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Membrane treatment applied to aqueous solutions containing atrazine photocatalytic oxidation products

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ABSTRACT

The present work aims to study the viability of combining heterogeneous photocatalysis and nanofiltration as an innovative strategy to improve atrazine elimination from aqueous solution by advanced oxidation processes. In order to promote the photocatalytic oxidation of atrazine, the selective separation of the intermediate products was explored by means of membrane filtration. Two nanofiltration membranes (NF-90 and NF-270) were tested to study their performance for aqueous solutions of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine), desethyl-desisopropyl-atrazine (2-chloro-4,6-diamino-1,3,5-triazine) and ammeline (2-hidroxy-4,6-amino-1,3,5-triazine). The influence of membranes and solutes properties on the organic rejection and flux decline was evaluated. Experimental flux declines were systematically small, although the values obtained for NF-90 were slightly larger than those found for NF-270. The highest difference was observed in the case of atrazine which is the most hydrophobic solute. NF-90 membrane exhibited high solute rejection for all compounds, reaching 98% for atrazine; however, rejection selectivity was poor. Conversely, NF-270 membrane showed significant differences in solute rejection between atrazine and the other studied compounds, systematically higher than 30%. In addition, rejection selectivity was enhanced al low transmembrane pressure. Experimental NF-270 rejection values suggest the use of this nanofiltration membrane to achieve the effective separation of aqueous atrazine from the other selected compounds originated in its photocatalytic oxidation.

Keywords: nanofiltration; rejection; selectivity; atrazine; pollutant removal

1. Introduction

Atrazine is one of the most common herbicides found in ground water sources and drinking water supplies. It has been included in the priority substances list of the European Commission (EC) [1]. This pollutant is not readily biodegradable and exhibits a high aqueous resistance with lifetime in the environment ranging from days to years, therefore causing problems in water detoxification processes. Heterogeneous photocatalysis has been demonstrated as a good alternative to the treatments usually applied to effluents contaminated with pesticides including the s-triazine herbicides [2,3]. It has been reported that the photocatalytic degradation occurs by several steps, as displayed in Fig. 1, leading to cyanuric acid as final product. In general, the latest oxidation products of the degradation pathway are increasingly refractive to chemical oxidation [3].

In addition, previous studies have shown that these less substituted triazine products and cyanuric acid are

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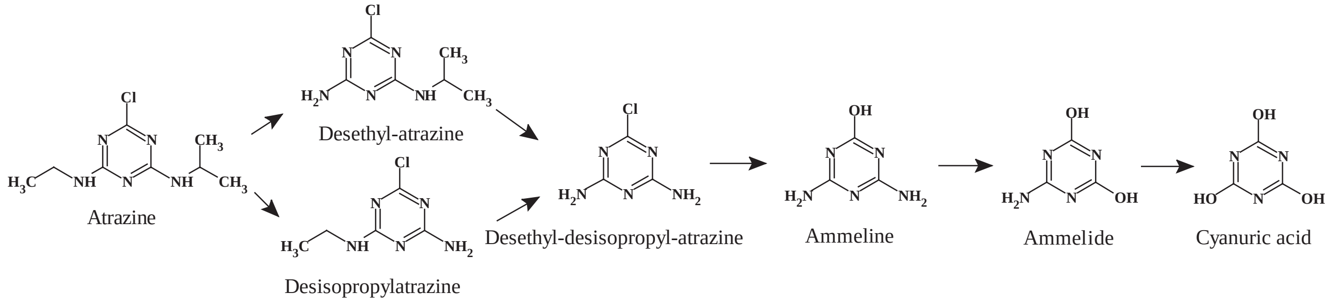

Fig. 1. Scheme of photocatalytic atrazine degradation.

