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MEMBRANE FILTRATION EFFICIENCY ON TRIAZINE HERBICIDES IN ORGANIC AND AQUEOUS SOLUTIONS

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Abstract

The filtration efficiency of organic contaminants like triazine herbicides class (simazine, atrazine and propazine) has been tested using more types of filter membranes (PTFE, glass, cellulose acetate, regenerated cellulose) from synthetic solutions with variable content of organic modifiers (acetonitrile and methanol). Thus, 2 mL of synthetic solutions (10%, 25%, 50%, 75% and 100% methanol and respectively acetonitrile) were filtered on each of the membrane filters. Simazine pesticide responds very well on PTFE, glass and regenerated cellulose filter membrane when the organic modifiers was acetonitrile. An excellent recovery was obtained when filtering simazine with 25% ACN on PTFE, glass and regenerated cellulose. In case of atrazine was observed a good recovery on the four filters when the solution contained 100% acetonitrile and 75% methanol. The propazine has an efficient filtration on all four membranes, on hydrophobic and hydrophilic membranes, contrary to theoretical prediction. For the samples prepared in 100% organic solvent (methanol), PTFE filters provided excellent recovery (>95%) for all three pesticides (simazine, atrazine and propazine). The study is useful in the filtration stage of organic extracts resulting from processing of environmental samples (water / soil).

Keywords: *environmental, liquid chromatography, membrane filters, pesticides*

Introduction

Triazine herbicides (simazine, atrazine and simazine) 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 (Grover 1988). Current research documents with increasing frequency show that many synthetic organic micro- pollutants, such as pesticides are present in drinking water sources throughout the world (Novotny 1999). The presence of pesticides in water sources and soil 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 performed on laboratory animals have shown that a series of pesticides is involved in endocrine disruption, while many of the well-known herbicides (such as atrazine) are blamed for long term toxicity and carcinogenicity. For this reason, they are considered as the most thoroughly tested and regulated substances in use today.

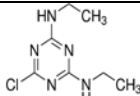
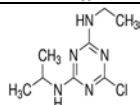
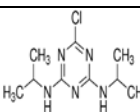
Simazine ($C_7H_{12}ClN_5$) is adsorbed especially in particulate form and rarely in gaseous form (gas/particle ratio may be in the range of 20%/80%) (Tissier et al 2005). It is used to control broad-leaved weeds and annual grasses and it remains active in the soil for 2-7 months after application. Atrazine ($C_8H_{14}ClN_5$) use was denied by the EU, due to its contamination of drinking water and subsequent problems for humans (Ackerman 2007). 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 ($K_d=3.7$ L/kg) (Smalling & Aelion 2006).

The large use of triazines and the similarity of their physicochemical properties such as water solubility, high polarity, low degree of adsorption in soils and high persistence, are the cause of the frequent occurrence of these chemicals and their metabolites in groundwater.

Micro-membrane filtration is a mandatory step in developing new chromatographic methods for the detection of organic pollutants in the environment (Galaon et al 2017, Kim et al 2017, Popescu et al 2017).

The objective of this work is to study the performance of membrane filters in the filtration of organic extracts from processing of environmental samples (water, soil). In Table 1 the chemical structure and the IUPAC chemical name of the selected pesticides are presented.

Table 1. Chemical structure and IUPAC chemical name of the pesticides

Compounds/ IUPAC chemical name	Molecular formula	Chemical structure	Molecular weight (g/mol)	Log Kow	Aqueous solubility (mg/L)
Simazine 6-chloro-2-N,4-N- diethyl-1,3,5- triazine-2,4-diamine	$C_7H_{12}ClN_5$		201.7	2.18	5.0
Atrazine 6-chloro-4-N-ethyl- 2-N-propan-2-yl- 1,3,5-triazine-2,4- diamine	$C_8H_{14}ClN_5$		215.7	2.61	33
Propazine 6-chloro-2-N,4-N- di(propan-2-yl)- 1,3,5-triazine-2,4- diamine	$C_9H_{16}ClN_5$		229.7	2.93	8.6

Solvent type, membrane filters type and percent of solvent volume were examined respectively. The reverse-phase high performance liquid chromatography (RP HPLC) separation with Multi-Wavelength Detection (MWD) was applied for the determination of triazines from the samples. Selection of a filtration device with an appropriate pore size ensures effective particulate removal while minimizing sample loss. In table 2 the membrane filter used on filtration was described.

