

# Elimination of Phenyl-urea Herbicides in Water Matrices by Combined Chemical Oxidation-Filtration Processes

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**Abstract** - Four selected phenyl-ureas herbicides (linuron, diuron, chlortoluron and isoproturon), dissolved in two water matrices (a groundwater and a reservoir water), were subjected to sequential combinations of chemical treatments and membrane filtration processes. Two specific sequences were conducted: firstly, a chemical oxidation stage (where UV radiation, ozone and ozone plus hydrogen peroxide were used) followed by a nanofiltration process; and secondly, a membrane filtration stage (by using UF and NF membranes) followed by an ozonation stage.

Values for the herbicide removals in the oxidation stages and for the rejection coefficients in the filtration stages are provided, and the partial contribution of the different stages is established for each combined treatment.

High removals (over 80%) were reached for the phenyl-ureas elimination by most of the combined processes tested. In the combined chemical oxidation/nanofiltration processes, the most effective was an ozonation pretreatment ( $[O_3]_0=1.5$  mg/L) followed by a NF step. In the opposite sequence filtration/chemical oxidation, the most effective was a NF pretreatment followed by the ozonation treatment ( $[O_3]_0=2$  mg/L).

**Index Terms**— Phenyl-urea herbicides, chemical oxidation, membrane filtration, combined treatments, removals, rejection coefficients.

## I. INTRODUCTION

Phenyl-urea herbicides have been detected in wastewater treatment plant effluents and raw drinking water sources in concentrations that exceed the drinking water quality value proposed by the EU; i. e. 0.1  $\mu\text{g/L}$  for each individual pesticide and 0.5  $\mu\text{g/L}$  for the total concentration of pesticides and related products, foreseen in the European Drinking Water Directive 98/83.<sup>1</sup> Due to their potential risks even at low concentrations, such as toxicity and possible carcinogenic properties for humans and wildlife, the removal of phenyl-ureas constitutes a priority objective in the water industry.

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Physical treatments are frequently used for the purification of surface waters and wastewaters, due their low costs and small environmental impacts. Among them, membrane separation processes have gradually gained popularity because they effectively remove a wide variety of contaminants from raw waters. While microfiltration (MF) and ultrafiltration (UF) membranes can mainly remove suspended particles, nanofiltration (NF) membranes constitute an effective technology to eliminate dissolved organic contaminants with molecular weights larger than 200 Da, as well as ions, by electrostatic repulsion (charge effect), size exclusion (sieving effect) and a combination of rejection mechanisms.<sup>2</sup>

In recent years, several studies have demonstrated that phenyl-urea herbicides can be readily removed from natural waters by ozonation<sup>3</sup> and by membrane procedures, mainly NF<sup>4-5</sup> when individually applied. However, there has not been report on the ozone/membrane hybrid process for the removal of phenyl-urea herbicides from natural waters. The present work was designed for the development of an efficient elimination of four selected phenyl-ureas herbicides (linuron (L), diuron (D), chlortoluron (C), and isoproturon (I)), which are present in some water matrices, by applying combinations of chemical treatments and membrane processes. Specifically, two sequences were explored: the first one started with a chemical oxidation stage (by using UV radiation, ozone and ozone plus hydrogen peroxide); and the effluent was fed to a NF process. In the second sequence, the first membrane filtration stage was carried out by using UF and NF membranes; and the permeate obtained was subjected to an ozonation stage.

## II. MATERIALS AND METHODS

The herbicides were dissolved in two water systems: a groundwater, and a surface water collected from the reservoir "Peña del Aguila" (Extremadura Community, south-west Spain). The membranes used were commercial flat-sheet membranes provided by GE Osmonics, Inc. (Florida, USA), with an effective surface area of 28 cm<sup>2</sup>. Specifically, the NF membrane (denoted DK membrane) had a MWCO in the range 150-300 Da, and the UF membrane (denoted PT membrane) had a MWCO of 5,000 Da.

The photochemical oxidation stage of the waters containing the selected herbicides was carried out by using a low pressure mercury vapor lamp (Hanau TNN 15/32, electrical power 15 W), which emitted monochromatic radiation at 254 nm. The reaction lasted 30 min, and samples were regularly withdrawn from the reactor (every 5 min) for herbicides analysis.

The ozonation stages were carried out in homogeneous conditions. Each run was initiated by injecting into the reaction flask containing the herbicide solutions the necessary volume of the ozone stock solution (or ozone plus H<sub>2</sub>O<sub>2</sub>) to achieve the desired initial O<sub>3</sub> concentration.