more biodegradable than atrazine and the intermediate products formed in the first steps of its photocatalytic oxidation [4,5]. For this reason, it should be very interesting to integrate the photocatalytic treatment of atrazine-polluted water with a technology that allows the separation of non-biodegradable species from those further amenable to biological degradation. Membrane processes, such as nanofiltration, appear as a feasible option to achieve this objective, since they have been successfully applied to separation of a wide variety of organic pollutants [6,7]. Nevertheless, to the best of our knowledge, application of integrated membrane-oxidation processes has been limited up-to-date to systems where the molecular weights of the initial organic compounds are several times greater than their partially oxidized products, *e.g.*, the oxidation of polyethyleneglycol as a model compound representing polymer manufactures wastewater [8]. On the contrary, small differences in the molecular weights are found between the above indicated intermediates formed in the photocatalytic treatment of wastewater containing atrazine.

On this basis, the purpose of the present work has been to explore the performance of nanofiltration membranes for the separation of atrazine and the less substituted triazine compounds formed in its photocatalytic oxidation in order to improve the removal of this pesticide. Membrane selectivity could be a useful tool to divide the photocatalytic solution discharge in two streams. The rejected stream containing the biorecalcitrant organics should be recirculated back to the photocatalytic reactor, whereas the permeate stream including the more biodegradables oxidation products could be biologically treated.

2. Materials and methods

2.1. Chemicals

All organic solvents were of analytical grade and used as received. Atrazine 99% (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) was obtained from Riedel-de Häen. The standards cyanuric acid 98% (2,4,6-trihydroxy-1,3,5-triazine) and desethyl-desisopropyl-atrazine (95%) were obtained from Sigma-Aldrich. Ammeline 95% (2-hydroxy-4,6-diamino-1,3,5-triazine) was purchased from ABCR. Table 1 lists some physicochemical properties of the tested herbicide and derivatives. Both photocatalytic and membrane experiments were conducted with synthetic solutions prepared by using organic-free de-ionized water (Milli-Q SP) and a single solute. The organic concentrations for filtration experiments of the model compounds were fixed at 20 mg/L, in accordance to the concentration used in the photocatalytic oxidation experiments.

2.2. Photocatalysis procedure

Photocatalytic reactions were carried out in a batch Pyrex reactor irradiated by a 150 W medium pressure

Table 1
Physico-chemical characteristics of the model compounds evaluated in this study

Compound	Molecular formula	MW (Da)	Solubility (mg/L)	logK_{ow}[a]
Cyanuric acid	$C_3H_3N_3O_3$	129.07	2000	−1.2
Ammeline	$C_3H_5N_5O$	127.11	75	−0.8
Desethyl-desisopropyl-atrazine	$C_3H_4ClN_5$	145.55	66	−0.1
Atrazine	$C_8H_{14}ClN_5$	215.68	33	2.6

[a] Logarithm of octanol-water partition coefficient.

Table 2
Relevant properties of investigated NF membranes

Membrane	R_{NaCl} (%)	R_{MgSO4} (%)	MWCO (Da)	PWP[a] (L/m^2 h bar)	Contact angle
NF-270	40	97	340	13.5	28°
NF-90	85	97	180	11.3	63°

[a]Pure water permeability.

mercury lamp (Heraeus TQ-150), placed inside a quartz jacket and provided with a cooling tube. Aqueous solutions of atrazine (25 mg/L) were irradiated in the presence of the catalyst (TiO_2 P25 supplied by Degussa), which was maintained in suspension by a magnetic stirrer placed at the bottom of the vessel. Aliquots were taken at time intervals, following filtration through 0.22 μm Nylon filters in order to remove the suspended solids before being analyzed.

2.3. Membranes

Two commercial nanofiltration membranes, NF-270 and NF-90, both provided by Dow Filmtec®, were evaluated in this investigation. These membranes were selected on the basis of their distinct average pore size and hydrophobicity (contact angle). According to the manufacturers, both membranes are polyamide thin-film composite with a microporous polysulfone supporting layer. The specifications of the membranes indicate that they can achieve a high removal of divalent salts and organic compounds from feed water. Table 2 summarizes some of the most relevant characteristics of the selected membranes.