Table 2. Description of membranes used to filter solutions

Membrane	Diameter (mm)	Pore Size (µm)	Resistance of membrane	Hydrophobicity/ Hydrophilicity
PTFE	25	0.45	All kinds of solvents	Hydrophobic
Glass Microfiber	13	0.45	Aqueous and/or organic	Hydrophilic
Cellulose acetate	25	0.45	Aqueous and/or alcohols	Hydrophilic
Regenerated cellulose	25	0.45	Aqueous and/or organic solvents	Hydrophilic

Materials and Methods

Reagent and solvents

Pesticides: simazine (99.2 purity), atrazine (99.2 purity) and propazine (99.2 purity) were all purchased from Riedel-de Haën (Germany), with certified quality. HPLC-grade acetonitrile, methanol was supplied by Scharlab (Barcelona, Spain) and Merck (Darmstadt, Germany). High purity water was produced by passing double distilled water through Milli-Q water purification system (Millipore, Bedford, MA, USA). The filters were purchased as follows: glass microfiber filters (0.45 µm GMF) from Whatman (United Kingdom); membrane filters (0.45 µm Cellulose Acetate) from Frisette (Denmark); membrane filters (0.45 µm PTFE) from Macherey-Nagel (Germany) and Econofilter (0.45 µm RC) from Agilent Technologies (Romania). Stock standard solutions of simazine, atrazine and propazine were prepared in methanol to achieve the final concentration of 500 µg/mL each. Standard mix solutions (synthetic) were prepared at 5 µg/mL in 10%, 25%, 50%, 75% and 100%, v/v methanol/ultrapure water and acetonitrile/ultrapure water. From each of the mixed solutions a volume of 0.25 mL was taken and then diluted in a 25 mL volumetric flask. All stocks and diluted standard solutions were protected against light in amber vials and were stored at 4°C.

Equipment

The samples were analyzed by using a liquid-chromatographic Agilent 1100 (Agilent Technologies, USA). The system was equipped with a degasser, quaternary pump, autosampler, a column thermostat and multiple wavelength detectors (MWD). The separations were performed on a BDS Hypersil C8 analytical column (150 mm length, 4 mm i.d., 5 µm particle size) acquired from Thermo Scientific (Waltham, Massachusetts, USA) protected by a BDS Hypersil C8 (10 mm x 4.6 mm i.d., 5 µm) guard column. System control and data acquisition were achieved by means of a computer equipped with an Agilent Chem Station program.

HPLC-MWD conditions and calibration

For this study a rapid LC-UV method was developed for the determination of the three pesticides (atrazine, simazine and propazine) in the synthetic solution. The optimized conditions were as follows: a mobile phase flow rate of 1 mL/min and an injection volume of 5 µL were used. Solvent A is ultrapure water (H₂O) and solvent B is acetonitrile (ACN). The elution of analytes was isocratic with 52.5% H₂O and 47.5% ACN, performed over a time of 6 minutes. The temperature of the column was 20°C. The detection was performed at 223 nm for all compounds which was determined to be at the optimum wavelength in preliminary studies performed

on a scanning spectrometer. There were compounds identified in the chromatograms comparing the retention time of the peaks with that of the corresponding compounds in the standard solution. Five concentration levels injected in triplicate were used to build the calibration curves, by means of an external standard method based on peak areas. Good linearity was found for all compounds in the concentration range of 0.57-11.97 $\mu\text{g/mL}$ with correlation coefficient (R^2) values higher than 0.99. Table 2 shows the quality parameters of the analytical procedure for each compound: regression equations, correlation coefficients, concentration range, repeatability (intra-day precision).

Table 3. Figures of merit for the analytical procedure of simazine, atrazine and propazine

Compound	Regression equation	R^2	Concentration range ($\mu\text{g/mL}$)	Repeatability (RSD) (n=4)
Simazine	$y=51.51x- 4.69$	0.99963	0.57-11.40	3.2
Atrazine	$y=48.01x- 5.07$	0.99961	0.52-10.40	3.9
Propazine	$y=47.70x- 6.72$	0.99953	0.59-11.97	3.6

Filtration of synthetic solutions

A volume of 2 mL for each synthetic solution with different percent of solvent (10%, 25%, 50%, 75% and 100% v/v methanol/ultrapure water and acetonitrile/ultrapure water) was manually passed through PTFE filter, glass filter, cellulose acetate and regenerated cellulose using 2 mL glass syringe. The filtrate was collected into an autosampler vial and was injected in the LC system.

