Anica Pavlinović[1], Iva Ćurić[2], Davor Dolar[3]

Original scientific paper
DOI: 10.5937/VIK26141P

NANOFILTRATION AND REVERSE OSMOSIS FOR PESTICIDE REMOVAL FROM GROUNDWATER

Abstract: Pesticides and their transformation products migrate through environmental compartments, contaminating soil, air, and water. Because of their stability and low biodegradability, their presence in groundwater poses a high risk to human health. This study investigated the removal of atrazine and its transformation products from groundwater using nanofiltration and reverse osmosis, with the aim of selecting the more suitable membrane for drinking water production. Reverse osmosis showed better removal of atrazine and its transformation products than nanofiltration due to its lower molecular weight cut-off, i.e., smaller pore size. The removal of transformation products is lower than that of atrazine because of their lower molecular weight.
Key Words: atrazine, transformation products, nanofiltration, reverse osmosis, groundwater

NANOFILTRACIJA I REVERZNA OSMOZA ZA UKLANJANJE PESTICIDA IZ PODZEMNE VODE

Rezime: Pesticidi i njihovi transformacijski produkti migriraju kroz različite dijelove okoliša, kontaminirajući tlo, zrak i vode. Zbog njihove stabilnosti i niske biorazgradivosti, ulazak u podzemne vode predstavlja visok rizik za ljudsko zdravlje. U ovom radu ispitano je uklanjanje pesticida atrazina i njegovih transformacijskih produkata iz podzemne vode primjenom nanofiltracije i reverzne osmoze, s ciljem odabira optimalne membrane za dobivanje pitke vode. Reverzna osmoza pokazala je bolje uklanjanje atrazina i njegovih transformacijskih produkata od nanofiltracije s obzirom na manju graničnu molekulsku masu, tj. manju veličinu pora. Uklanjanje transformacijskih produkata je manje od atrazina s obzirom na njihovu manju molekulsku masu.
Ključne reči: atrazin, transformacijski produkti, nanofiltracija, reverzna osmoza, podzemna voda

1. Introduction

The increasing use of pesticides in agriculture, driven by global population growth and rising food production, has led to growing environmental consequences. Depending on the application method, pesticides can migrate through environmental compartments via differe

[1] *University of Zagreb, Faculty of Chemical Engineering and Technology, apavli@fkit.unizg.hr, ORCID: 0000-0002-4909-3709*
[2] *University of Zagreb, Faculty of Chemical Engineering and Technology, icuric@fkit.unizg.hr, ORCID: 0000-0001-5219-0748*
[3] *University of Zagreb, Faculty of Chemical Engineering and Technology, dolar@fkit.unizg.hr, ORCID: 0000-0002-4699-1298*

rent pathways. A major concern regarding pesticides is their stability, low biodegradability, and, in most cases, high mobility, which leads to their occurrence in groundwater. Pesticides can also undergo various transformation processes, leading to the formation of transformation products (TPs) that can be more persistent and less biodegradable [1, 2]. Atrazine, a pesticide banned for use in the European Union (EU) since 2004, is still one of the most frequently detected pesticides in groundwater, alongside its transformation products, due to its stability and low biodegradability, with their presence in groundwater leading to various health concerns [3]. The EU has established directives to protect groundwater from pollution and to ensure safe drinking water, thereby preventing further health issues. The quality standard for groundwater and drinking water was set at a concentration of 0.10 µg/L for individual pesticides and their relevant transformation products and 0.50 µg/L for the total sum of pesticides [4, 5]. The new directive from 2024 sets a target for 80% micropollutant removal, further emphasizing the need for successful treatment [6].

Membrane separation processes, specifically nanofiltration (NF) and reverse osmosis (RO), have been established as successful treatment methods for micropollutant removal [7]. Various studies on pesticide removal from different water matrices have confirmed the efficiency of NF and RO, often exceeding 80% removal, depending on membrane characteristics, pesticide properties, and operating conditions [8, 9]. Removal of pesticide TPs has not been investigated as extensively as the removal of parent compounds but is equally important for preserving water quality [10].

This study aimed to investigate the removal efficiencies of the pesticide atrazine and its transformation products from groundwater using NF and RO membranes. Since salt removal was not experimentally determined in this study, an analysis based on manufacturer provided data for both membrane processes was conducted as a final step to identify the more suitable membrane for pesticide removal and the production of safe drinking water.

2. Materials and methods

2.1. Materials

The membranes used in the experiments were commercially available DK (Suez, France), an NF membrane, and XLE, an RO membrane (Dow-Filmtec, USA). Their characteristics, as provided by the manufacturers, are shown in Table 1.

Table 1. Membrane characteristics according to manufacturer
Tablica 1. Karakteristike membrana od proizvođača

Membrane	Maximum working pressure, bar	pH range	R^a (%)	Zeta potential[b] pH 8, mV
DK	41	3 – 9	98.0 ($MgSO_4$)	-15.82
XLE	41	2 – 11	97.0 (NaCl)	-24.13

[a] Concentrations of $MgSO_4$ were 2000 mg/L, and NaCl 2000 mg/L.
[b] Experimentally determined.