2.4. Crossflow membrane filtration protocol

The whole experimental procedure was previously described in detail elsewhere [9]. The main aspects are briefly mentioned here. Membranes were tested as flat sheet membrane specimens in a commercial SEPA II crossflow filtration test cell (Osmonics, Minnetonka, MN). The effective membrane area in the test unit was 139 cm^2. The experiments were operated in a recycle mode in which all concentrate and permeate streams were flowed back to the feed vessel.

A new membrane sample was used for each essay to avoid the influence of previous experiments. Fresh membranes were first soaked in distilled water for approximately 24 h to remove chemicals used for membrane preservation. Prior to each experiment, the membrane was stabilized (precompacted) at 20 bar using Milli-Q water for 1 h until there was no further variations in permeate flux to avoid the influence of compaction during filtration experiments. The operation time required for the membrane system to reach steady state was usually about 30–60 min. During the experiments, conducted under pressure conditions ranging between 2 and 12 bar, samples of permeate and concentrate solutions were collected every 20 min after the membrane system reached steady state. The permeate flux was determined by measuring the volume of permeate collected in a given time interval. The volume of samples withdrawn for solute analysis was 5 mL. The feed crossflow velocity was set at 1.5 m/s in all the experiments.

To compare the flux decline between selected compounds, relative fluxes (Eq. (1)) were defined as the relation of the organic solution flux (J_v) to the pure water flux (J_w):

$$\mathrm{RF} = \frac{J_v}{J_w}, \tag{1}$$

where the pure water flux (Milli-Q water) was measured before the filtration experiments for each compound.

The rejection of every organic compound was calculated as:

$$R\,(\%) = \left(1 - \frac{C_p}{C_c}\right) \times 100, \tag{2}$$

where C_p and C_c are the permeate and concentrate concentrations, respectively.

The temperature was controlled by circulating feed water through a stainless-still coil immersed in the thermostatic bath and was maintained in all experiments at 25°C.

2.5. Analysis

High Performance Liquid Chromatography (Varian Polaris Prostar 320) with the UV-VIS detector set at 215 nm was used to identify and quantify the products obtained in the photocatalytic reactions and also for concentrate and permeate samples. Toxicity was evaluated by means of the luminescent inhibition of *Vibrio fischeri* bacteria using a BioTox® equipment (Aboatox).

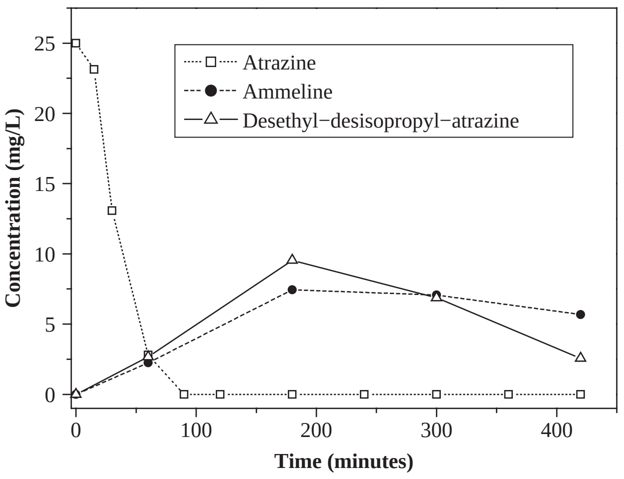

Fig. 2. Concentration profiles of atrazine, ammeline and desethyl-desisopropyl-atrazine during the photocatalytic degradation of atrazine with TiO_2.