Results and Discussion

The efficiency of acetonitrile solutions filtration

The significance of each parameter in case of pesticides filtration is directly related to the particular solute properties (molecular weight, molecular dimensions: length and width), the polarity (dipole moment), the acid dissociation constant (pKa), and hydrophobicity/hydrophilicity ($\log K_{ow}$) which determines the strength of the pesticide-membranes physicochemical interaction.

The filtering behaviour of the triazine herbicides class on the membranes filters: PTFE, glass, cellulose acetate and regenerated cellulose using different percentages of organic solvent (acetonitrile) is shown in Figure 1. The data consists of percentages indicating the recovery of compounds passed through the filters, as calculated from the peak areas integrated in the HPLC chromatograms.

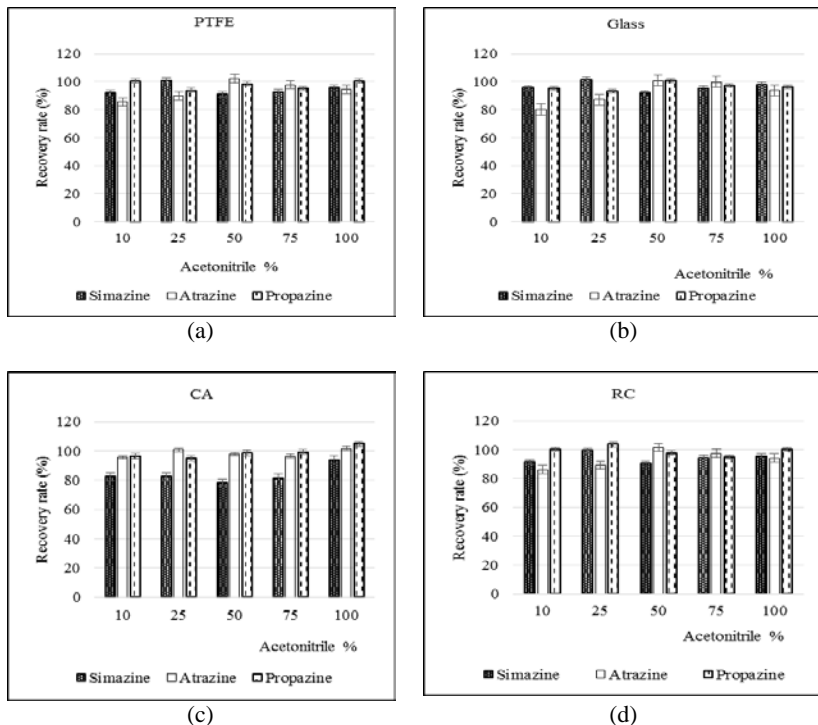


Figure 1. Filtration recovery evaluation results for aqueous/ acetonitrile sample media on PTFE (a), glass (b), cellulose acetate (c) and regenerated cellulose (d)

Adsorption of the selected chlorinated herbicides (atrazine, simazine and propazine) was observed on all four membrane filters employed. The adsorption is different, depending on the solute and the membranes properties, but it is mainly facilitated in the hydrophobic region of membrane materials due to hydrophobic interactions.

From Figure 1 it was observed that the simazine has an efficient filtration on PTFE, glass and regenerated cellulose (recovery between 90.4 and 101.7) compared to the CA for which were obtained lower values (78.4% - 94.0%). The maximum recovery rate was obtained when filtering the solutions with 25% ACN (PTFE, glass and regenerated cellulose). In the case of PTFE membranes it was achieved a recovery in the range 90% -101% for solutions in ACN% between 10 and 100%.

