APPLICATION OF MEMBRANE TECHNOLOGY
IN THE TREATMENT AND ANALYSIS
OF TRIAZINE PESTICIDES IN WATER

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Abstract. The quality of consumable water is decreasing due to increasing water pollution caused by the production and use of human-made chemicals. A significant part of these chemicals are pesticides from the class of triazines since they are widely used in agriculture as herbicides. Water treatment techniques mainly rely on separation science, where the membrane technology has been identified as the most useful. Membrane processes used in water treatment are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In general, the pollutant retention/rejection by membranes depends on the physicochemical properties of the membrane i.e. membrane material, porosity, pore size and on the properties of the pollutant molecule i.e. size, length, width, molecular weight, hydrophobicity or dipole moment. The pollutant retention also depends on the feed-water composition (organic matter and salt presence, solute concentration, water pH). Thus, effective water treatment depends on the selection of an appropriate type of membrane for a particular type of pollutants. Membrane technology is also significant because it is used in polluted water analysis, more precise as a part of a liquid-phase or solid-phase microextraction. Among several developed membrane-based microextraction methods, in triazine polluted water analysis common are membrane-protected solid-phase microextraction and hollow-fiber liquid-phase microextraction. In this field, researchers tend to achieve membrane-pollutant compatibility through the synthesis of polymeric materials with molecular recognition properties i.e. through a technology called molecular imprinting.

Key words: membrane technology, triazines, water treatment, water pollution

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1. INTRODUCTION

Despite the fact that water is the most common substance on the planet, only 3% of water resources is fresh water and only 1% of it is available for human use. The quality of consumable water is decreasing due to increasing water pollution, mainly caused by human activities. Water treatment techniques used to improve water quality and taste by removing pathogens and undesirable compounds mainly rely on separation science, where the use of membrane technology has been identified as the most robust and flexible one.

Advantages of membrane technology over the conventional ones are that membrane treatment takes place at ambient temperature without phase changing, the separation occurs without substance accumulation inside the membrane and membrane processes are technically simpler and more energy efficient than conventional separation processes (Karabelas and Plakas, 2011). The disadvantages would be potential membrane fouling and damaging, which why membrane treatment requires costly feed-water pretreatment (Karabelas and Plakas, 2011). The main fouling categories are organic, inorganic, particulate and biological fouling. Harmful substances can damage membrane (acids, bases, (pH), free chlorine, bacteria, free oxygen), block membrane by fouling (metal oxides, (Fe$^{2+}$, Mn$^{2+}$), colloids (organic, inorganic) biological substances (bacteria, microorganisms) or by scaling (calcium sulfate, calcium carbonate, calcium fluoride, barium sulfate, silica) (Rautenbach and Albrecht, 1989).

1.1. General Principles of Membrane Technology

The membrane separation process is based on the physicochemical nature of the membrane material which acts as a semipermeable barrier between two homogeneous phases i.e. membrane separation is characterized by simultaneous retention of species and product flow through the membrane (Singh, 2015). The driving force of membrane separation is the difference in concentration, electrical potential or pressure between the feed and product side. The key factors of a membrane performance are the membrane selectivity and productivity, which have a trade-off relationship (Singh, 2015; Yoshikawa et al., 2016). Selectivity can be expressed as the ratio between permeability coefficients of two substances i.e. a parameter called retention or separation factor, while productivity is expressed as a parameter called flux (Singh, 2015; Yoshikawa et al., 2016). For the pressure-driven separation processes flux can be expressed with Eq. (1) (Singh, 2015) where, as can be seen, depends on transmembrane pressure ($\Delta P$) and the membrane thickness ($t$).

$$J = k \times \Delta P \times t$$  \hspace{1cm} (1)

The membrane transport phenomena can be explained in different ways depending on the membrane pore size. Molecules of solutes are first incorporated into the membrane’s pores and subsequently transported through the membrane by diffusion (Yoshikawa et al., 2016). The step of solute incorporation into the pores is affected by the pore size and may occur due to solubility or partition. Therefore, the transport phenomena through a dense membrane (characterized by a molecular weight cut-off less than 100 Da) can be understood by means of solution-diffusion whereas through a porous membrane by the partition-diffusion mechanism (Yoshikawa et al., 2016).
1.2. Membrane Processes in Water Treatment

Membrane processes used in water treatment (figure 1) are usually defined according to the membrane pore size. The separation mechanisms vary depending on the physicochemical properties of the solute and the membrane and can be explained either with physical (size exclusion or steric hindrance) or chemical selectivity (hydrophobic/hydrophilic interactions), where for the polar organic compounds separation is not so simple due to potential polar interactions between organic species and membrane surface (Karabelas and Plakas, 2011).

