

Peroxydisulfate Activation by Carbon Materials for the Degradation of the Herbicide Ametryn in Waters

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ABSTRACT: Brazil, the largest global sugar cane producer, utilizes approximately 10 million hectares for cultivation. However, the increased use of agrochemicals in this industry raises concerns about environmental and human health impacts. Inclusive, ametryn (AMT), a pesticide intensively used in sugar cane plantations, has been detected in several water matrices at concerning levels, which evidences the urgent need for the development of technologies capable of removing this pesticide from the environment. This study investigated the removal efficiency of AMT from aquatic environments via oxidation promoted by persulfate (PS) activation mediated by carbon-based materials, such as graphene, carbon nanotubes, and activated carbon. Granular activated carbon (GAC) emerged as the most suitable material due to its clear catalytic role. A central composite design was used to evaluate and optimize the factors influencing AMT degradation and mineralization, revealing that the initial PS concentration and GAC dosage strongly impact the degradation rate and organic carbon removal in different directions. GAC was submitted to surface functionalization with N- and O-precursors to investigate how this impacts PS activation, and positive enhancements were noted with the latter, with a mineralization degree 9% superior. Experiments with real water matrices evidence the impact of other water constituents on the degradation rate of the target pollutant (k'_{300}), which was reduced by half when performed in groundwater. Notwithstanding, the system still demonstrated a consistent capacity to remove organic content, ranging from 60 to 50% $\text{TOC}_{\text{removal}}$, regardless of the water matrix, indicating that the system might be effective in real contamination scenarios. This research highlights the potential of GAC and its modified version for remediation of AMT-contaminated water remediation.

1. INTRODUCTION

Brazil is the largest sugar cane producer in the world, and according to a report published by UNICA in 2023, approximately 10 million hectares were solely dedicated to planting this crop in 2021.¹ The worldwide increasing demand for sugar and biofuels incentives the growth of sugar cane plantations, which is consequently followed by increased consumption of agrochemicals, thereby raising concerns regarding the potential environmental and human health impacts associated with these substances.

Among the pesticides utilized in sugar cane cultivation, ametryn (AMT) (4-*N*-ethyl-6-methylsulfanyl-2-*N*-propan-2-yl-1,3,5-triazine-2,4-diamine) is one of the most intensively employed. As a consequence, this pesticide has been frequently

detected in various aquatic environments at alarming concentrations. For instance, it has been found at a concentration of $0.3 \mu\text{g L}^{-1}$ in Australian surface waters,² $0.35 \mu\text{g L}^{-1}$ in groundwater samples in France,³ 207 ng L^{-1} in surface water in Mexico,⁴ and even as high as 168.3 mg L^{-1} in activated sludge from wastewater treatment plants.⁵ In Brazil,

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concentrations ranging from 2 to 2900 ng L⁻¹ have been detected in surface water.⁶

The high occurrence of AMT in the environment suggests that it is a persistent pollutant. In fact, it has already been reported that conventional water and wastewater treatment processes do not effectively eliminate triazine herbicides,⁶ which is a class to which AMT belongs. This highlights the need to implement new water treatment technologies capable of degrading this pollutant as a means to diminish environmental impacts associated with its presence in the aquatic environment. The scientific community has been making efforts in this sense. Physical removal processes, such as nanofiltration,^{6,7} reverse osmosis,⁶ and adsorption⁸ have been explored, although achieving almost complete AMT removal, these do not offer a definitive solution for the pollution cause, since AMT is only transferred from one medium (aqueous phase) to another (filtration membrane or adsorbent).

Several studies have explored the biodegradation of AMT using various microorganisms and microbial processes achieving remarkable AMT abatement results (>99.7%),⁹ but these processes are usually time-consuming, requiring a treatment period of days to obtain considerable pollutant removal rates.

Advanced oxidation processes (AOPs) are known for their capacity to degrade persistent pollutants from aqueous media since they involve the generation of highly reactive free radicals such as hydroxyl ($\bullet\text{OH}$) and sulfate ($\text{SO}_4^{\bullet-}$) radicals⁷ that attack a wide class of organic molecules, even those that are more resistant to conventional water treatment. Comparing physical and biological processes, AOPs present several advantages such as requiring less time to achieve high removal rates and not producing secondary waste. Some AOPs were already explored for the degradation of AMT, such as hydrogen peroxide activated by ultraviolet radiation (UV/H₂O₂ AOP)¹⁰ and heterogeneous photocatalysis using TiO₂ as a solid catalyst and solar light as an activator.¹¹ These are $\bullet\text{OH}$ -driven processes widely explored for the degradation of many persistent pollutants. More recently, $\text{SO}_4^{\bullet-}$ -driven processes have been preferred to $\bullet\text{OH}$ -driven ones due to some advantages of the former for practical application: the $\text{SO}_4^{\bullet-}$ lifespan is longer, potentially reaching longer distances and consequently promoting the degradation of more pollutants; $\text{SO}_4^{\bullet-}$ are more selective, thus being less likely to be attacked by other organic molecules present in the medium that decrease the process efficiency; cheaper reactants and less energy-consuming reactions are usually associated. The literature approaching these processes for AMT degradation is still scarce.¹²