3. Results

3.1. Photocatalysis

Fig. 2 displays the kinetics of the photocatalytic degradation of atrazine. An effective decrease in the pesticide concentration was observed with the irradiation time, with complete disappearance after ~90 min. HPLC analysis of the aliquots taken during the reaction showed that a number of intermediate compounds were formed as the concentration of atrazine decreased. Among them, the concentration profiles of major products ammeline and desethyl-desisoproyl-atrazine for 7 h of irradiation have been included. They reach a maximum concentration within 180–200 min of photocatalytic treatment, following afterwards their conversion to more hydroxylated compounds. Conversion to cyanuric acid was not detected until 14 h of irradiation.

The toxicity evaluation of the aliquots withdrawn along the reaction showed a gradual decrease in toxicity, according to the values in the inhibition percentage of *Vibrio fischeri* bacteria: 93.5% in the initial sample constituted by 25 mg L^{-1} of atrazine, and 59.56% in the sample obtained after seven hours of reaction.

3.2. Nanofiltration

To study the membrane performance on relative flux and organic rejection, experiments were carried out for a time interval of three hours at 5.5 bar and 25°C (experimental conditions recommended by the manufacturer). For comparison purposes the experimental data at 3 h were selected, time at which the membranes showed stable values in flux and rejection.

As illustrated in Fig. 3, the flux declines were minor and rather similar for both tested membranes, although the lowest relative fluxes thoroughly occurred for NF-90. In addition, atrazine solutions exhibited the larger flux decline difference between both membranes. Previous studies have suggested that flux decline during filtration of aqueous solutions containing organic compounds is mainly related to adsorption processes which can be promoted by hydrophobic interactions. Adsorption on the pores and membrane surface results in a reduction of the free volume in the membrane, what leads to flux variations [10,11]. Therefore, the observed difference for atrazine, the more hydrophobic solute (see $\log K_{ow}$ in Table 1), could be attributed to the stronger hydrophobic interaction between this solute and NF-90, the more hydrophobic membrane (contact angle 63°).

Rejection of the selected organic compounds in aqueous solution for NF-90 and NF-270 membranes is shown in Fig. 3. Solute rejection systematically follows the expected order $R_{NF\text{-}90} > R_{NF\text{-}270}$, which is consistent

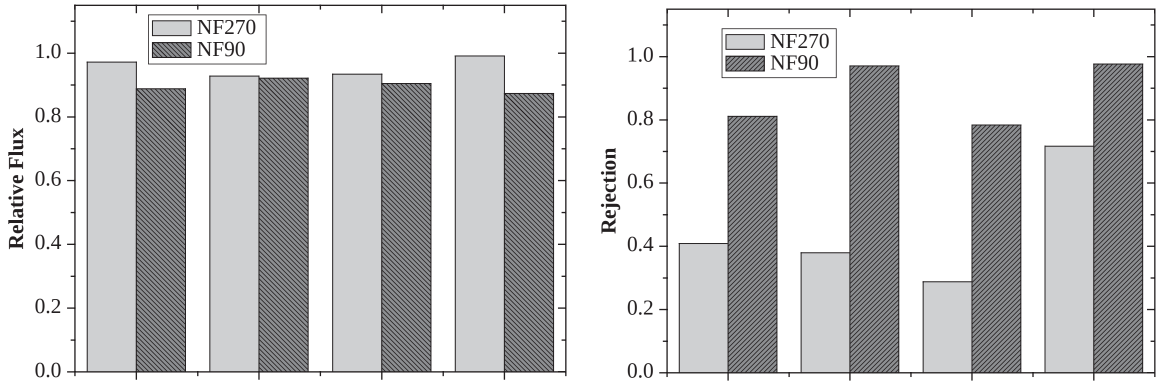

Fig. 3. Flux decline and rejection after 3 h of filtration with a feed concentration of 20 mg/L for NF-270 and NF-90 membranes.