The pesticide used in the experiment was atrazine from Thermo Fisher Scientific (USA) and its TPs, desethylatrazine (DEA) and desisopropylatrazine (DIA), from Sigma-Aldrich (USA), all of analytical purity grade. Their physico-chemical properties are summarized in Table 2. Stock solutions of the standards (1 g/L) were first prepared in methanol due to their low water solubility. A mixture solution of the pesticide and its transformation products was prepared in groundwater, with an atrazine concentration of 100 µg/L and 50 µg/L of each transformation product. The pH value of the solution was 8.00. The physico-chemical characteristics of groundwater obtained from Vrbovec, Croatia, are presented in Table 3.

Table 2. Physico-chemical characteristics of the investigated compounds
Tablica 2. Fizikalno-kemijske karakteristike ispitivanih spojeva

	Atrazine	DEA	DIA
CAS no.	1912-24-9	6190-65-4	1007-28-9
Molecular weight, g/mol	215.69	187.63	173.60
Water solubility, mg/L	34.7	3200	980
log $K_{O/W}$	2.61	1.51	1.15
pK_a	1.60	n.a.	n.a.

n.a. – not available

Table 3. Physico-chemical characteristics of groundwater.
Tablica 3. Fizikalno-kemijske karakteristike podzemne vode.

	Unit	Value
pH	-	7.50
Conductivity	µS/cm at 20°C	600
Chloride	mg/L	9.8
Sulphate	mg/L SO_4^{3-}	35.7
Total hardness	mg/L $CaCO_3$	275
Magnesium	mg/L Mg^{2+}	21.7
Calcium	mg/L Ca^{2+}	74.1
Sodium	mg/L Na^{2+}	21.5
Potassium	mg/L K^+	0.97

2.2. Methods

The removal of atrazine and TPs from a groundwater solution was carried out on a laboratory-scale RO/NF system described in detail by Dolar et al. (2011) [11], at a working pressure of 10 bar and with a membrane area of 11 cm^2. Before the removal experiment, the membranes were pressurized at 12 bar until the flux stabilized. Treatment with the groundwater mixture lasted 3 hours in batch circulation mode, with both permeate and concentrate circulated back into the feed stream.

The zeta potential of the membranes was determined using a SurPASS Electrokinetic Analyzer-type A from Anton Paar (Austria). Membrane samples were fixed to the sample

holder with in an Adjustable Gap Cell using double-sided adhesive tape. The pH dependence of the zeta potential was investigated over the pH range 2.5-9.

Atrazine and its TPs were quantified using an ACQUITY UPLC H-Class System (Waters, USA) coupled to a Xevo TQ-S micro triple quadrupole mass spectrometer (Waters, USA) with electrospray ionization in positive ion mode. Separation was performed at 40 °C on an XBridge Premier BEH C18 column (100×2.1 mm i.d., 2.5 µm particle size). The injection volume was set to 1 µL. The mobile phase consisted of 0.1 % v/v formic acid in water (A) and methanol (B), delivered at a flow rate of 400 µL/min with a gradient of 45 % to 95% B (0-3 min), 95 % B (3-4 min), and 45 % B (4-5 min). The optimized MS parameters were a capillary voltage of 3.0 kV, a cone voltage of 25 V, a source temperature of 150 °C, a desolvation temperature of 450 °C, a desolvation gas flow rate of 1000 L/h, and a cone gas flow rate of 50 L/h.

3. Results and discussion

Rejection factors for the atrazine and TPs mixture from groundwater after 3 h of treatment with the NF and RO membranes are presented in Figure 1. Higher removal of atrazine and its TPs was expected with the RO membrane XLE than with the NF membrane DK due to the difference in MWCO, i.e., the pore size of the membranes. The XLE membrane has an MWCO ranging from 100 Da to 200 Da, whereas the MWCO of DK membrane ranges from 150 Da to 300 Da. Atrazine, with a molecular weight of 215.69 g/mol, DEA with 187.63 g/mol, and DIA with 173.60 g/mol fall within both of these MWCO ranges. Due to the differences mentioned, a clear difference in removal efficiency can be observed between the NF and RO membranes.

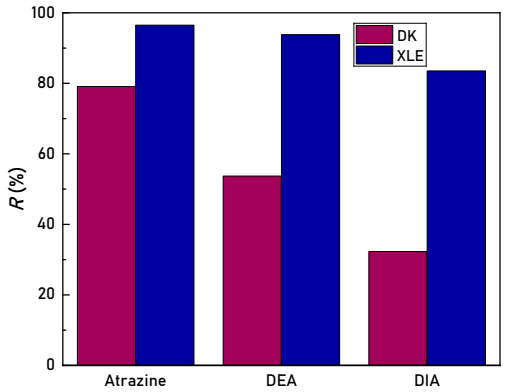


Figure 1. Removal efficiency of atrazine and its TPs removal using NF and RO
Slika 1. Faktor zadržavanja atrazina i transformacijskih produkata pomoću NF i RO

For all three compounds, removal with the XLE membrane exceeded 80%, whereas with the DK membrane atrazine removal reached approximately 80% and removal of its TPs was below 55%. The difference in MWs of atrazine and its TPs also affects removal with the NF membrane, with the lower MWs of the TPs leading to lower removal effi-

ciency. Since the MWs of atrazine and its TPs are close to or within the MWCO range of both membranes, partial passage of these components is possible, causing lower rejection.

