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Activated Carbon and Ozone to Reduce Simazine in Water

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Abstract: In this study, the reduction of the pesticide simazine at an initial concentration of 0.7 mg L^{-1} in water has been investigated using two different technologies: adsorption with powdered and granulated activated carbon, advanced oxidation processes with ozone and finally, the combination of both technologies. The results obtained for a carbon dose of 16 mg L^{-1} show that powdered activated carbon, with contact times of 60 min, obtained 81% of reduction and in 24 h 92%, while granulated activated carbon at 60 min obtained a reduction of 2%, rising to 34% after 24 h of contact time. Therefore, powdered activated carbon achieves better reductions compared to granulated; when ozone was applied at a dose of 19.7 mg L^{-1}, with a reaction time of 18 min, a reduction of 93% was obtained, achieving a better reduction in less time than with adsorption treatments; however, during oxidation, by-products of simazine were produced. In the combined treatments, with the same doses of carbon and ozone mentioned above, the treatment that starts with ozone followed by activated carbon powder is recommended due to the adsorption in the last phase reaching a 90% reduction of the simazine and its by-products in 38 min of time.

Keywords: simazine; powdered activated carbon (PAC); granulated activated carbon (GAC); ozone; combined treatments; emerging contaminants

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1. Introduction

Emerging organic pollutants (EOCs) are known as micro-organic compounds, which are defined in Directive 2013/39/EU [1]. There is a wide range of compounds that are EOCs: drugs, pesticides, hormones, etc. [2]. These compounds are found in the environment, due to the increase in their consumption and/or production by humans [3–5].

2-chloro-4-ethylamino-6 isopropylamino-s-triazine, known as simazine (CAS No. 122-34-9), is a selective herbicide [6]. This substance is used to eliminate the weeds in different types of crops [7]. Simazine applied to soil as an herbicide has contributed to surface and groundwater contamination due to its leaching tendency [8]. The presence of simazine in the soil–water system is considered an environmental hazard due to its estrogenic effect [9,10].

The United States Environmental Protection Agency (USEPA) considers simazine an endocrine disruptor and a possible carcinogen for humans and animals [11–13]. The lethal concentration 50 (LC50) for fish varies from units to hundreds of milligrams per liter [14]. Several researchers have detected the presence of simazine in water. Kim and Homan [15] detected the presence of simazine in the waters of Erie's Lake. Li et al. [16] identified simazine in the Taizi River waters in concentrations of up to 1150 ng L^{-1}. The USEPA detected its two main metabolites (desisopropyl-s-atrazine and diaminochlorotriazine) in soil and groundwater samples in California [17]. The European Union has established a regulation that limits herbicide residues in drinking water to 0.1 μg L^{-1} for individual herbicides, and 0.5 μg L^{-1} for the sum of herbicides [18], while the USEPA has established this limit at 4 μg L^{-1} [19].

Conventional wastewater treatment plants (WWTPs), based mainly on biological processes, are not specifically designed for EOCs reduction. By aerobic or anaerobic biological treatment in WWTPs, simazine is only partially eliminated; therefore, biodegradation is not the most effective technology for its removal. In addition, the presence of this type of contaminants has a negative effect on the survival and reproduction of the microorganisms that allow the water treatment [20,21]. There are different studies in which simazine has been detected in the effluents of WWTPs [22]. Bueno et al. [23] detected concentrations of 105 and 1242 ng L^{-1} in the effluents of the WWTPs that treated urban and industrial wastewater in the city of Almeria, Spain.

Active carbon (AC) is used as an adsorbent for pesticides and other compounds in natural water and wastewater. ACs are highly porous and have a wide range of pore sizes. There are two main types of carbon: powdered activated carbon (PAC) and granulated activated carbon (GAC). PAC is most applicable for inclusion in those systems that already have a number of processes including tanks for mixing, precipitation or sedimentation and filtration, PAC is mainly added directly to water from WWTPs with an average contact time of 30 min to 4 h. While GAC is used in filter beds, it can be used in small residential treatment systems (individual supply), or for large volumes in commercial units, such as water treatment for community supply systems. Bataller et al. [24] reported that, in drinking water, the current trend is to incorporate post-ozonization to interozonization, followed by granular-activated carbon or biofiltration, with the aim to remove pesticides, biodegradable dissolved organic carbon and ozonation by-products. The EPA recommends the use of GAC for atrazine pesticide removal [25]. Lladó et al. [26] tested three different types of activated carbons to eliminate carbamazepine and atrazine in water. Gardi et al. [27] studied the elimination of 3 g L^{-1} of simazine with 1 g L^{-1} of GAC (Hydraffin 30N); they found a reduction of 38% at a contact time of 10 min. In other studies, novel porous carbon composites were used; these adsorbents were applied to farmland waters, achieving improvements in the adsorption of triazine group herbicides present in the soil [28].

In general, the AC's adsorption effectiveness depends on their physicochemical characteristics such as: surface, size and number of pores, functional groups, etc.; and also depends on the physicochemical properties of the contaminant such as: molecular size, hydrophobicity, polarity, functional groups, etc. [29]. In the Water Treatment Plants (WTP) located in Benidorm (Alicante, Spain) [30], PAC is used to reduce color and odor in the treatment of natural water that the plant captures before distribution to the public supply network. As per Di Bernardo and Dantas [31], it cannot be generalized that any type of carbon (powder or granular) can adsorb any undesirable organic substance from the water. Therefore, it is essential to carry out laboratory tests, to obtain previous knowledge of the main characteristics of the different types of active carbon and to make the appropriate selection of the active carbon, analyzing the removal of specific substances.

Ozonization is effective in the degradation of a wide range of organic contaminants (pharmaceuticals, synthetic substances, pesticides and herbicides, etc.) [28]. The degradation of organic substances is achieved mainly in two ways: by direct reaction with molecular ozone, or by indirect reactions with free radicals. Ozone treatment has been applied for the reduction of natural organic matter [32,33], inactivation of microorganisms [34] and reduction of EOCs in waters [35,36]. Simazine is considered a low oxidation microcontaminant; its reduction is greater when both direct and indirect reaction ways are used, the indirect one being the most sensitive. Mathon et al. [37] applied a dose of ozone of 1.6 g O_3 g DOC^{-1} to an initial concentration of simazine of 9000 ng L^{-1}; in this study they obtained a concentration of simazine of 6000 ng L^{-1} after 800 s of treatment. This means a reduction of 33%. Rate constants of reactions of ozone and hydroxyl radical with simazine were found to be 8.7 M^{-1} s^{-1} and 2.1×10^9 M^{-1} s^{-1}, respectively [38]. For example, carbamazepine had a reaction rate constant of ozone (K_{O3}) and hydroxyl radical (K_{OH}) of 3.0×10^5 M^{-1} s^{-1} and 8.8×10^9 M^{-1} s^{-1}, respectively [39], while the reaction rate constants of metoprolol were 2.0×10^3 M^{-1} s^{-1} and 7.3×10^9 M^{-1} s^{-1}, respectively [40].