The membrane filtration stages (UF or NF) were conducted in a laboratory cross-flow membrane filtration unit and a batch concentration mode procedure was followed, with the permeate stream collected separately, and the retentate stream recycled to the feed tank.<sup>6</sup> It was followed a standard protocol which firstly measured the water permeate flux (J<sub>w</sub>), and the membrane hydraulic permeability (L<sub>p</sub>): the final L<sub>p</sub> values obtained were 3.05 and 27.5 L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup> for the DK (NF) and the PT (UF) membranes, respectively. Secondly, the phenyl-urea herbicides membrane experiments were performed, registering its weight accumulated with time, what allowed to determine the permeate flux (J<sub>v</sub>) of the solution. Then, samples of the feed, retentate and permeate streams were simultaneously collected and the herbicide concentrations were analysed in these samples by HPLC.

### III. THEORETICAL BACKGROUND

The efficiencies of the different treatments conducted in this research, chemical oxidations and membrane filtration processes, were evaluated by determining the reduction in the concentrations obtained for the selected phenyl-ureas during each process. Specifically for the chemical oxidation stages, these reductions were quantified by the conversions:

$$X = \frac{[\text{Ph}]_0 - [\text{Ph}]_f}{[\text{Ph}]_0} \cdot 100 \quad (1)$$

where [Ph]<sub>0</sub> and [Ph]<sub>f</sub> represent the measured initial and final concentrations for each phenylurea. Similarly, the removal in the membrane filtration processes was determined by measuring the rejection coefficient (f) for each compound, which can be defined in the form:

$$f = \frac{[\text{Ph}]_F - [\text{Ph}]_P}{[\text{Ph}]_F} \cdot 100 \quad (2)$$

where [Ph]<sub>F</sub> and [Ph]<sub>P</sub> represent the concentrations measured in the feed and permeate streams respectively.

In the filtration experiments, the permeate fluxes were determined at regular processing times by the equation:

$$J_v = \frac{\Delta V_p}{\Delta t \cdot A} \quad (3)$$

where ΔV<sub>p</sub> is the accumulated permeate volume during the time difference Δt, and A is the membrane area. This parameter decreased with the processing time, until a constant value was reached: it is the permeate flux at the steady state J<sub>vss</sub>. Another interesting parameter in filtration processes is the flux reduction factor FRF, which relates the permeate flux of the polluted solution J<sub>vss</sub> with respect to the permeate flux of ultra-pure water J<sub>w</sub>, and is calculated by the expression:

$$\text{FRF} = \frac{J_w - J_{vss}}{J_w} \times 100 \quad (4)$$

It must be remarked that this FRF parameter is directly related to the fouling of the membrane: an increase of the reduction in the permeate flux is a direct consequence of an increase in the membrane fouling.

### IV. RESULTS AND DISCUSSION

The first stages of this combined treatment consisted in the use of three chemical oxidants applied to the oxidation of the phenyl-ureas present in the two selected natural waters: UV radiation, ozone (with two different initial doses) and the advanced oxidation process constituted by ozone plus H<sub>2</sub>O<sub>2</sub>.

The results obtained reveal that the use of UV radiation provided much higher removals (calculated by Eq. [1]) than by using ozone or ozone plus H<sub>2</sub>O<sub>2</sub>. Thus, almost total removals were reached with the exception of isoproturon, because its quantum yield is significantly lower than those corresponding to the three remaining herbicides. In effect, as it has been previously reported,<sup>7</sup> the quantum yields at 20 °C were: 36.0×10<sup>-3</sup> mol E<sup>-1</sup> for linuron, 31.9×10<sup>-3</sup> mol E<sup>-1</sup> for chlortoluron, 11.5×10<sup>-3</sup> mol E<sup>-1</sup> for diuron, and 3.7×10<sup>-3</sup> mol E<sup>-1</sup> for isoproturon

On the contrary, the ozonation process yielded higher conversion for isoproturon, due to its higher ozonation rate constant: The rate constants for the ozonation reaction of these compounds have also been published previously:<sup>8</sup> 1.9 M<sup>-1</sup> s<sup>-1</sup>, 16.5 M<sup>-1</sup> s<sup>-1</sup>, 393.5 M<sup>-1</sup> s<sup>-1</sup> and 2191 M<sup>-1</sup> s<sup>-1</sup>, for linuron, diuron, chlortoluron and isoproturon, respectively, at 20 °C. Specifically for these ozonation experiments, it is observed the following sequence of degradations: isoproturon > chlortoluron > diuron > linuron, which exactly agrees with the sequence of the mentioned ozonation rate constants.