1.3. Pesticide Water Pollution

The significant part of an increasingly complex mixture of human-made organic chemicals that pollute water bodies are the pesticides. They can cause a list of health effects, including cancer, birth defects, and disruption of the endocrine system. About 50% of pesticides applied in agriculture are related to herbicides (Abate and Masini, 2005) and among them, triazine compounds are the most common. They are easily introduced into the water flows since a larger amount of herbicides applied is dispersed in the air, contaminating the surface waters or on the soil, contaminating groundwater, than it is in contact with plants. Once introduced into the environment, pesticides can cause long-term negative effects due to their persistence. For example, some European countries have stopped using atrazine before 2004 but still detect its concentrations above 0.1 µg/l in aquifers (La Cecilia and Maggi, 2017). Another issue is the easy distribution of pesticides into another parts of the environment, especially from soil into groundwater which are the main sources of drinking water. It was found that the frequency of herbicide detection in groundwater is directly related to the soil half-life of the herbicide (Ritter et al., 1994).

Since membrane technology is one of the most robust and beneficial among the purification technologies, the aim of this paper was to present the aspects of its application in treatment and analysis of the most frequent water pollutants, triazine herbicides.

Fig. 1 Overview of the main features of membrane technology
2. MEMBRANE TECHNOLOGY IN TREATMENT OF TRIAZINE POLLUTED WATER

Several factors, like membrane (porosity, pore size, MWCO) or pesticide properties (molecule size, length, width, hydrophobicity, dipole moment) affect membrane treatment of water polluted with pesticides. On the membrane pore size, for example, depends hydropermeability, where the bigger pore size is the higher is permeability, as shown for three different nanofiltration membranes (Palma et al., 2016). In order to efficiently purify water from pesticides, one of the most important items is to match the membrane pore size and pesticide size.

2.1. Influence of Pesticide Properties

Pesticides usually have molecular weights above 200 Da and the size in the range of 1 nm, thus convenient membrane techniques for their removal would be nanofiltration (NF) or ultra-low-pressure reverse osmosis (ULPRO) (Karabelas and Plakas, 2011). NF membranes, like NF99HF, show rejection of large triazines (atrazine, bentazon) above 90 %, but these are not efficient in removal of small triazine transformation products like 2,6-dichlorobenzamide (BAM) or desethyldeisopropyl atrazine (DEIA) whose sufficient removal is achieved with low-pressure membranes i.e. with XLE (Extra-Low Energy) membrane (Madsen and Søgaard, 2014). These authors (Madsen and Søgaard, 2014) described the triazine retention with the steric model, suggesting that the main effect of the triazine transformation is changing (decreasing) their steric hindrance, which explains the worse retention of pesticides by membranes with the bigger pores (in this case with NF99HF). The higher retention of heavier and bigger triazine molecules is confirmed by other authors, where among atrazine (MW=215.7), propazine (MW=229.7) and prometryn (MW=241.4), prometryn displayed the highest rejection (Rakhshan and Pakizeh, 2015, 2016), but the molecule size is not the single factor affecting retention. The retention also increases as molecule length and width increases, with the greater influence of the length (Musbah et al., 2013). As mentioned before, separation of polar organics is complex due to interactions with the membrane surface. For example, desethylatrazine (DEA) retention is better than simazine retention-at 10 bars DEA retention is about 62 %, while for simazine is about 50%, although DEA has lower MW than simazine (Musbah et al., 2013). This is probably due to greater simazine-membrane affinity. Furthermore, triazines rejection by NF270 membrane, with MWCO of 340 Da is lower than by NF-90 membrane, with MWCO of 180 Da, as expected, but NF270 showed higher selectivity and rejected each triazine in a different way, with differences between atrazine and others within 30-40 % (Sotto et al., 2010). In general, when the molecule is larger than the membrane pore size its retention is affected by sieve mechanism, but when it is in the range of a membrane pore size, the membrane-surface interactions have a greater role in rejection (Chen et al., 2004).