Beltrán et al. [41] studied the by-products generated during the oxidation process of simazine with ozone. The main oxidation by-products detected in this study were: 2-chloro−4-acetamide-6-ethylamino-s-triazine (CDET), 4.6-diamine-2-hydroxy-s-triazine (OAAT) and 2.4.6-trihydroxy-s-triazine or cyanuric acid (OOOT). These by-products could in some cases be as hazardous as simazine, which would require further treatment.

In recent years, combined treatment processes are being used to remove pollutants from water [42]. Bernal Romero del Hombre Bueno [43] studied at laboratory scale the elimination of simazine in wastewater, using a combination of several treatments. For an initial simazine concentration of 7 µg L^{-1}, a reduction of 25% was obtained when they applied a membrane bioreactor (MBR) treatment, and around 43% when they used an Upflow Anaerobic Sludge Blanket (UASB) treatment. With the combined treatment of MBR + Nanofiltration (NF), they obtained reductions of greater than 90%. When they used the MBR + Reverse osmosis (RO), they observed a reduction of 97%. The combined treatment of MBR + Ozone (O_3) reached yields above 92%. The simazine removal rate with the UASB + MBR treatment, to treat a dose of contaminant of 2.9 µg L^{-1}, was 72%. In this research, the combination of three treatments was also studied: The UASB + MBR + NF treatment achieved a percentage of 90% for an initial concentration of simazine of 1 µg L^{-1}. When the combined treatment was UASB + MBR + IO, they obtained a 97.2% reduction when the initial simazine dose was 0.3 µg L^{-1} [43]. Flores et al. [44] studied the photocatalytic degradation of simazine using zinc oxide/graphene oxide composite materials under visible light irradiation. In this study, they achieved percentages above 80% depending on the catalyst dose and pH range. Catalkaya and Kargi [45] investigated the removal of simazine from aqueous solution by Fenton's reagent oxidation. The optimal H_2O_2/Fe (II)/simazine ratio to obtain the maximum pesticide removal (100%) was 55/15/3 (mg L^{-1}) [45].

No bibliographic references have been found that discuss the reduction of simazine with carbon followed by ozone or vice versa. For this reason, the main objective of this research was to study the effect of the combination of active carbon followed by ozone and vice versa, to achieve the maximum reduction of simazine. For this purpose, an initial dose of contaminant of 0.7 mg L^{-1} was chosen. In the first part of the research, the optimal dose of carbon and ozone was determined. Two types of active carbon were used (PAC and GAC). Finally, for the combined treatments AC/O_3 and O_3/AC, the optimal time that allowed a reduction of 90% of simazine was determined.

2. Materials and Methods

2.1. Reagents

The simazine standard was supplied by the manufacturer Sigma-Aldrich. Simazine concentrations were obtained from the standard by dilution with methanol to concentrations of 2500 mg L^{-1} and for lower concentrations with acetonitrile and ultrapure water (*v*:*v* = 55:45). All reagents were of HPLC quality grade, supplied by the Sigma Chemical company with a purity of 98–99% respectively (acetonitrile and methanol). The physico-chemical characteristics of simazine [46] are shown in Table 1.

Table 1. Physico-chemical characteristics of simazine.

Chemical Name	EC_{50}, 336 h (mg L^{-1})	Molecule Size (nm)	Width (Å)	Depth (Å)	Molar Mass (g moL^{-1})	Solubility in Water (mg L^{-1})	Log Kow	pKa
Simazine	0.592 [A]	0.784 [B]	7.49 [C]	10.34 [C]	201.66	6.20(20 °C)	2.18	1.62

[A] [47] [B] [48] [C] [49].

2.2. Activated Carbon

Two types of AC have been used in this study: Powdered Activated Carbon—PAC (Pulsorb PWX HA) and Granular Activated Carbon—GAC (Calgon Filtrasorb 400). To characterize PAC, the methodology suggested according to the standards of the American Society for Testing and Materials (ASTM), D5158-98 [50] was used and for the characterization of the GAC, the standards recommended by the American Water Works Association (AWWA), B604-12 [51]. Before each test, the AC was subjected to the following conditioning: screening of the AC, washing with ultrapure water several times to a constant pH, drying at 105 °C for 3 h, storage in a desiccator until required for use.

2.3. Characterisation of Activated Carbons

To determine the adsorption isotherm of N_2 77 K, an Autosorb-6 automatic volumetric instrument for the physical adsorption of N_2 and an Autosorb degasser from Quantachrome Instruments, model Quadrasorb-Kr/MP, were used.

To determine functional groups, the Fourier-transform infrared spectroscopy (FTIR) technique was used. The equipment used in the investigation was a spectrometer from Jasco, an FTIR-4700 series, capable of working with a resolution of up to 0.5 cm^{-1} equipped with a medium IR source, a germanium encapsulated KBr beam splitter and a DLaTGS detector for routine measurements. It has a measurable frequency range between 7800 and 400 cm^{-1}.

2.4. Analytical Method

The simazine concentration was determined using High-Performance Liquid Chromatography (HPLC) equipment from Agilent technologies, specifically, an Agilent 1100 Series machine (Bad Homburg, Waldbronn, Germany). The equipment has a 5 µm Ascentis RP-Amide column (150 mm × 4.6 mm) from Sigma-Aldrich as its stationary phase and an ultraviolet detector (UV), with a working wavelength of 220 nm. The mobile phase consisted of a mixture of acetonitrile and water (v:v = 55:45), at a flow of 1.0 mL min^{-1} with a detection time of 225s. The matrix used for the study was Type I ultrapure water [52], supplied by Milli-Q Academic (Millipore), with a pH of 6.7. The limits of detection (LOD) and quantification (LOQ) for simazine were measured at signal-to-noise ratios of 3 and 10, respectively. The LOD were 0.015 mg L^{-1} and LOQ 0.045 mg L^{-1}, respectively.

2.5. Adsorption Experiments

Batch adsorption experiments were performed using both types of activated carbon. The adsorption experiments were carried out in order to study the influence of the carbon dose and the contact time for the reduction of simazine. The adsorption tests were carried out according to the ASTM standard [53]. Each experiment was carried out in a 500 mL reactor with a set stirring speed of (300 rpm ± 10 rpm), temperature (25 °C ± 2 °C) and initial pH (6.7 ± 0.1). An initial simazine concentration for all experiments was set at 0.7 mg L^{-1}. The variables studied were: type of AC (PAC or GAC), the dose of AC (4, 8, 12, 16 and 20 mg L^{-1}) and experiment time.