In this single ozonation process, it is observed an increase in the herbicide removals with the increase in the initial ozone dose (from 20 to 30 μM). The additional presence of H<sub>2</sub>O<sub>2</sub> also yielded an increase in the removals in relation to the single ozonation experiment with the same initial dose of ozone, due to the generation of hydroxyl radicals from the decomposition of O<sub>3</sub> promoted by H<sub>2</sub>O<sub>2</sub>.

In addition, it is generally observed a higher conversion of the herbicides by the chemical oxidation when the phenylureas were dissolved in the groundwater than in the reservoir water. This effect is due to the amount of dissolved organic matter (DOM) present in each water, which also consumes ozone. In effect, the reservoir water had a higher content in DOM than the groundwater, and this DOM competes with the phenyl-ureas in the consumption of UV radiation, ozone or hydroxyl radicals. Therefore, more UV radiation, ozone or hydroxyl radicals are available in the groundwater for the oxidation of the herbicides, and the removals obtained are higher.

The effluents of the preceding chemical oxidation stage constituted the feed stream for the nanofiltration stage by using a hydrophilic DK membrane (MWCO in the range 150-300 Da). The rejection coefficients were determined by Eq. [2], and the values obtained for each herbicide were above 60 % in all cases.

By considering the different phenyl-ureas, their rejection coefficients followed the sequence: isoproturon > linuron > chlortoluron > diuron. This trend is explained by considering the influence of the polarity of the molecules on the retention in nanofiltration processes. In order to check this hypothesis, the dipole moment of the selected herbicides was determined by using the computer program Hyperchem, and the values obtained were: 3.31, 4.76, 4.92 and 5.87 Debye for isoproturon, linuron, chlortoluron and diuron respectively. Then, as diuron is the most polar compound it is expected that presents the lowest retention; on the contrary, isoproturon, which is the least polar compound, must reach the highest retention. As the results obtained followed this trend, this hypothesis is confirmed.

On the other hand, it is also observed a slight increase in the herbicide rejection coefficients in the reservoir water in comparison to the groundwater. It is due to the higher content in natural organic matter of this reservoir water, which could partially block the pores of the membrane, favouring the retentions of the herbicides.

This group of filtration experiments lasted around 30 min, with a significant decrease in the permeate flux  $J_v$  during the first min of the process; and later, the flux remained almost constant: then, it is considered the permeate flux at the steady state  $J_{vss}$ . The permeate fluxes  $J_v$  and  $J_{vss}$ , and the flux reduction factor FRF were determined according to Eqs. (3) and (4). The results obtained for  $J_{vss}$  and FRF in the NF experiments showed that the influence of the chemical pretreatment stage on  $J_{vss}$  is not significant. However, the effect of the chemical pretreatments on the fouling of the membranes can be deduced from the FRF values, which demonstrated that this reduction is lower in the experiments performed with the chemically pretreated waters in comparison to the experiment without chemical pretreatment.

This effect was expected, because the pretreated waters presented lower organic matter content than the raw waters. Consequently, they promoted a lower fouling of the

membranes, which is the main cause of the decay in the permeate flux through a membrane in a filtration process. Particularly, the lowest FRF value, as a consequence of a lower fouling, was obtained for the pretreated water with the highest ozone concentration 30  $\mu\text{M}$ , which produced a higher oxidation of the herbicides and the natural organic matter in the ozonation pretreatment.

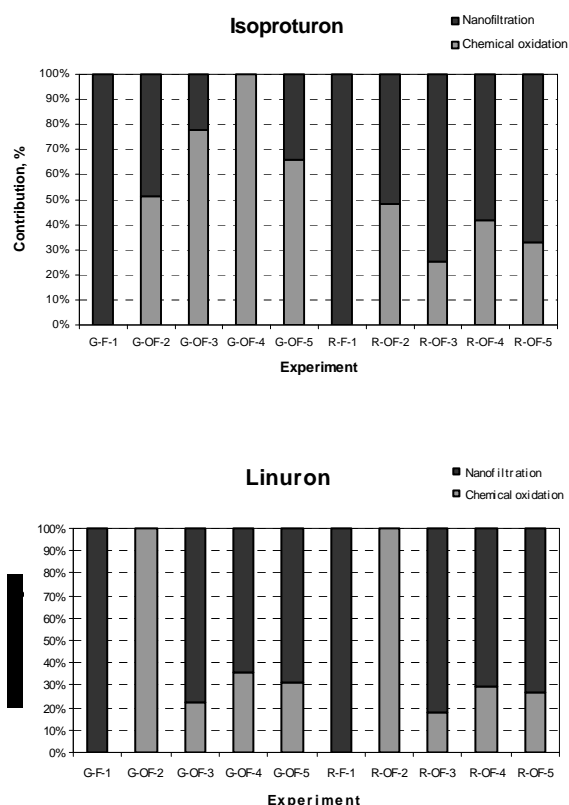
By considering the water matrices, the fouling effect (and consequently, the FRF) was slightly higher in the groundwater, because this water presented a higher content in dissolved solids and ions which are also retained by the membrane, and led to an increase in its fouling. However, these small differences due to the chemical pretreatment are not significant in comparison to the high herbicide rejections reached in the NF treatment stage.

