Molecular weight cut-off (MWCO) is defined as the corresponding molecular weight to 95% rejection. The values of MWCO obtained are 170 Da and 330 Da respectively for NF and OPMN-K. Finally, pore