During the contact phase, 1 mL samples were periodically extracted for subsequent analysis. Once the samples were extracted, they were filtered with a Hydrophilic PVDF filter of pore size 0.22 µm and diameter 25 mm from the Filter-Lab company, and were subsequently subjected to analysis using HPLC-UV.

2.6. Oxidation Experiments

The equipment used was an Anseros COM-AD-01 ozone generator (Dischingerweg, Tubinga, Germany). The equipment was coupled to an external industrial oxygen supply whose purity quality by volume was ≥99.5% and with H_2O of ≤30 vpm, at a constant flow of 100 L h^{-1} at a pressure of 1 bar. Each experiment was carried out in a 500 mL reactor with set stirring speed (300 rpm ± 10 rpm), temperature (25 °C ± 2 °C) and initial pH (6.7 ± 0.1). The variables studied were: O_3 dose (5.6, 10.5, 15.4, 19.7 and 24 mg L^{-1}) and experiment times of 0–20 min. In all experiments, an initial simazine concentration of 0.7 mg L^{-1} was established. During the contact phase, 1 mL samples were periodically extracted for subsequent analysis once filtered.

2.7. Combined Experiments

The effect of applying AC/O_3 and conversely O_3/AC was studied for the two types of activated carbon. The time set for the first treatment was that which managed to reduce the contaminant by 50% ± 5%. This time was previously estimated from the individual experiments. In the second phase of treatment, the experiment was maintained until reaching final values greater than 90%. All experiments were carried out for a PAC and GAC dose of 16 mg L^{-1} and an O_3 dose of 19.7 mg L^{-1}. The initial concentration of simazine studied was 0.7 mg L^{-1}. The same methodologies were maintained as those for each of the individual experiments and the combinations studied were PAC/O_3, O_3/PAC, GAC/O_3, and finally O_3/GAC.

3. Results and Discussion

3.1. Characterisation of the Pulsorb PWX HA and Calgon Filtrasorb 400

According to the classification of pore distribution by the International Union of Pure and Applied Chemistry (IUPAC) [54], it can be seen that the activated carbons studied in this research have the following characteristics: PAC has 63% of the pores with a diameter greater than 2 nm, while GAC has only 26%. PAC and GAC have a surface area (based on the shape of the Brunauer, Emmett and Teller (BET)) of 824.688 m^2 g^{-1} and 1070.089 m^2 g^{-1}, respectively. The average particle diameter in the PAC and GAC is 1.18 nm and 1.24 nm. The volume of mesopores of the PAC is slightly higher than the GAC one (0.18 and 0.14 cc g^{-1}). This difference in the volume of mesopores means that, so far the size of the simazine particles is less than 1 nm (see Table 1), they are more easily accessible in the PAC than in the GAC.

These data have been contrasted with other studies that use the same types of coals [30,55]. The data have been found to be in concordance with them.

When we observe both carbons to scale 1 μm, differences can be clearly seen at the surface level. Figures 1 and 2 show the SEM photographs obtained. Figure 1A (PAC) shows a relatively smooth surface with small bodies of amorphous morphology. Figure 2A (GAC) presents a different morphology, a less smooth and homogeneous surface can be seen. At an increase of 100 nm, differences are observed in the distribution of the pores. In Figure 1B, a greater number of pores predominate, most of these being mesopores, than in Figure 2B.

Figure 3 shows the photographs obtained by TEM at a size of 5 nm in which we can see the micropores of the coals used in this research. In the GAC (Figure 2B), more micropores are observed than in the PAC (Figure 2A). Therefore, there are important differences between both ACs. Although PAC has fewer micropores than GAC, it has in its favor a greater number of mesopores than GAC on the surface.

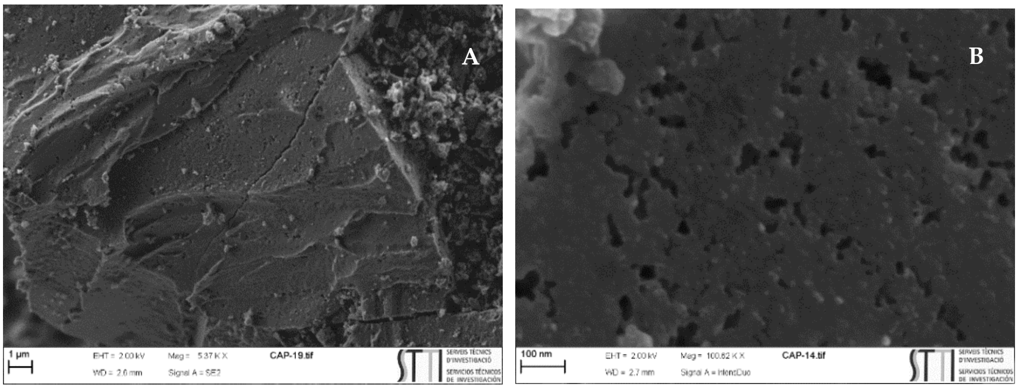

Figure 1. SEM images of PAC at different scales: (**A**) 5370 magnification. (**B**) 100,620 magnification.

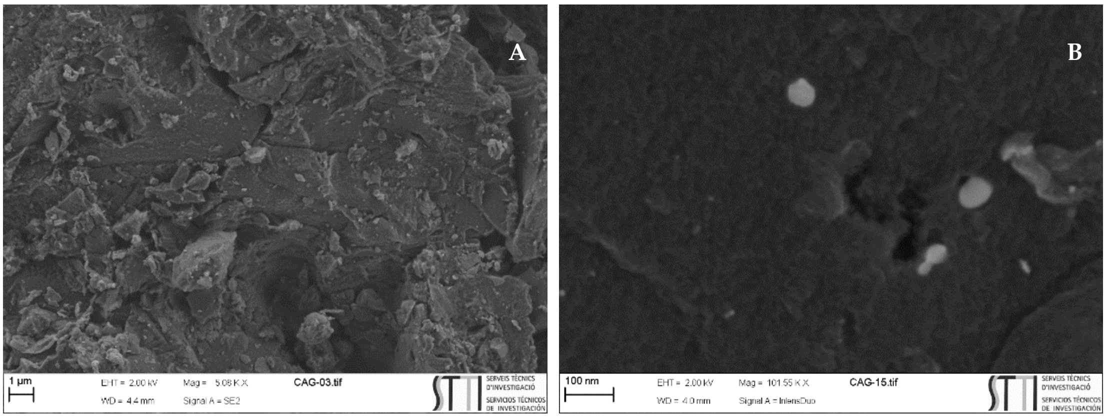

Figure 2. SEM images of GAC at different scales: (**A**) 5080 magnification. (**B**) 100,155 magnification.