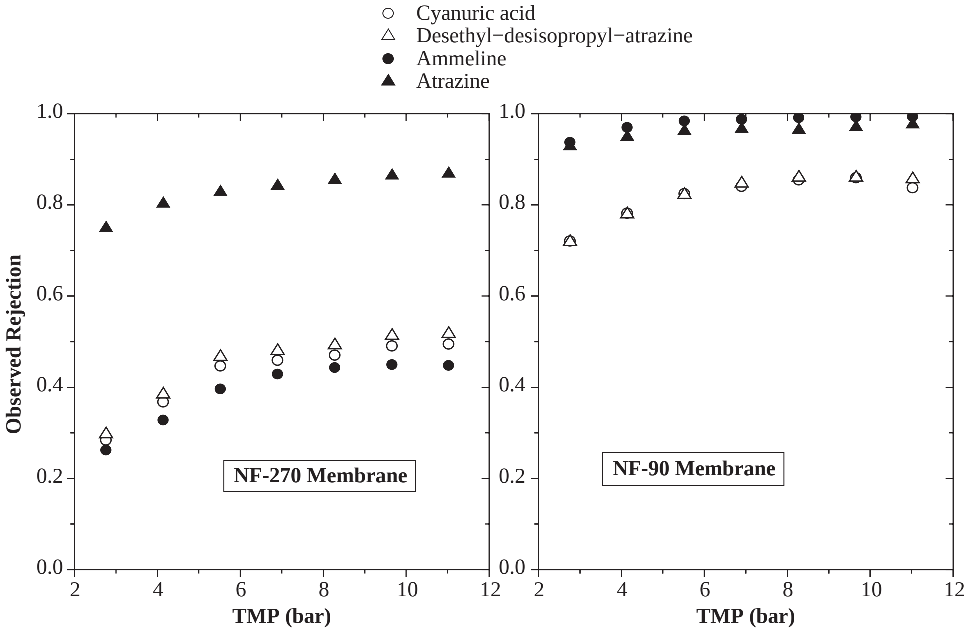

Fig. 4. Observed rejection plotted against transmembrane pressure (TMP) of selected compounds for NF-270 and NF-90.

with the sieving characteristics of the membranes, such as MWCO and pore size [7]. Therefore, steric interactions between membrane and organic compounds are a determining feature for the solute transport across the membrane.

As observed in Fig. 3, NF-90 exhibits a high rejection for the selected compounds (over 80% in all cases) and NF-90 behaves as a quasi-ideal semi-permeable membrane for atrazine ($R = 98\%$). However, NF-90 solute rejection is not selective enough to separate atrazine from its oxidation products. Conversely, NF-270 exhibits a distinctive performance for atrazine in comparison to the products formed during the photocatalytic degradation of the pesticide with rejection differences higher than 30%. Thus, NF-270 can act as a selective barrier between the parent pesticide and its degradation intermediates in order to implement processes that combine membrane technology with photocatalytic/biological treatments.

3.3. Influence of transmembrane pressure (TMP)

To improve the selective rejection of the selected compounds, it was explored the influence of the transmembrane pressure (TMP) on filtration performance, since this variable can become an important operational parameter. The rejection dependence upon TMP can be observed in Fig. 4 for NF-90 and NF-270 membranes.

Effect of TMP on rejection was studied from 2 to 12 bar. Experimental rejection systematically increased up to 8 bar; from this pressure rather steady rejection values were generally found.

In order to combine membrane processes with photocatalysis technology, Fig. 4 confirms that NF-90 is not suitable for separating atrazine and their oxidation products; conversely, NF-270 can act as a selective barrier for atrazine at all TMP values. To achieve the optimal operational conditions, the lower TMP range studied in this work should be used, where the selective rejection for atrazine against its oxidation products by NF-270 membrane exhibits the widest differences.