When it comes to pesticide hydrophobicity, researches have shown that triazine retention cannot be correlated only with this factor, but also with molecule’s dipole moment (Rakhshan and Pakizeh, 2015, 2016). The triazine rejection decreases as dipole moment increases, which was shown by experiments conducted with propazine, atrazine, and prometryn (Rakhshan and Pakizeh, 2015, 2016). The possible explanation is that the molecule’s dipole tends to orient parallel to the pore length, thereby the molecule easier enters the pore and permeates through the membrane (Van der Bruggen et al., 1999).
2.2. The Role of Feed-water Composition

The role of the feed-water composition in membrane treatment efficiency includes the role of pH and ionic strength of the solution, solute concentration and the presence of organic matter. pH affects pesticide retention due to membrane surface functional groups dissociation (Karabelas and Plakas, 2011), where the higher ionic content leads to an increase in triazine rejection due to ion adsorption on the membrane, which narrows the membrane pore size, as indicated by an increase in membrane zeta potential (Madsen and Søgaard, 2014). The triazine rejection increases as the feed concentration increases (Musbah et al., 2013; Rakhshan and Pakizeh, 2015, 2016), probably due to pesticide adsorption onto the membrane surface (Rakhshan and Pakizeh, 2015). Research on the presence of organic matter in water and its influence on triazine rejection by NF90, NF270 and XLE membrane, conducted by Plakas and Karabelas (2009, 2011) revealed several important facts. First, organic matter deposition on the membrane causes changes in membrane surface characteristics which affects flux and triazine rejection. Membrane fouling and triazine rejection depend on the type and concentration of humic material and the presence of calcium ions i.e. the rejection is improved in the presence of ions and with increasing humic material concentration. The concluding is that triazine rejection, with the presence of humic substances, is improved due to complexation between pesticide and much larger organic matter that leads to a solute with higher MW, which is better retained. Figure 2. represents a brief review on triazine rejection by several membranes (commonly used commercial membranes (XLE, NF90, NF270) and two laboratory prepared LabPrep1 (Oleic acid-modified SiO2/cellulose acetate nanocomposite membrane, fabricated via the phase inversion method (Rakhshan and Pakizeh, 2016)) and Lab-Prep2 (Thin film nanocomposite (TFN) membrane containing oleic acid modified silica nanoparticles, synthesized via interfacial polymerization on polysulfone asymmetric membrane (Rakhshan and Pakizeh, 2015))).

Fig. 2. A review on rejection percentage of several triazines
3. APPLICATION OF MEMBRANE TECHNOLOGY IN ANALYSIS OF TRIAZINES IN WATER

Considering the sample preparation as a multistep process, its main problem is the risk of analyte loss and sample contamination, so an ideal preparation technique should be single-step, with minimal use of solvent and energy. Such technique nearly matches with the combination of membrane-based separation, which can be performed continuously, under mild conditions and microextraction, which can reduce the number of errors and it is eco-friendlier. Therefore, the main purpose of membrane technology in triazine analysis is in the sample preparation step, as an alternative to conventional extraction techniques. In order to increase the membrane selectivity and enhance the separation performance, it is necessary to introduce specific binding sites i.e. to give the membrane a recognition ability for a specific molecule. This is achieved through molecular imprinting technology, which is usually related to polymers. Molecularly imprinted polymer (MIP) is a type of material in which recognition sites for a specific molecule are created through physicochemical interactions between functional groups of polymer and template molecule, then are further stabilized through structure stabilization and at the end are activated by the target molecule extraction (Yoshikawa et al., 2016). In brief, the functional monomer forms a complex with the template molecule, which is followed by further polymerization of monomer and cross-linker, leading to a highly cross-linked polymeric network that keeps the template in a position (Gkementzoglou et al., 2013). Template removal at the end, reveals recognition sites. Several preparation methods of MIPs used in triazine analysis are given in Table 1.

As functional monomers frequently used are acrylic (AA) and methacrylic acid (MAA), which are hydrogen-bonding and proton-accepting compounds (Yoshikawa et al., 2016) convenient for interaction with polar compounds, like triazines. Although, non-covalent imprinting, based on weak non-covalent forces between template and monomer is more common as an imprinting technique (Yoshikawa et al., 2016), the resulting MIPs often have poor recognition ability in water due to the presence of polar solvent which easily disturbs hydrogen bonds formed via non-covalent imprinting (Chen et al., 2011). Researchers tend to develop a water compatible MIPs, by using 2-hydroxyethyl methacrylate (HEMA) as functional monomer (Benito-Peña et al., 2009) or by enhancing MIPs surface’s hydrophilicity through hydrophilic functional groups bonding or hydrophilic polymer grafting process (Yang et al., 2009; Ma et al., 2012; Xu et al., 2014). Xu et al. prepared MIP with hydrophilic core and shell, so-called double water compatible MIP (DWC-MIP), using HEMA as co-monomer and grafting poly (2-hydroxyethyl methacrylate) (PHEMA) to MIP particles by reversible addition fragmentation chain transfer precipitate polymerization. DWC-MIP had the highest triazine binding capacity and fastest binding kinetics, among other MIPs, because polymer particles due to good water compatibility can uniformly disperse in water, providing better contact between pesticide and MIP.
### Table 1. MIP preparation methods