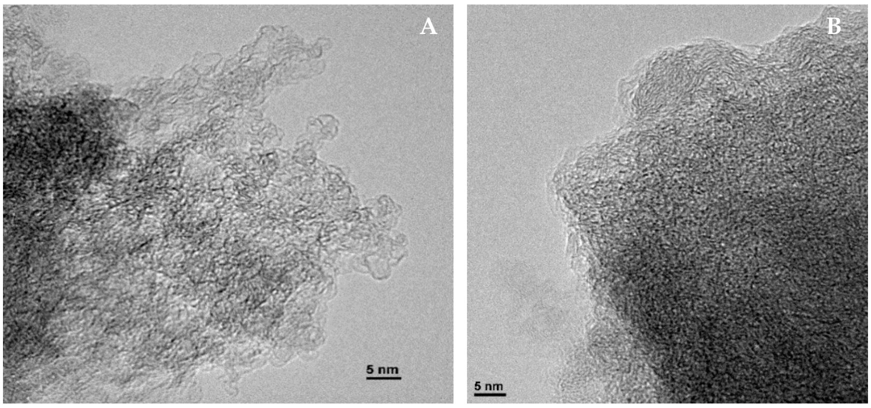

Figure 3. TEM images of activated carbons: (**A**) PAC; (**B**) GAC.

3.2. Simazine Adsorption with Powdered Activated Carbon

In Figure 4, the percentage of simazine reduction is plotted against time for different doses of PAC. As can be seen, at whichever dose of PAC, a rapid reduction of simazine occurs at the beginning of the experiment until around minute 30–45. For a contact time of 60 min and carbon doses of 4, 8, 12, 16 and 20 mg L^{-1}, a reduction of simazine of 6%, 36%, 53%, 64% and 79% is achieved. After 60 min, the reduction continues to increase, but with a less pronounced slope. After 10 h of contact time, the reduction of the contaminant increases very slightly, but does not show an increase of more than 28% in the period up to the completion of the experiment. This slowing down of the simazine adsorption rate at higher contact times can be attributed to the decrease in the active sites of the PAC, which generates a reduction in the driving force of adsorption [56,57].

In all cases, a higher dose of PAC obtains better reduction yields, with more significant differences being observed when going from the lowest dose studied of 4 mg L^{-1} to 8 mg L^{-1}.

In the research by Matsui et al. [58], they studied the reduction of different pesticides in different waters, like river water. For an initial simazine concentration of 92 µg L^{-1} and a dose of 5 mg L^{-1} of PAC achieved, a 40% reduction was achieved after 30 min and a ≈50% reduction after 60 min. Also, for a PAC dose of 10 mg L^{-1}, the reduction of simazine increased to 60% in 30 min and 75% in 60 min. Meanwhile, Jiang and Adams [59] achieved ≈90% reductions with two different PACs at 5 h of contact time with an initial concentration of 3 µg L^{-1} in a mixture of six chlorine-s-triazines in distilled water (pH 7.5), including simazine. Both studies show the effectiveness of reducing simazine by using PAC. Comparing the results obtained with other researches, it is observed that PAC has a high enough adsorption capacity to be able to retain higher concentrations of simazine than the usual ones in water and with similar doses to achieve reductions in an optimal time.

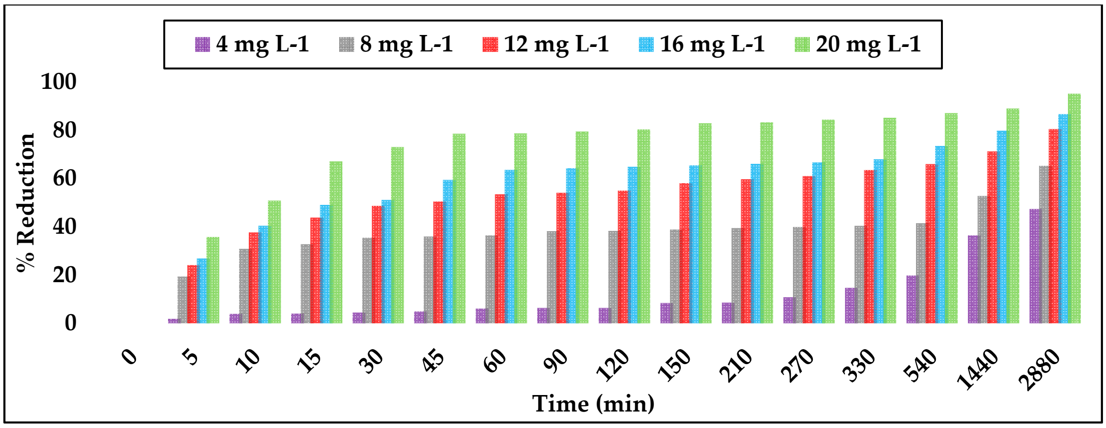

Figure 4. Evolution of simazine reduction over time with different doses of PAC. Experimental conditions: [Simazine$_0$] = 0.7 mg L^{-1}; [PAC] = 4, 8, 12, 16 and 20 mg L^{-1}; pH$_0$ 6.7; T = 25 °C.

3.3. Simazine Adsorption with Granular Activated Carbon

In Figure 5, the percentage of simazine reduction over time is represented for all the doses of GAC studied. As can be seen, for a contact time of 168 h, at the highest dose of GAC studied, better contaminant reduction performances were obtained. At low doses of GAC, increases of 4 mg L^{-1} significantly improve the reduction yields, an effect that can be observed for doses of 4 and 8 mg L^{-1}. In contrast, when the increase occurs at higher doses of GAC (16–20 mg L^{-1}), there are no significant differences. In the same way as what happened with PAC, at higher doses of GAC, there are a greater number of active sites where adsorption can occur for a constant number of simazine molecules [60–62]. Simazine reductions greater than 10% do not occur at any GAC concentration with contact times less than 540 min. After 24 h of experimentation, at 20 mg L^{-1}, the highest dose of GAC studied, the reduction of simazine is less than 28%. At the lowest dose of GAC studied and after 7 days of contact, the yield was less than 38%. For a concentration of 16 mg L^{-1}, reduction values greater than 50% are obtained after the fourth day of experimentation. In general, it can be concluded that GAC reduction would require high doses and long contact times to be considered a valid industrial process in itself that was deemed efficient.

