

# A study of selected herbicides retention by nanofiltration membranes—The role of organic fouling

K.V. Plakas<sup>a,b,\*</sup>, A.J. Karabelas<sup>a</sup>, T. Wintgens<sup>b</sup>, T. Melin<sup>b</sup>

<sup>a</sup> Chemical Process Engineering Research Institute and Department of Chemical Engineering, Aristotle University of Thessaloniki, Univ. Box-455, Thessaloniki GR 541-24, Greece

<sup>b</sup> Chemical Engineering Department, RWTH Aachen University, Turmstrasse 46, 52056 Aachen, Germany

Received 16 April 2006; received in revised form 26 July 2006; accepted 27 July 2006

Available online 15 August 2006

## Abstract

This paper reports the results from a series of experiments investigating the retention of three selected herbicides (atrazine, isoproturon and prometryn) in single solute or dissolute solutions by three typical commercial nanofiltration membranes. Based on measured permeation rates and the rejection capacity for herbicides, one of the tested nanofilters is selected in order to study the role of organic matter and calcium concentration on herbicide retention. The effect of organic fouling, caused by humic substances, on the retention of atrazine and isoproturon in dead-end nanofiltration is also examined.

In the absence of other species, the retention of individually tested herbicides can be explained by the combined effect of their molecular size and dipole moment, whereas the simultaneous nanofiltration of two herbicides seems to be influenced by a competitive adsorption of solutes on the membrane surface. The extent of membrane organic fouling, depending on the nature and the relative concentration of humic substances as well as the presence of calcium, significantly affects the retention of the tested herbicides; additionally, nanofiltration of water where herbicides are present together with humic substances results in increased herbicide retention. This trend is less evident in the presence of calcium ions due to their possible interference with the humic substances–herbicides interactions.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Nanofiltration; Herbicides; Humic substances; Organic fouling; Drinking water

## 1. Introduction

Current research documents with increasing frequency that many synthetic organic micropollutants, such as pesticides, which have not historically been considered as contaminants, are present in drinking water sources throughout the world [1]. In parallel, statistical data from Europe show that there is a trend towards an increased dependency of agricultural activities on pesticide products and hence an increased exposure to pesticides, their “inert ingredients” and metabolites [2]. In Greece and Germany, many of the pesticides found in water sources are herbicides, often detected in surface waters. Furthermore, many of these herbicides are fairly mobile in soil and readily migrate into ground waters [3–5]. Triazines are the most widely used group of herbicides since their discovery in the 1950s, constituting a

group of chemically similar compounds used to control certain annual broadleaf weeds and grasses throughout the world [6]. Monitoring studies of surface waters as well as ground waters in Greece and Germany have shown widespread occurrence of these herbicides, since this kind of crop protection products appears to hold the largest share of the pesticide market in the two countries [2]. Two triazine compounds, atrazine and prometryn, and the phenylurea derivative, isoproturon, are the most frequently identified herbicides, in concentrations that exceed the drinking water quality value proposed by the European Union; i.e. 0.1 µg/L for each individual pesticide and 0.5 µg/L for the total concentration of pesticides and related products, foreseen in the European Drinking Water Directive 98/83/EC [3,5].

The presence of pesticides in water sources is becoming a concern in drinking water production, wastewater treatment, and water reuse applications due to potentially adverse health effects associated with these compounds. Numerous studies with laboratory animals have shown that a series of pesticides is involved in endocrine disruption, while many of the well known

\* Corresponding author. Tel.: +30 2310 996214; fax: +30 2310 996209.  
E-mail address: [kplakas@cperi.certh.gr](mailto:kplakas@cperi.certh.gr) (K.V. Plakas).

herbicides (such as atrazine) and insecticides are blamed for long term toxicity and carcinogenicity [7–9]. For this reason, they are considered as the most thoroughly tested and regulated substances in use today.

In view of the problems inherent to conventional water treatment processes to cope with the removal of synthetic organic chemicals, like pesticides, various researchers have turned their attention to pressure-driven membrane processes which emerge as a valuable alternative [10]. Since the majority of the compounds categorized as pesticides have molecular weights (MW) of more than 200 Da, reverse osmosis (RO) and nanofiltration (NF) are promising options for their removal from contaminated water sources. The application of RO membranes to retain hazardous organic pollutants such as pesticides is under investigation since the late 1960s [11,12]. The increasing interest for more cost-effective membrane processes, operating at lower pressure and with higher membrane flux, has led to the development of ultra low-pressure RO and NF membranes, which have been applied for the successful removal of pesticides in the last 10 years [13,14]. The need for partial softening of raw waters as well as the removal of hazardous organic micropollutants, has led to the adaptation of nanofiltration for serving this dual purpose; a notable example is the water facility of Mery-sur-Oise, France, where application of nanofiltration technology is reported to be a total success [15].