<table>
<thead>
<tr>
<th>Used as</th>
<th>Template</th>
<th>Monomer</th>
<th>Cross- linker</th>
<th>Initiator</th>
<th>Porogen</th>
<th>Template removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-LPME</td>
<td>propazine</td>
<td>MAA</td>
<td>EGDMA</td>
<td>AIMN</td>
<td>toluene</td>
<td>methanol: acetic acid=1:1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td>protected</td>
<td>atrazine</td>
<td>MAA</td>
<td>EDMA</td>
<td>AIBN</td>
<td>toluene + dodecanol</td>
<td>methanol</td>
<td>Chen et al., 2014</td>
</tr>
<tr>
<td>HF-LPME</td>
<td>propazine</td>
<td>MAA</td>
<td>DVB-80</td>
<td>AIBN</td>
<td>toluene: acetonitrile=25:75</td>
<td>methanol: acetic acid=1:1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td>SPE</td>
<td>atrazine</td>
<td>MAA-HEMA</td>
<td>EGDMA</td>
<td>AIBN</td>
<td>acetonitrile</td>
<td>methanol: acetic acid=9:1</td>
<td>Xu et al., 2014</td>
</tr>
</tbody>
</table>

Abbreviations: HF-LSME (hollow fiber liquid-solid microextraction), EDMA (ethylene dimethacrylate), EGDMA (ethylene glycol dimethacrylate), AIMN (2,2'-azobis-2-methylbutyronitrile), AIBN (2,2'-azobisisobutyronitrile)

### 3.1. MIPs Sorbent Efficiency

Prepared MIPs are powerful sorbents for triazine removal. For example, MIP loading capacity is 5.5 and non-imprinted polymer (NIP) capacity is 1.8 µg of pesticide per fiber (Barahona et al., 2016). The selectivity coefficients, defined as the extraction amount ratio of MIP to NIP are 9.7, 9.2, 9.1, 9.3 and 1.9 for atrazine, 2-amino-4-methoxy-6-methyl-1,3,5-triazine (TRI), ametryn, terbutylazine and metribuzin, respectively (Chen et al., 2014). The same authors (Chen et al., 2014) showed that the preconcentration factors for MIP fiber were 9.5, 11.8, 47.3 and 26.5 for TRI, atrazine, ametryn, and terbutylazine, respectively, leading to an effective enrichment by the developed method. In another study (Sanagi et al., 2015) enrichment factors for atrazine and sebumeton were 77.5 and 88, respectively. Furthermore, chromatograms obtained after classic solid-phase extraction of triazine from water showed a big hump corresponding to humic and fulvic acids and a dirty baseline, while after the supported-liquid membrane-protected-MIP-SPE procedure the obtained chromatograms were clean, indicating high selectivity of MIP fibers (Turiel et al., 2016).

### 3.2. Membrane-based Extraction Methods in Triazine Analysis

Among several developed microextraction membrane-based methods, such as membrane-protected solid-phase microextraction (MP-SPME), hollow-fiber liquid-phase microextraction (HF-LPME), thin film microextraction (TF-ME), electromembrane extraction (EME) (Carasek and Merib, 2015), in triazine polluted water analysis prevail MP-SPME and HF-LPME (Chen et al., 2014; Sanagi et al., 2015; Barahona et al., 2016; Turiel et al., 2016). In MP-SPME pollutants are adsorbed on SPME fiber which is inside the membrane which serves as protection, while in HF-LPME pollutants are firstly liquid-liquid extracted from the sample into a supported liquid membrane in the pores of a hollow fiber and then into acceptor solvent placed into the fiber’s lumen (Carasek and Merib, 2015). Pollutant extraction is a mass-transfer process, therefore the main factors affecting extraction efficiency are extraction time and stirring rate. Extraction time is a
compromise between sensitivity and repeatability of the analytical method (Carasek and Merib, 2015) and may vary, whereas diffusion of pollutants from water to the membrane is favored at higher stirring rates (Chen et al., 2014; Barahona et al., 2016). Table 2 represents the average triazine recoveries obtained with developed methods, under optimized conditions.