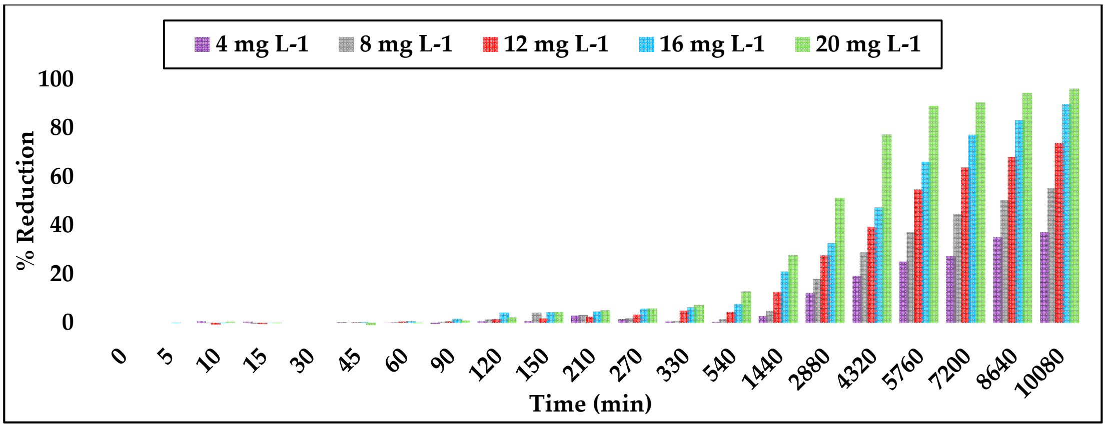

Figure 5. Evolution of simazine reduction over time with different doses of GAC. Experimental conditions: [Simazine $_0$] = 0.7 mg L^{-1}; [GAC] = 4, 8, 12, 16 and 20 mg L^{-1}; pH$_0$ 6.7; T = 25 °C.

Li et al. [63] studied the overall reduction of s-triazine herbicides (atrazine, simazine and promethrin), to an average concentration of 150–950 µg L^{-1}, by adsorption treatment with a GAC dose of 400 mg L^{-1}, studying the effect of water temperatures and matrices. Their results showed that adsorption was different depending on the physical–chemical properties of each EOC studied.

Simazine had a higher absorption capacity in distilled water than in other aqueous matrices such as mains or surface water. This lower removal of simazine in natural waters is due to the presence of natural organic matter (NOM) in natural waters, which tends to be adsorbed in the active centers of the carbon, reducing the removal efficiency. An increase in the temperature of the medium decreased the adsorption of s-triazine in the GAC [64].

Metcalf and Eddy [20] described that activated carbons have a low adsorption affinity for polar organic species with low molecular weight, such as simazine. Choi et al. [65] explained that the volume of pores, with a greater effect than the specific area, is one of the most important factors of adsorption. The GAC used in this study has a smaller volume of mesopores than the PAC (Figures 1 and 2); this hinders the access of simazine molecules to the active center. This is the main reason for the poor adsorption of simazine over the time for this carbon.

Nevertheless, it is observed in the results that, as the contact time increases, the reduction of simazine increases when it is treated with GAC. This is mainly due to the fact that GAC has C-H and C-O surface groups, which gives it an acidic character [66]. In addition, GAC has a greater number of C-O functional groups than PAC, providing GAC a greater polarity. This greater polarity of the GAC favors the adsorption of the simazine once it has entered into the pores.

3.4. Comparison of PAC versus GAC

In Figure 6, the percentage of simazine reduction is represented against 4 different reaction times (60, 540, 1440 and 2280 min) for the two activated carbons studied. The results show that, in all cases, the reductions achieved with PAC are much higher than those achieved with GAC. These differences are also more significant at lower contact times; for example, at a time of 60 min, the treatment with PAC achieves a reduction of more than 6% at all the carbon doses studied. However, when GAC was used, no results above 3% were obtained. For a dose of activated carbon of 16 mg L^{-1} with a contact time of 60 min, a reduction percentage for PAC of 64% was obtained, while that of GAC was only 2%. With a contact time of 540 min and carbon doses of 4, 8, 12, 16 and 20 mg L^{-1}, a reduction of simazine is obtained with PAC of 20%, 41%, 66%, 74% and 87%, accordingly, whereas in the case of GAC, with the highest dose (20 mg L^{-1}), only 13% reduction was reached; this is 74% less than the result achieved with PAC.

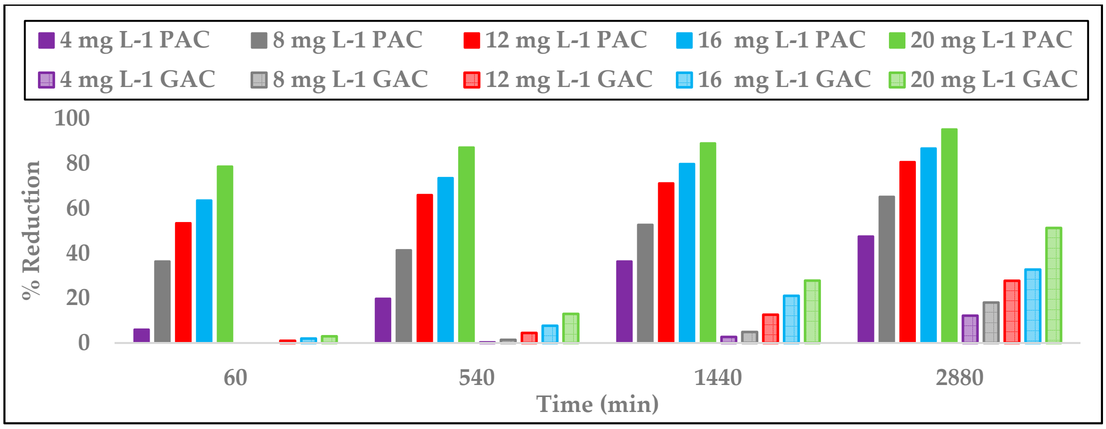

Figure 6. Simazine reduction using PAC and GAC with different contact times. Experimental conditions: [$Simazine_0$] = 0.7 mg L^{-1}; [PAC] and [GAC] = 4–20 mg L^{-1}; pH_0 6.7; T = 25 °C.

The differences between PAC and GAC are less marked at longer contact times; for example, with a contact time of 48 h at the highest dose of carbon studied, the reduction with PAC achieved is 95%, whilst using GAC it is 51%, a difference of 44%. This is due to the fact that the reduction with PAC is fast at lower contact times, but after 540 min, it tends to stabilize, showing an increase in a less pronounced way. In the case of GAC, contaminant reduction is more gradual throughout the entire experiment and requires times greater than 24 h to achieve reductions of more than 23%. Simazine has a low log Kow (Table 1), that is, it is hydrophilic, which promotes the solubility in water. PAC has a higher number of mesopores than GAC; this facilitates that simazine molecules reach the active centers of carbon. Therefore, PAC achieves a greater reduction of simazine than GAC in less time under the same doses studied.