The total effectiveness of this combined process, globally considered, can be deduced from the removals of the four herbicides, absorbance at 254 nm and conductivity, once both stages, chemical oxidation pretreatment and NF membrane treatment, were completed. From these results, it is observed that global reductions higher than 70 % were reached for the herbicides in all cases where the combined process was performed, as well as higher removals than 90 % for absorbance at 254 nm and higher than 60 % for conductivity.

Additionally, it must be remarked the increases obtained in the global reductions by these combined sequences, in comparison to the single NF experiments of the waters without any chemical pretreatment. More specifically, almost a total reduction of phenyl-ureas and absorbance, as well as conductivity in a great extent, were reached in the nanofiltration of both waters when the UV radiation was used in the pretreatment stage. Then, it can be concluded that the most effective sequence is a photodegradation pretreatment followed by a nanofiltration treatment, which eliminated most of the phenyl ureas present in both water matrices.

Finally, it is also interesting to establish the partial contribution of the two stages individually considered to the global effectiveness of the combined process. These contributions are represented in Figure 1 for isoproturon and linuron taken as examples. As it is observed, the first ozonation stage with an initial concentration of 30  $\mu\text{M}$  provided a major contribution to isoproturon elimination, specially in the groundwater; while the UV radiation pretreatment totally eliminated linuron in both water matrices, as was previously discussed according to the reactivity of the phenyl-ureas towards both oxidant agents, ozone and UV radiation.

Moreover, while the NF treatment presented a major contribution in the elimination of linuron (with the exception of the photochemically pretreated water), the oxidation pretreatments had a major contribution in the elimination of isoproturon in the groundwater, and slightly lower contribution in the reservoir water. These trends agreed well with the reactivities towards oxidants and retentions by NF of the selected herbicides.



**Figure 1.** Contribution of the chemical oxidation pretreatments to the elimination of phenyl-ureas in the sequences of chemical oxidation followed by nanofiltration experiments. a) isoproturon b) linuron.

The second sequence of treatments started with a filtration stage that was followed by an ozonation stage. In the filtration pretreatment, two different processes were conducted by using a ultrafiltration PT membrane (MWCO of 5 kDa), and the previously used nanofiltration DK membrane (MWCO in the range 150-300 Da). The effluent from these membranes filtration stages were oxidized in a second chemical stage by using ozone.

Focusing in the first filtration stage, it is observed two different trends; thus, in the NF process the sequence is: isoproturon > linuron > chlortoluron > diuron, which coincides with the results also obtained in the NF stage of the chemically pretreated waters. That is, the rejection by the hydrophylic DK membrane was inversely related to the polarity of the herbicides, as was previously discussed. However, in the UF stage, the rejection sequence was: linuron > diuron > chlortoluron > isoproturon. An explanation for this result can be given by considering that the hydrophobic nature of the substances is the predominant cause of the retention when an hydrophobic UF membrane is used,<sup>9-10</sup> as in the present case with the PT membrane. In effect, it is expected that the rejection of the selected pollutants may mainly be due to adsorption onto the membrane surface/pores by hydrophobic interactions.

In order to check this hypothesis, the hydrophobicity of the phenyl-ureas was evaluated by measuring their log  $K_{ow}$ , and the values obtained were: 3.20, 2.78, 2.35 and 2.32, for linuron, diuron, chlortoluron and isoproturon, respectively. As it is observed, the rejection sequence obtained in the present work agreed with this hydrophobic character, which confirms that adsorption constituted the most important mechanism for the rejection of the phenyl-ureas when using a hydrophobic UF membrane.