The atrazine pesticide has presented the following recovery range for use of acetonitrile as a solvent: PTFE 85.6% (10%) - 102.3% (100%); glass 80.1% (10%) - 100.9% (100%); cellulose acetate 95.8% (10%) - 101.9% (100%); regenerated cellulose 86.3% (10%) - 101.9% (100%). Low efficiency is shown for PTFE, glass and regenerated cellulose membranes in the case of a low percentage of organic modifier (10% and 25% acetonitrile). Starting with 50% ACN, the herbicide shows maximum efficiency on all membranes.

The propazine has an efficient filtration across all four membranes, both on hydrophobic PTFE membranes corresponding to the lowest polar character (log K_{ow} =2.93, Table 1) and on other hydrophilic membranes, contrary to theoretical prediction. The recoveries ranged for PTFE between 94.0% (25% ACN) and 100.7% (100% ACN); for glass 93.2% (25% ACN) and 100.9% (100% ACN); for cellulose acetate 94.9% (25% ACN) and 99.4% (100% ACN); and for regenerated cellulose 95.0% (25% ACN) and 103.8% (100% ACN).

It has been noticed that the use of ACN as a solution preparation solvent led to filtration efficiencies higher than MeOH of up to 16% (in case of atrazine the use cellulose acetate as a membrane filter with 100% ACN generated a recovery of 101.9% compared to 85.6% at 100% MeOH).

The efficiency of methanol solutions filtration

The potential adsorption of the triazines class on to membranes filters PTFE, glass, cellulose acetate and regenerated cellulose using different percent of organic solvent (methanol) is shown in Figure 2.

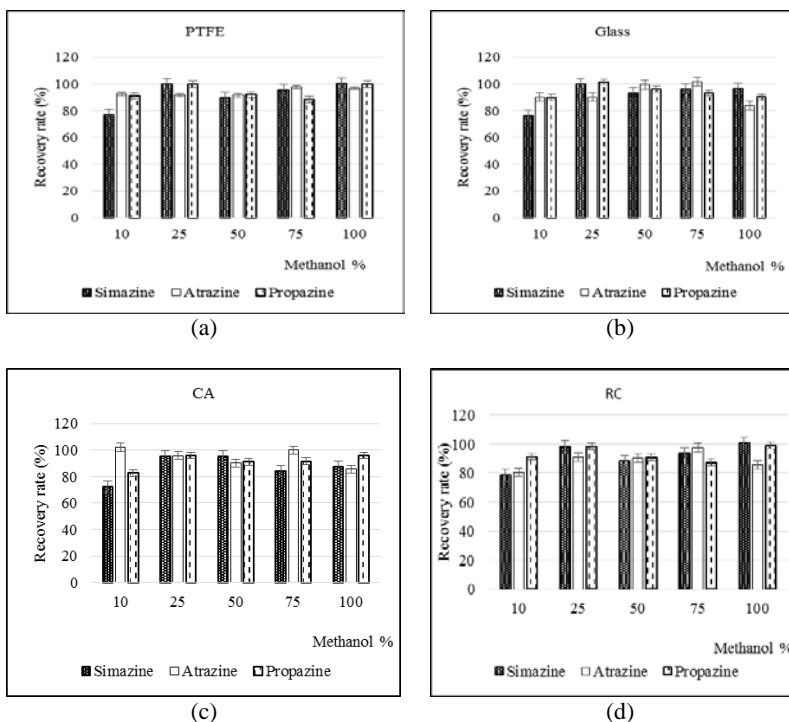


Figure 2. Filtration recovery evaluation results for aqueous/methanol sample media on PTFE (a), glass (b), cellulose acetate (c) and regenerated cellulose (d)

For the samples in 100% organic solvent (methanol) PTFE filters provided excellent recovery (>95%) for all pesticides (simazine, atrazine and propazine). However,

glass filter, cellulose acetate and regenerated cellulose (RC) caused loss of atrazine pesticide during filtration.

The simazine pesticide presented the following recovery ranges for use of methanol as solvent: PTFE 76.8% (10%) - 100.2% (100%); glass 76.6% (10%) - 99.6% (100%); cellulose acetate 72.4% (10%) - 95.3% (100%); regenerated cellulose 78.6% (10%) - 100.8% (100%). Excellent recovery was obtained for PTFE, glass and regenerated cellulose membranes in case of a high percentage of organic modifier (100% methanol). The retention of compounds in filters by adsorption in case of aqueous solution (10%) can be due physical interactions between simazine and sorbent. It is recommended to avoid filtering the simazine in aqueous solution by this type of membrane.