3.5. Simazine Oxidation with Ozone

In Figure 7, the simazine reduction percentage has been plotted against time for different ozone doses. It can be seen that, at any O_3 dose, a rapid reduction of simazine occurs throughout the experiment. With a contact time of 20 min and O_3 doses of 5.6, 10.5, 15.4, 19.7 and 24 mg L^{-1}, a simazine reduction of 47%, 60%, 81%, 87 and 93% is obtained, respectively. In all cases, increasing the ozone dose improves the efficiency of contaminant reduction [67,68]. At low ozone doses, increments in O_3 of around 5 mg L^{-1} significantly improve contaminant reductions, but with a dose of 15.4 mg L^{-1} of O_3, an increase of 5 mg L^{-1} does not imply a significant improvement in the reduction of simazine.

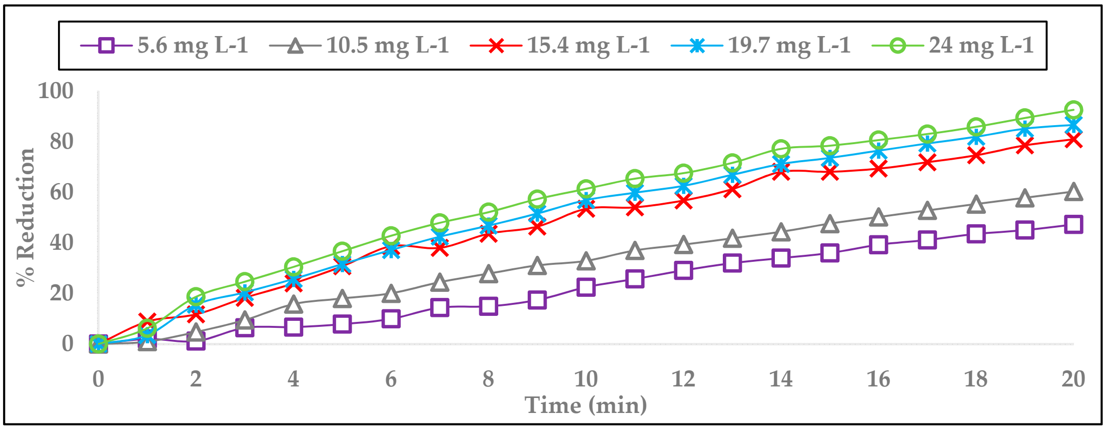

Figure 7. Evolution of simazine reduction over time at different doses of O_3. Experimental conditions: [$Simazine_0$] = 0.7 mg L^{-1}; [O_3] = 5.6, 10.5, 15.4, 19.7 and 24 mg L^{-1}; pH_0 6.7, $pH_{(20\ min)}$ 4.5–4.9; T = 25 °C.

Nahim-Granados et al. [69] investigated on a pilot scale the reduction of 6 EOCs, including simazine with a concentration of 100 µg L^{-1} in aqueous matrices. The study was carried out at different pHs between 6.25 and 11. In this study, better removal performances were obtained when using a 20 mg L^{-1} dose of O_3. In addition, they achieved a reduction of 50% at 30 min of contact and 85% at 120 min. It was further indicated that there had been an inactivation of pathogens. Ormad et al. [70] detected 44 different pesticides in the Ebro river basin, Spain. Simazine with an initial concentration of 536 ng L^{-1} was treated with an O_3 dose of 3 mg L^{-1} at pH 8, achieving a reduction of 23%.

The main mechanism of action of O_3 is electrophilic attack, however, simazine has a low ozonization efficiency with a low oxidation kinetic constant (k_{O3}) ($100 < k_{O3} > 10^3$ M^{-1} s^{-1}) [71,72]. This resistance that simazine presents to oxidation by O_3 in comparison with other pesticides that have some triazine ring may be due to the absence of S in their side chains and having a Cl group, which is less susceptible to electrophilic attack [73].

In Table 2, it is observed that the pH was not constant in the O_3 treatments. As the dose of ozone increases, the pH obtained at the end of the treatment decreases and is more acidic, obtaining a decrease with respect to the initial pH of 32.5% with the highest dose of ozone at 20 min of contact.

Table 2. The simazine concentration and the pH obtained in the ozone treatment at a contact time of 20 min and temperature of 25 °C.

	[O$_3$]									
	(mg L^{-1})									
	5.6		**10.5**		**15.4**		**19.7**		**24**	
Time	**[Simazine]**	**Reduction**	**[Simazine]**	**Reduction**	**[Simazine]**	**Reduction**	**[Simazine]**	**Reduction**	**[Simazine]**	**Reduction**
(min)	**(mg L^{-1})**	**(%)**	**(mg L^{-1})**	**(%)**	**(mg L^{-1})**	**(%)**	**(mg L^{-1})**	**(%)**	**(mg L^{-1})**	**(%)**
0	0.7	0	0.7	0	0.7	0	0.7	0	0.7	0
5	0.64	7.86	0.57	18.01	0.48	30.74	0.48	31.61	0.44	36.69
10	0.54	22.47	0.47	32.89	0.33	53.46	0.30	56.88	0.27	61.35
15	0.45	35.99	0.37	47.60	0.22	68.09	0.19	73.57	0.15	78.40
20	0.37	47.28	0.28	60.29	0.13	80.93	0.09	86.64	0.05	92.57
pH$_{(0\ \mathrm{min})}$	6.7 ± 0.1		6.7 ± 0.1		6.7 ± 0.1		6.7 ± 0.1		6.7 ± 0.1	
pH$_{(20\ \mathrm{min})}$	5.2 ± 0.1		5.0 ± 0.1		4.8 ± 0.1		4.5 ± 0.1		4.2 ± 0.1	

3.6. Combined PAC/O_3 and O_3/PAC Experiments

In Figure 8, the percentage of simazine reduction over time has been represented for the two combined treatments studied, namely PAC/O_3 and O_3/PAC. As already observed in the PAC experiments, to obtain a reduction of simazine of 50% ± 5%, the contact time necessary to treat an initial concentration of 0.7 mg L^{-1} at a 16 mg L^{-1} dose of PAC was 16 min (see Figure 4). Subsequent treatment with O_3 makes it possible to achieve a simazine reduction greater than 90% beyond 38 min (total time). In the second treatment (O_3/PAC), it is observed, in the first phase of contact with O_3, that a reduction of 50% ± 5% is achieved at 10 min. In the second phase of treatment with PAC, to achieve a contaminant reduction of more than 90%, we must maintain the adsorption for a total time of 40 min. If we compare both experiments (PAC/O_3 and O_3/PAC), it can be concluded that the application of PAC/O_3 requires a considerably shorter treatment time.