In this sense, the main objective of this study was to investigate the removal of AMT from aquatic environments through a sulfate radical ($\text{SO}_4^{\bullet-}$)-based AOP. Persulfate (PS) ions can be activated in various ways, including temperature elevation, the employment of different catalysts (both metallic and nonmetallic), and UV radiation, among others.^{13,14} In this research, the potential of carbon-based catalysts was explored, including graphene, carbon nanotubes (CNTs), and activated carbon. Their metal-free nature, high availability, superior resistance, ultrahigh pore volumes, and large specific surface areas make carbon materials appealing alternatives to metal-based catalysts for PS activation. Although the activation mechanism is not completely demystified, the defects in hybrid sp²/sp³ structure and oxygen groups at the surface of carbonaceous catalysts are likely to be responsible for the

activation of PS, generating radicals such as sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\bullet\text{OH}$), and/or superoxide ion radicals ($\text{O}_2^{\bullet-}$),^{15,16} which are expected to degrade the target pollutant.

Among the three carbon materials tested, the best performing one in PS activation was then submitted to a more in-depth investigation in which its dosage was varied concurrently with PS concentration using an experimental design, with the goal of optimizing the degradation rate and mineralization of AMT. The same material underwent surface modification using nitrogen and oxygen precursors to enhance its catalytic activity^{17,18} and was tested under more suitable operating conditions identified in the experimental design. Moreover, the system was validated for practical application using AMT dissolved in real water matrices.

To the best of our knowledge, there are no records in the literature exploring this process for the elimination of AMT from waters; thus, this study brings practical advancements and opens up new opportunities for future research.

2. EXPERIMENTAL SECTION

2.1. Chemicals. AMT (analytical standard, C₉H₁₇N₃S, 227.3 g mol⁻¹) was purchased from Sigma-Aldrich; methanol (HPLC grade, CH₃OH) and sodium dihydrogen phosphate anhydrous (>99.7%, NaH₂PO₄) from VWR chemicals were used for HPLC analyses; sodium peroxydisulfate was also supplied by VWR chemicals (99.6%, Na₂S₂O₈); sodium sulfide (>98.5%, Na₂SO₃) was from Across.

Deionized water (18.2 MΩ cm from a Milli-Q Direct-Q system, Merck Millipore) was used in the experiments except when the effect of the water matrix was studied. For that, two other water matrices were tested, namely, bottled mineral water commercially obtained and groundwater collected from a Cartesian well. According to the information available by the supplier, the bottled mineral water has the following composition: Cl⁻ (10 mg·L⁻¹), HCO₃⁻ (11.2 mg·L⁻¹), Na⁺ (11 mg·L⁻¹), Ca²⁺ (5.6 mg·L⁻¹), SiO₂ (14 mg·L⁻¹), total dissolved solids/minerals (75 mg·L⁻¹), and pH = 6.14. The collected groundwater has the following composition: PO₄³⁻ (<0.0067 mg P·L⁻¹), NO₂⁻ (<0.012 mg NO₂⁻·L⁻¹), NO₃⁻ (33.04 mg NO₃⁻·L⁻¹), turbidity (0.1 NTU), conductivity (269 μS/cm), pH = 6.18, and total organic carbon (TOC) = 1.463 mg·L⁻¹.

Three carbon materials were used as catalysts in this study, namely, granular activated carbon (GAC) provided by Cabot (Norit GAC 1240 Plus M-2059), graphene nanoplatelets (GRAF) provided by Alfa Aesar, and CNTs (>95% C) provided by Nanocyl. Functionalization of carbon material surfaces with oxygen-containing groups was made using nitric acid (HNO₃, ≥65%) from Sigma-Aldrich and nitrogen-containing groups using urea [(NH₂)₂CO, 98%], and melamine (C₃H₆N₆, 98%, TCI Chemicals) from Thermo Scientific or melamine (C₃H₆N₆, 99%) from Aldrich.