At the same time, it is clearly seen the influence of the membrane pore size on these coefficients, with an increase in the retention when the pore size was decreased. Thus, the coefficients obtained with the NF membrane were higher than those of the UF membrane with a higher MWCO, with the exception of linuron in the ground water. In effect, in this case the higher hydrophobic nature of this herbicide resulted in a great adsorption by the hydrophobic PT membrane, which overpassed the retention capacity of the DK membrane, although the MWCO of the last one was much lower. Finally, the results obtained show slightly higher rejection coefficients in the groundwater than in the reservoir water, which can be explained by a slightly greater fouling caused on the membrane by the adsorption and pore blocking of dissolved solids and ions, which are present in a major extent in the groundwater. This membrane fouling mentioned decreased the pore size and increased the herbicide retention.

The permeate stream of the preceding filtration stage (UF or NF), constituted the feed for the following chemical ozonation stage. In general, high conversions were obtained for the herbicides, specially in the case of the pretreated water with the NF process which reached almost total removal of herbicides. It is also observed that the sequence of conversions (isoproturon > chlortoluron > diuron > linuron) again agreed with the rate constants for the direct reactions between each herbicide and ozone, whose values were previously reported.<sup>13</sup> At the same time, the lower conversion values obtained for the groundwater in comparison to those from the equivalent experiments with the reservoir water are due to the lower ozone dose used: 2 mg L<sup>-1</sup> for the groundwater vs. 3 mg L<sup>-1</sup> for the reservoir water.

On the other hand, the conversions in the ozonation of waters from the UF pretreatment are lower than those reached in the single ozonation experiments without filtration pretreatment, specially for the most refractory substances to the direct ozone attack (linuron and diuron). It can be explained by the decrease in the generation of OH radicals that took place in the pretreated waters by the UF stage. As von Gunten pointed out,<sup>19</sup> an important source of OH radicals is the reaction between ozone and the organic matter present in a natural water, being these substances promoters of a chain mechanism for the decomposition of ozone into OH radicals. In the present process, it seems that the UF membrane mainly retained the most hydrophobic compounds, and therefore, their presence was diminished in the effluent that was fed to the ozonation stage.

This organic substances decrease in the solution led to a decrease in the production of OH radicals through their reaction with ozone. Similar effects have been described in the ozone treatment of permeates from hydrofobic membranes.<sup>11</sup> However, the ozonation of permeates from NF pretreatment, resulted in an almost total elimination of the herbicides, with an enhancement in the conversions in comparison to the single ozonation experiments, as could be expected. The absence of organic matter in the NF permeate led to a decrease of ozone consumption (higher ozone stability), and also, to its decomposition into OH radicals, both factors favouring the oxidation of herbicides.

Finally, the total effectiveness of this combined process is determined by the final removals obtained for the herbicides, absorbance at 254 nm and conductivity after the filtration and ozonation stages were completed. Thus, removals higher than 80% were reached for all the phenyl-ureas in the combined treatment, with total eliminations in the specific cases of isoproturon and chlortoluron. Additionally, clear improvements were obtained in relation to the single ozonation treatments, specially for diuron and linuron. Then, it can be concluded that the sequence constituted by a NF stage followed by the ozonation of the permeate effluent was the most effective, with almost total elimination of the phenyl-ureas in both water matrices, and an effluent of higher quality than any other treatment is generated.

## V. CONCLUSIONS

In this research, combinations of chemical oxidation stages followed by filtration stages, as well as the inverse sequence, filtration stages followed by chemical oxidation stages were tested for the elimination of four selected phenylurea herbicides (linuron, diuron, chlortoluron and isoproturon) from two natural water systems (a groundwater and a reservoir water). Although these sequences have been used by several authors for removing different micropollutants from water matrices, no specific report is found in the literature for the elimination of these compounds.

By only considering an efficiency point of view, and without economical considerations, it is deduced that both sequences provided high level of elimination for the individual herbicides, as well as for the global absorbance and conductivity of the water matrices tested. Thus, in the sequence chemical oxidation/filtration, when using UV radiation in the pretreatment stage followed by a nanofiltration stage, almost a total reduction of phenyl-ureas and absorbance at 254 nm were reached in both water matrices, although the processing time of this photochemical stage was high (30 min). If using ozone based pretreatments, the processing time was 10 min, and an ozone dose of 1.5 mg L<sup>-1</sup> was enough to decrease membrane fouling in the subsequent NF step.

In the opposite sequence filtration/chemical oxidation, a NF stage followed by the ozonation (with an initial concentration of 2 mg L<sup>-1</sup>) of the permeate effluent

provided in the groundwater total removals of isoproturon and chlortoluron, as well as of absorbance at 254 nm; removals higher than 90% of diuron and linuron, and 70% of conductivity. This removals were higher in the case of the reservoir water with an initial ozone concentration of 3 mg L<sup>-1</sup>.

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