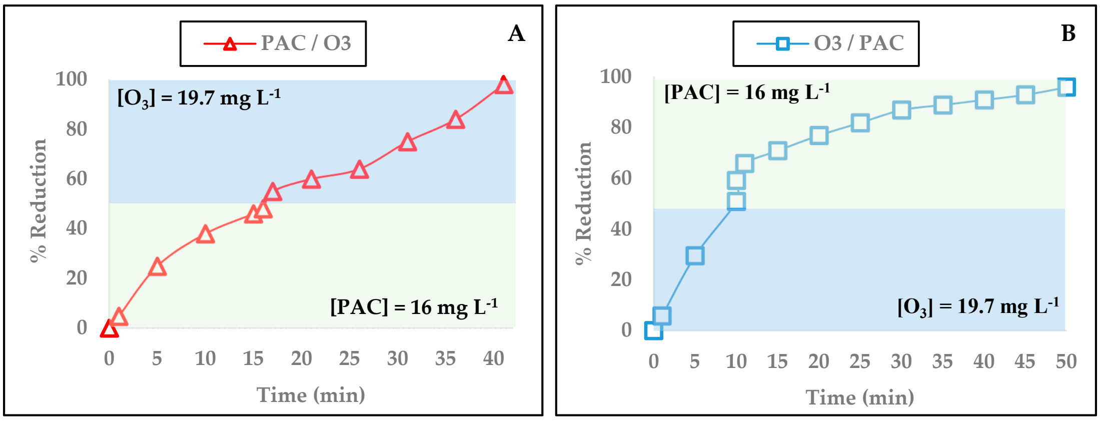

Figure 8. Evolution of simazine reduction over time for combined treatments: (**A**) Experimental conditions PAC/O_3: [$Simazine_0$] = 0.7 mg L^{-1}; [PAC] = 16 mg L^{-1}; [O_3] = 19.7 mg L^{-1}; pH_0 6.7; $pH_{(20\ min)}$ 4.3–4.5; T = 25 °C. (**B**) Experimental conditions O_3/PAC: [$Simazine_0$] = 0.7 mg L^{-1}; [O_3] = 19.7 mg L^{-1}; [PAC] = 16 mg L^{-1}; pH_0 6.7; $pH_{(20\ min)}$ 5.0–5.2; T = 25 °C.

With regards to the results, for an initial contaminant concentration of 0.7 mg L^{-1} and dose of O_3 at 19.7 mg L^{-1}, it is observed that, as time increases, simazine decreases due to O_3 action, until reaching final values greater than 90% reduction; however, whilst reducing the main contaminant, new chemical species are being created. Beltrán et al. [41] studied the ozonization process of simazine, identified 2-chloro4-ethylamino-6-amino-1,3,5-s-triazine (CEAT) and 2-chloro-4,6-bis(amino)-1,3,5-s-triazine (CAAT). In other works where hydroxyl radicals were used as the main oxidants of s-triazine herbicides in water [74–77], they identified other possible intermediates such as: 2-chloro-4-acetamide-6-ethylamino-s-triazine (CDET), 4.6-diamine-2-hydroxy-s-triazine (OAAT) and 2.4.6-trihydroxy-s-triazine or cyanuric acid (OOOT).

When ozone reacts with the pesticide, in addition to reducing simazine, by-products are generated in this reaction. Therefore, when the combination O_3/PAC is carried out, at the end of the first treatment with O_3, the simazine that has not been reduced in this process is still present in the water but with its by-products, but when the second treatment with activated carbon begins, it adsorbs the simazine and the by-products. However, when the combination is PAC/O_3, in the second treatment, the ozone reduces the simazine present in water, but it generates new chemical species with negative effects on the aquatic environment.

3.7. Combined GAC/O_3 and O_3/GAC Experiments

In Figure 9, the percentage reduction of simazine over time has been plotted for the two combined treatments GAC/O_3 and O_3/GAC. As already observed in the GAC experiments, to obtain a 50% ± 5% reduction in simazine, the contact time necessary to treat an initial concentration of 0.7 mg L^{-1} at a

16 mg L^{-1} dose of GAC was around 3 days (Figure 5). Subsequent treatment with O_3 makes it possible to achieve a simazine reduction value greater than 90% from the minute 4338 onwards (total time). In the second treatment (O_3/GAC), for the simazine concentration studied, it is observed in the first phase of contact with O_3 that a reduction of 50% ± 5% is achieved at 10 min. In the second phase of contact with GAC, to achieve a total reduction of contaminant greater than 90%, the phase must be longer. A 90% reduction is achieved with a total experiment time of 5772 min. If we compare both experiments (GAC/O_3 and O_3/GAC), it can be concluded that the application of GAC/O_3 requires a considerably shorter treatment time. Therefore, it is observed that the combination of GAC/O_3 in terms of treatment time is more favorable than when treatment is initiated with O_3, due to the same explanation as in the combined PAC/O_3 and O_3/PAC trial of simazine. The application of O_3 generates a series of by-products [78,79] and OH [80], which compete for the active carbon centers, decreasing the adsorption of simazine against time.

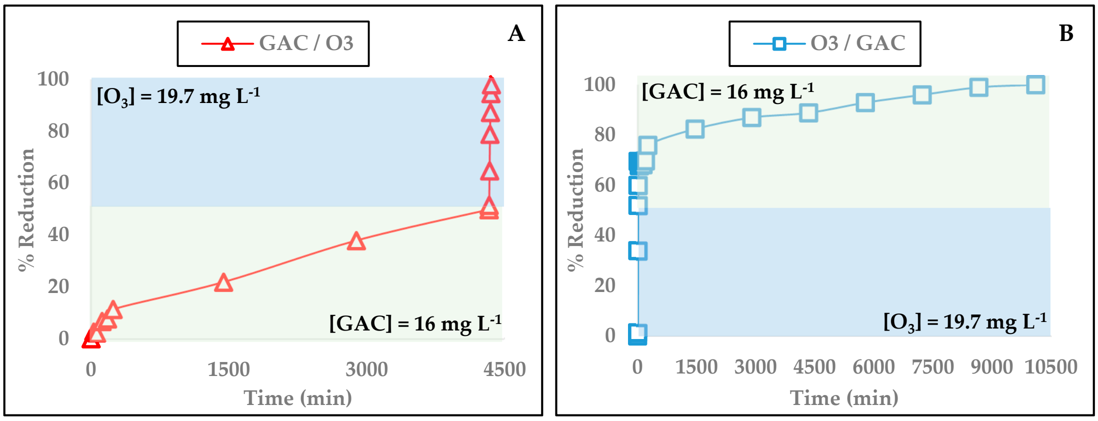

Figure 9. Reduction of simazine during the course of the combined experiment: (**A**) Experimental conditions GAC/O_3: [$Simazine_0$] = 0.7 mg L^{-1}; [GAC] = 16 mg L^{-1}; [O_3] = 19.7 mg L^{-1}; pH_0 6.7; $pH_{(20\ min)}$ 4.2–4.5; T = 25 °C. (**B**) Experimental conditions O_3/GAC: [$Simazine_0$] = 0.7 mg L^{-1}; [O_3] = 19.7 mg L^{-1}; [GAC] = 16 mg L^{-1}; pH_0 6.7; $pH_{(20\ min)}$ 4.8–5.1; T = 25 °C.