Excellent and consistent recoveries (>95%) were evident for atrazine when using all syringe filters with a proportion of methanol/water 75:25 (v/v). The results showed a decrease of recovery (<92%) when using PTFE, glass and regenerated cellulose filters with low percentage of methanol. Similar behavior was observed in case of simazine and propazine by use of aqueous (10%) solutions on PTFE, glass and regenerated cellulose.

In case of propazine, good overall recovery (>95%) in all three filter materials (PTFE, CA and RC) was obtained when the proportion of MeOH in the sample was 100%. For glass filter the best recovery was obtained at 50% (96.3%). Propazine recoveries were in the following ranges: for PTFE 88.2% (75% MeOH) - 100.0% (25% MeOH); for glass 90.3% (10% MeOH) - 101.6% (25% MeOH); for cellulose acetate 82.6% (10% MeOH) - 91.6% (75% MeOH); and for regenerated cellulose 87.32% (75% MeOH) - 99.1% (100% MeOH).

The PTFE, glass and RC filters gave the worst recovery when the samples contained MeOH at 10%. Once the MeOH concentration was increased to at least 25%, all three filters gave similar high recovery results for all analytes. This study showed that if the sample needs filtration, the sample should contain at least 25% MeOH to prevent recovery losses due to filter absorption.

Conclusions

Filtration using syringe filters was shown to be a simple, easy and efficient step for the analysis of triazine pesticides. The membrane can affect the potential adsorption of pesticide during filtration, and therefore selection of the appropriate filters, including membrane type, pore size and filter dimension is critical to achieve accurate and precise results.

The performance of PTFE, glass, cellulose acetate and regenerated cellulose membrane filters in retaining three pesticides (atrazine, simazine and propazine) from synthetic solutions was studied. The results showed that the recovery varied according to the proportion of water/solvent (acetonitrile and methanol) and the material of the membrane. The recovery of pesticides increased when the percentage of solvent was higher. The results confirm that the PTFE membrane shows a better performance for all pesticides compared to the glass membrane.

In conclusion, PTFE syringe filters were shown to be an excellent choice for filtering of triazine pesticides, by providing excellent filtration recovery.

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References

- Ackerman, F 2007, 'The economics of atrazine', *International Journal of Occupational and Environmental Health*, vol. 13, no. 4, pp. 441-449.
- Galaon, T, Petre, J, Iancu, V & Niculescu, M 2017 'Determination of estrogenic steroids in sewage sludge samples from eight domestic wastewater treatment plants', *20th International Symposium "The Environment and The Industry", SIMI 2017*, National Research and Development Institute for Industrial Ecology ECOIND, Bucharest, pp. 237-241.
- Grover, RA 1988, 'Environmental Chemistry of Herbicides', CRC Press, Boca Raton, Florida, pp. 45-88.
- Kim, L, Muresan AM, Cuciuoreanu A, Guta, D, Arama, M, Cristea, NI & Dediu, V 2017 'Experimental models of characterization and analysis of industrial waste', *20th International Symposium "The Environment and The Industry", SIMI 2017*, National Research and Development Institute for Industrial Ecology ECOIND, Bucharest, pp. 142-150.
- Novotny, V 1999, 'Diffuse pollution from agriculture-A worldwide outlook', *Water Science and Technology*, vol. 39, no. 3, pp. 1-13.
- Popescu, M, Puiu, D, Mihalache, M, Borde, N, Raiciu, AD, Cristea, I, Galaon, T & Pascu, LF 2017, 'A study of the content in volatile oils and their composition of various aromatic herbs from ecological soils', *20th International Symposium "The Environment and The Industry", SIMI 2017*, National Research and Development Institute for Industrial Ecology ECOIND, Bucharest, pp. 206-212.
- Smalling, KL & Aelion, CM 2006 'Biological and chemical transformation of atrazine in coastal aquatic sediments', *Chemosphere*, vol. 62, no. 2, pp. 188-196.
- Tissier, C, Morvan, C, Bocquené, G, Grossel, H, James, A & Marchand, M 2005, 'Les substances prioritaires de la Directive cadre sur l'eau', Ifremer, Fiches de synthèse.