**Table 2.** A review on triazine recoveries from water spiked at different levels

<table>
<thead>
<tr>
<th>Triazine</th>
<th>Determination technique</th>
<th>Limit of Detection (µg/L)</th>
<th>Recovery (%)/Spike level (µg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ametryn</td>
<td>HPLC/UV</td>
<td>0.32</td>
<td>76.4/10</td>
<td>Chen et al., 2014</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>3.8</td>
<td>80.7/50</td>
<td>Xu et al., 2014</td>
</tr>
<tr>
<td>Atrazine</td>
<td>HPLC/UV</td>
<td>30</td>
<td>6.2/1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/UV</td>
<td>0.18</td>
<td>77.9/10</td>
<td>Chen et al., 2014</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.024</td>
<td>101.3/0.1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.028</td>
<td>92.5/0.5</td>
<td>Xu et al., 2014</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>HPLC/UV</td>
<td>100</td>
<td>7.9/1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.027</td>
<td>88.1/0.1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td>Propazine</td>
<td>HPLC/UV</td>
<td>100</td>
<td>7.9/1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.024</td>
<td>96.2/0.1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.026</td>
<td>89.6/0.5</td>
<td>2016</td>
</tr>
<tr>
<td>Secbumeton</td>
<td>GC/MS</td>
<td>0.42</td>
<td>91/10</td>
<td>Sanagi et al., 2015</td>
</tr>
<tr>
<td>Simazine</td>
<td>HPLC/UV</td>
<td>100</td>
<td>6.8/1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.022</td>
<td>82.4/0.1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.026</td>
<td>77.6/0.5</td>
<td>2016</td>
</tr>
<tr>
<td>Simetryn</td>
<td>HPLC/DAD</td>
<td>4.5</td>
<td>81.2/50</td>
<td>Xu et al., 2014</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>HPLC/UV</td>
<td>50</td>
<td>8/1</td>
<td>Barahona et al., 2016</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.35</td>
<td>72.8/10</td>
<td>Chen et al., 2014</td>
</tr>
<tr>
<td></td>
<td>HPLC/DAD</td>
<td>0.026</td>
<td>102.9/0.1</td>
<td>Turiel et al., 2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.024</td>
<td>94.8/0.5</td>
<td>2016</td>
</tr>
</tbody>
</table>

*Lake water; *Tap water; *River water; *Well water; *Stream water;
Membrane technology is an indispensable part of the water treatment. In this treatment membrane technology takes the final position due to possible pore blocking and membrane fouling which why is necessary to have an effluent of a certain purity degree. When the significant part of impurities (suspended matter, bigger particles) is removed, the next step is fine water purification of low-molecular or low-concentration pollutants, by membrane techniques. Efficient removal of organic micro-pollutants can be achieved considering the properties of the membrane and pollutant, but also of the feed-water.

Matching the pollutant and membrane pore size, membrane processes that can be used for the removal of triazine pesticides are NF and ULPRO. With these, the percentage of triazine retention is satisfactory i.e. in most of the cases above 85 %. But studies have shown that membrane selection versus pesticide size is not the only important factor, because membrane-surface-pesticide interactions also participate in pesticide retention. These interactions become significant especially when the pesticide size is in the range of the membrane pore size. Although it is better to have an effluent of certain purity, due to membrane productivity maintenance, it was shown that membrane fouling with natural organic matter positively affects triazine retention.

In addition to productivity, selectivity is also important for membrane performance. The higher selectivity of the membrane usually means a 100 % removal of a pollutant and nowadays selectivity is improved through the molecular imprinting technology. This technology has especially found its application in triazine analytical determination, because MIPs that are used as membranes have high selectivity towards template-triazine and its analogs, providing high enrichment factors and therefore leading to greater sensitivity and accuracy of determination technique. These polymers, used in different microextraction techniques (MP-SPE, HF-LPME) through validation studies have shown high triazine removal percentage.

REFERENCES

PRIMENA MEMBRANSKIH TEHNOLOGIJA U TRETMANU I ANALIZI PESTICIDA IZ KLASE TRIAZINA U ZAGAĐENIM VODAMA


Ključne reči: membranske tehnologije, triazini, prečišćavanje vode, zagađenje vode