3.8. Comparison AC/O_3 versus O_3/AC

Table 3 shows a summary of the simazine reduction percentages for the combined tests for an initial contaminant concentration of 0.7 mg L^{-1}. In the table, the yields obtained at the end of each of the treatments can be observed. As can be seen, the total time is substantially less when PAC is applied initially than when GAC is applied initially. In both cases, percentages greater than 96% reduction of simazine are achieved, but in the case of using GAC/O_3, the times would exceed 3 days, whilst the total time is significantly shorter when PAC is applied after ozonation than when GAC is applied. In both cases, high percentages of contaminant reduction are achieved, but at very different times. While with O_3/PAC the treatment times are around 49 min, in the case of O_3/GAC, the required contact time is greater than 7 days.

Table 3. Comparison of simazine reduction percentages for AC/O_3 and O_3/AC. Initial Conditions: [$Simazine_0$] = 0.7 mg L^{-1}; [O_3] = 19.7 mg L^{-1}; [PAC] y [GAC] = 16 mg L^{-1}.

	PAC		**O_3**		**GAC**		**O_3**	
AC/O_3	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**
	15	46	25	98	4320	50	25	98
	O_3		**PAC**		**O_3**		**GAC**	
O_3/AC	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**	**Time (min)**	**Reduction (%)**
	10	51	39	96	10	52	10,080	99

In view of the results obtained, the combined treatments studied in this research are all effective in reducing simazine; however, the treatment that is initiated with O_3 followed by AC is recommended, because during the ozonization process, as well as reducing simazine, new chemical species are generated which are just as toxic or harmful as the main contaminant. The final adsorption treatment would allow both the simazine and its by-products to be retained in the AC. This would benefit the ecological status of the waters and also the health of living beings [81]. In addition to the GAC treatments needing greater contact times than PAC, they may also impair the ability of WWTPs to function correctly. Therefore, the best treatment for simazine reduction, with respect to time and effectiveness, would be the combined O_3/PAC version.

No studies have been found based on the combination of AC adsorption treatments followed by ozonation (PAC/O_3 and GAC/O_3) or vice versa (O_3/PAC and GAC/O_3). The vast majority of studies about the reduction of simazine have been based on combination and not by phases.

4. Conclusions

In view of the results obtained by the isotherm of N_2 adsorption at 77 K, it indicates that GAC has more micropores than PAC; however, GAC has less mesopores. The SEM images reflect the similarity on the surface of the coals, while the TEM images make the difference by showing a higher number of micropores in the GAC carbon. Therefore, although GAC has a greater volume of micropores, it also has fewer mesopores on its surface, which makes it difficult for simazine to access the active center and be adsorbed, in contrast to PAC.

In the PAC adsorption experiments, simazine shows a rapid reduction in the first 30–45 min. With the lowest and highest dose of PAC studied (4 mg L^{-1} and 20 mg L^{-1}) for an initial simazine concentration of 0.7 mg L^{-1}, a reduction of 6% and 79% is achieved for a contact time of 60 min. In the same way, but with a contact time of 24 h, a reduction of 36% and 89% is achieved, respectively. When GAC was used, simazine did not show significant reductions above 10% until after 540 min. With the lowest and highest dose of GAC (4 mg L^{-1} and 20 mg L^{-1}), for an initial simazine concentration of 0.7 mg L^{-1} and 24 h of contact, a reduction of 3% and 28% was achieved, respectively. When the time was increased to 7 days of contact, the percentages obtained were 38% and 96%, respectively. Therefore, adsorption treatments for simazine achieve better reduction performance against contact time when treated with Pulsorb PWX HA than with Calgon Filtrasorb 400.

In the oxidation experiments, for the lowest and highest dose of O_3 studied (5.6 mg L^{-1} and 24 mg L^{-1}), an initial simazine concentration of 0.7 mg L^{-1} and a contact time of 20 min, reduction percentages of 47% and 93% were achieved, respectively. O_3 oxidation achieves higher reduction percentages with less contact time than when treating with PAC and GAC, but the oxidation of simazine with O_3 generates a series of by-products with negative effects for the aquatic environment and the health of living beings.

With the combined AC/O_3 experiments, in order to achieve a simazine reduction greater than 90%, an average contact time of 38 min for PAC/O_3 and 3 days for GAC/O_3 was required.

Whilst in the experiments where the treatment was initiated with O_3 and terminated with PAC or GAC, the time was 40 min and 4 days, respectively. These differences are due to the fact that the application of O_3 generates a series of by-products that compete for the active center of the carbon, hindering the adsorption of simazine.

Both treatments are favorable for simazine reduction, taking into account the characteristics of the adsorbent or oxidant with the dose and contact time for each one. However, to achieve a reduction of more than 90% of simazine, any of the GAC combination treatments would not be optimal, since it requires a high treatment time due to the characteristics of the activated carbon, unless it increases the doses of GAC to achieve the adsorption of a greater number of simazine molecules in less time. The best combination treatment would be the one that uses PAC (PAC/O_3 and O_3/PAC). The O_3/PAC treatment is recommended, because the contact time to achieve a reduction of more than 90% of simazine is similar to that of PAC/$O_{3,}$ and, at the end of the treatment with activated carbon, the adsorption of the by-products of the ozonization of simazine would be achieved, avoiding the negative effects to the aquatic environment and the health of any living being.

In conclusion, the individual treatments studied to reduce simazine present in the water show to be effective, except for the treatment with GAC for its low reduction in short times, while for the combined treatments, the best option is the O_3/PAC reaching optimal reductions in low time. Considering that the concentration of the contaminant in this study (mg L^{-1}) is higher than the concentration detected in aquatic environments, and also that the maximum concentration of simazine allowed in drinking water in the European Union is 0.1 µg L^{-1}, the results obtained by the combined treatment O_3/PAC, allow us to propose that this could be a treatment to be considered for the reduction of simazine in natural water for human consumption.

For future researches, the study could be extended to other EOCs present in the aquatic environment and include real water to determine the effectiveness when other substances are also present in the water.

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