4. Conclusions

A number of s-triazine intermediate compounds were formed as a consequence of photocatalytic oxidation of the herbicide atrazine in aqueous solution. In particular, ammeline and desethyl-desisopropyl-atrazine exhibited high concentration profiles as intermediate oxidation products during degradation process. This work investigated the viability of separating by nanofiltration atrazine from its photocatalytic degradation derivatives. In this way, atrazine, ammeline, desethyl-desisopropyl-atrazine and cyanuric acid, the expected final degradation product, were chosen to explore the retention selectivity of two nanofiltration membranes, NF-90 and NF-270.

Observed flux declines were of little significance for both membranes, although the relative fluxes for NF-270 were steadily larger than those found for NF-90. It was especially notable the difference for atrazine. This behavior is attributed to adsorptive effects of the organic solutes on the nanofiltration membranes which are enhanced through hydrophobic interactions, since atrazine and NF-90 are the most hydrophobic solute and membrane, respectively, within the materials here studied. Rejection performance was highly depending on the membrane used. Solute rejection by NF-270 were lower than NF-90 for all studied compounds. NF-90 systematically showed high retention capacity, more than 80% for every solute, reaching around 98% for atrazine. However, differences between individual solute rejections were not marked. Conversely, NF-270 membrane rejected each solute in a distinctive way with significant differences between atrazine and the other compounds (within 30–40%). To optimize the rejection selectivity in order to combine photocatalytic and membrane technologies, the effect of transmembrane pressure was also analyzed. Low pressure conditions revealed to be the more adequate.

Acknowledgments

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References

[1] Directive 2000/60/EC of the European Parliament and of the Council of October 23, 2000 establishing a framework for Community action in the field of water policy (L327 of 22-12-2000).

[2] V. Hequet, C. Gonzalez and P. Le Cloirec, Photochemical processes for atrazine degradation: Methodological aproach, Water Res., 35 (2001) 4253–4260.

[3] C.L. Bianchi, C. Pirola, V. Ragaini and E. Selli, Mechanism and efficiency of atrazine degradation under combined oxidation processes, Appl. Catal. B: Environ., 64 (2006) 131–138.

[4] C. Ernst and H.J. Rehm, Development of a continuous system for the degradation of cyanuric acid by adsorbed *Pseudomonas* sp. NRRL B-12228, Appl. Microbiol. Biotech., 43 (1995) 150–155.

[5] M. Radosevich, S.J. Traina, Y.L. Hao and O.H. Tuovinen, Degradation and mineralization of atrazine by a soil bacterial isolate, Appl. Environ. Microbiol., 61 (1995) 297–302.

[6] K.O. Agenson, J.H. Oh and T. Urase, Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process, J. Membr. Sci., 225 (2003) 91–103.

[7] J.M. Arsuaga, M.J. López-Muñoz, A. Sotto and G. del Rosario, Retention of phenols and carboxylic acids by nanofiltration/reverse osmosis membranes: sieving and membrane-solute interaction effects, Desalination, 200 (2006) 731–733.

[8] R. Hellebrand, D. Mantzavinos, I.S. Metcalfe and Livingston, Integration of Wet Oxidation and Nanofiltration for Treatment of Recalcitrant Organics in wastewater, Ind. Eng. Chem. Res., 36 (1997) 5054–5062.

[9] M.J. López-Muñoz, A. Sotto, J.M. Arsuaga and B. Van der Bruggen, Influence of membrane, solute and solution properties on the retention of phenolic compounds in aqueous solution by nanofiltration membranes, Sep. Purif. Technol., 66 (2009) 194–201.

[10] L. Braeken, B. Van der Bruggen and C. Vandecasteele, Flux decline in nanofiltration due to adsorption of dissolved organic compounds: Model prediction of time dependency, J. Phys. Chem., 110 (2006) 2957–2962.

[11] L. Braeken, R. Ramaekers, Y. Zhang, G. Maes, B. Van der Bruggen and C. Vandecasteele, Influence of hydrophobicity on retention in nanofiltration of aqueous solutions containing organic compounds, J. Membr. Sci., 252 (2005) 195–203.