Results on the retention of pesticides by NF membranes are often reported and the related articles are reviewed in recent papers [16,17]. Researchers agree that size exclusion is the most important mechanism of pesticide retention, while several studies show that there are also other solute parameters, such as the dipole moment and the hydrophobicity, influencing the adsorption on the membrane surface and therefore retention [18,19]. Additionally, feed water properties such as pH, ionic strength, hardness and the presence of organic matter are identified as having an influence on pesticide rejection [20–23]. Surveying the literature, however, reveals the lack of studies on the effect of fouling of NF/RO membranes on pesticide retention. Indeed, numerous studies have been reported on organic and colloidal fouling with emphasis on permeate flux decline and salt rejection [24–26], but studies on simultaneous micro-pollutants rejection behaviour are rather limited. Ng and Elimelech [27] report that membrane fouling tends to degrade the permeate water quality; more specifically, they find that the decline in steroid hormone rejection with time is much more severe if colloidal fouling takes place. In a recent study, Xu et al. [28] show that membrane fouling, caused by secondary effluents from a municipal wastewater treatment plant, significantly affects the rejection of organic solutes by cellulose triacetate RO membranes, NF and ultra low-pressure RO membranes, whereas it is less important for thin film composite RO membranes. These authors attribute the difference in the rejection values between virgin and fouled membranes to the modified membrane characteristics. Therefore, the need for systematic studies of the influence of various types of fouling on the rejection characteristics of organic micropollutants such as pesticides is evident.

The scope of this paper is to assess the capability of three commercially available NF membranes to retain three com-

mon herbicides (i.e. atrazine, isotroturon and prometryn) and to investigate the effect of an already fouled (by humic substances) membrane on the retention characteristics of atrazine and isotroturon. Moreover, the retention characteristics of selected herbicides are studied when treated in the presence and absence of humic substances and/or calcium ions.

## 2. Experimental work

### 2.1. Materials and methods

#### 2.1.1. Membranes and characterization

Three types of flat sheet nanofiltration membranes, listed in Table 1, are used in this study; ESNA is an aromatic polyamide membrane while NF200 and NF270 are polypiperazine-based membranes. In all membranes the active layer is supported by a porous polysulfone layer reinforced with a non-woven polyester fabric. The flux,  $J_w$ , of pure water (i.e. water free of ions and organic carbon), is measured before each separation experiment and the results are summarised in Table 1. Since the observed  $J_w$  fluctuates, the values presented in Table 1 correspond to average ones over a period of 1–5 h depending on the membrane used. The NF270 membrane exhibits greater permeability than the other two.

The hydrophobicity of the membrane surface is analysed by sessile drop contact angle measurements, performed with a Contact Angle Measuring Instrument G10 (Krüss). These measurements with clean membranes show that NF270 and NF200 are hydrophilic, while ESNA is relatively hydrophobic.

Characterisation of the composite NF membranes was carried out by measuring the membrane streaming potential at various pH values (Fig. 1). The measurements were performed with a PAAR EKA-Electro Kinetic Analyzer RV. 4.0, over the pH range of 3–9, using an electrolyte solution of 2 mM KCl. From Fig. 1 it can be concluded that the two Filmtec membranes are negatively charged for  $\text{pH} > 3$  (NF200 is slightly positively charged for  $\text{pH} \leq 3$ ) whereas the ESNA membrane is positively charged for  $\text{pH} < 5$ . At higher pH, however, ESNA exhibits a greater negative charge, followed by NF270 and NF200.

The surface condition of the virgin and fouled NF270 membranes was examined by scanning electron microscopy (SEM). A JEOL (JSM-6300) Scanning Microscope was used; images

Table 1  
Characteristics of the membranes used in this study

	NF270	NF200	ESNA
Manufacturer	Dow (Filmtec)	Dow (Filmtec)	Hydranautics
MWCO <sup>a,b</sup> (Da)	300	300	200
Contact angle (°)	28 ± 2	26 ± 2	60 ± 2
Specific flux <sup>c</sup> (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	10.59	3.65	5.6
Stabilized CaCl <sub>2</sub> passage <sup>b</sup> (%)	40–60	50–65	20

<sup>a</sup> Molecular weight cut-off.

<sup>b</sup> As reported by manufacturer.

<sup>c</sup> Determined at 5 bar (filtration of deionised water at 25 °C).

Download English Version:

<https://daneshyari.com/en/article/639052>

Download Persian Version:

<https://daneshyari.com/article/639052>

[Daneshyari.com](https://daneshyari.com)