In addition, when comparing other physico-chemical characteristics of atrazine with its TPs, DEA, and DIA primarily log $K_{O/W}$, a difference in hydrophobicity is evident. Atrazine can be considered hydrophobic, with a tendency to adsorb to the membrane's polymeric matrix, whereas the TPs have log $K_{O/W}$ <2, which indicates their hydrophilicity.

Since atrazine has a higher molecular weight and higher log $K_{O/W}$ compared to DEA and DIA, which are more hydrophilic and have lower molecular weight, the NF membrane showed higher rejection of the parent compound. Consequently, the TPs may interact less strongly with the membrane polymer and pass more readily through the membrane structure.

At the measured groundwater pH, atrazine and its TPs were expected to occur predominantly in their neutral form [12]. Therefore, electrostatic interactions were unlikely to be the dominant rejection mechanism, and the differences in rejection were most likely governed by size exclusion and possible hydrophobic interactions.

4. Conclusion

This study investigated the removal of atrazine and its transformation products from groundwater using two membranes: an NF membrane (DK) and an RO membrane (XLE). The XLE membrane achieved higher rejection of all investigated compounds, confirming its greater suitability for treating groundwater containing atrazine and its TPs. NF was less effective, particularly for DEA and DIA, which may be attributed to their lower molecular weights and greater hydrophilicity.

The results indicate that size exclusion and hydrophobic interactions were more important for compound rejection than electrostatic interactions under the investigated conditions. However, the final suitability of the permeate for drinking water production must be assessed using measured values in the treated water.

Acknowledgement:

This research was funded by the NATO Science for Peace and Security Programme under grant id. G6087 and the Croatian Science Foundation project DOK-NPOO-2023-10-8063.

5. References

[1] Fao, *Pesticides use and trade – 1990–2023.* 2025, FAO: Rome, Italy. p. 13 DOI: https://doi.org/10.4060/cd5968en, 20205.

[2] Hassaan M. A. and El Nemr A, *Pesticides pollution: Classifications, human health impact, extraction and treatment techniques.* Egyptian Journal of Aquatic Research, 46(3): p. 207-220 DOI: 10.1016/j.ejar.2020.08.007, 2020.

[3] European Comission, *Consolidated text: Commission Decision 2004/248/EC of 10 March 2004 concerning the non-inclusion of atrazine in Annex I to Council Directive 91/414/EEC.* OJ L 78, 16.3.2004. p. 53, 2024.

[4] European Parliament and Council, *Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration*. European Union, 2006.

[5] European Parliament and Council, *Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast)*. European Union, 2020.

[6] European Parliament and Council, *Directive (EU) 2024/3019 of the European Parliament and of the Council of 27 November 2024 concerning urban wastewater treatment (recast)*, in *OJ L, 2024/3019, 12.12.2024*. 2024.

[7] García-Ávila F, Zambrano-Jaramillo A, Velecela-Garay C, Coronel-Sánchez K. and Valdiviezo-Gonzales L, Effectiveness of membrane technologies in removing emerging contaminants from wastewater: Reverse Osmosis and Nanofiltration. *Water Cycle*, 6: p. 357-373 DOI: https://doi.org/10.1016/j.watcyc.2024.12.004, 2025.

[8] Rodríguez-Alegre R, Pérez Megías L, Sanchis S, Andecochea Saiz C, and You X. J. D. E, *Nanofiltration & reverse osmosis technical assessment for pesticides removal.* 2(1): p. 52, 2024.

[9] Fujioka T, Kodamatani H, Yujue W, Yu K. D, Wanjaya E. R, Yuan H, Fang M. and Snyder S. A, Assessing the passage of small pesticides through reverse osmosis membranes. *Journal of Membrane Science*, 595: p. 117577 DOI: https://doi.org/10.1016/j.memsci.-2019.117577, 2020.

[10] Zakhia A, Balestra L. B, Dhainaut J, Merlier F. and Boussetta N. Review on the removal and degradation methods of chloridazon and its metabolites. *Separation and Purification Technology*, 376: p. 133998 DOI: https://doi.org/10.1016/j.seppur.2025.133998, 2025.

[11] Dolar D, Vuković A, Ašperger D, and Košutić K, Effect of water matrices on removal of veterinary pharmaceuticals by nanofiltration and reverse osmosis membranes. *Journal of Environmental Sciences*, 23(8): p. 1299-1307 DOI: https://doi.org/10.1016/S1001-0742-(10)60545-1, 2011.

[12] Lago A, Silva B, and Tavares T, *Cleaner Approach for Atrazine Removal Using Recycling Biowaste/Waste in Permeable Barriers.* 2021. 6(2): p. 41.