2.2. Experimental Section. **2.2.1. Functionalization of Carbon Materials.** **2.2.1.1. Treatment with Nitric Acid.** The carbon material treated with HNO₃ was prepared according to the procedure detailed in Ramalho et al. (2023),¹⁷ with some adaptations, as follows: 4 g of carbon material was placed inside a 250 mL capacity Soxhlet. This was connected to a boiling flask and a condenser. The boiling flask consisted of a 500 cm³ Pyrex round-bottom flask containing 300 mL of 6 M HNO₃ that was heated until boiling. This system was kept in reflux for 3 h. Then, the treated carbon material was washed

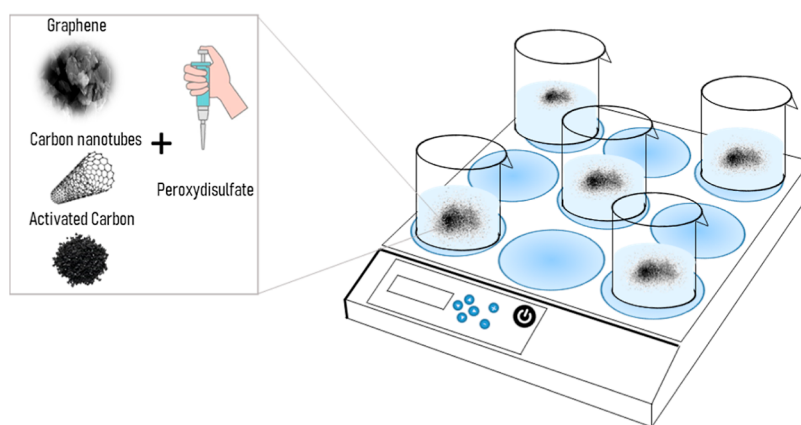


Figure 1. Scheme of the experimental apparatus.

with distilled water until a neutral pH and dried in an oven at 120 °C for 24 h.

2.2.1.2. Treatment with Urea. 0.5 g of carbon material was immersed in 100 mL of an aqueous solution of 1 M urea and kept under constant agitation for 24 h. After this period, the material was collected in filter paper (particle retention 5–13 μm , VWR, Germany) and left to dry in the oven. The material was then thermally treated in a vertical furnace under N_2 flow ($100 \text{ cm}^3 \cdot \text{min}^{-1}$). The temperature was elevated to 600 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and held at this temperature for 50 min. Then, the sample was cooled down to room temperature, also under a N_2 atmosphere, and stored. This procedure was adapted from Sousa, Pereira, and Figueiredo (2013).¹⁸

2.2.1.3. Treatment with Melamine. 2 g of carbon material was mixed with a melamine suspension (1.3 g of melamine in 100 mL of ethanol) and stirred at room temperature for 5 h. Then, the same procedure as that described for the treatment with urea was followed.

2.3. Characterization of the Carbon Samples. The textural characterization of the treated materials, namely, specific surface area, volume of pores, and pores diameter, was carried out through the nitrogen adsorption–desorption isotherms determined at $-196 \text{ }^\circ\text{C}$ with a Quantachrome Instruments Autosorb-iQ2 Series. The specific surface area of the mesopores (S_{meso}) and the volume of micropores (V_{micro}) were calculated by t-method using the appropriate standard isotherm, and the specific surface area was calculated by the BET method (S_{BET}). Additionally, the total volume of pores was extrapolated from a single point of the adsorption isotherm where $p/p_0 = 0.95$ ($V_{p/p_0=0.95}$).

2.4. AMT Degradation Experiments. Experiments were carried out in 250 mL beakers containing 100 mL of AMT solution ($20 \text{ mg} \cdot \text{L}^{-1}$), the catalyst, and PS at the desired doses. The beakers were placed onto a magnetic stirrer plate with multiple positions, in order to explore simultaneously different conditions. A scheme of this experimental apparatus can be seen in Figure 1. The reaction starts when the PS is added, and then 1 mL aliquots are withdrawn at determined times, for 300 min of reaction. To separate the catalyst from the solution, the aliquots were centrifuged in a MicroStar 12 centrifuge (VWR, Belgium) at $12,300 \text{ g}$ for 5 min (room temperature). Before doing so, the reaction was stopped in the Eppendorf containing the aliquot at the moment of sampling with 10% MeOH.⁴ It is worth mentioning that the laboratory where the experiments were performed was temperature controlled (~ 20

$^\circ\text{C}$) to avoid PS thermal activation¹⁵ and to guarantee the same experimental conditions in all experiments.

Initially, reactions were carried out with each of the three carbon catalysts that aimed to be studied (GRAF, GAC, or CNT). In these experiments, a fixed catalyst concentration of $0.5 \text{ g} \cdot \text{L}^{-1}$ was used, while the PS concentration was kept at $10 \text{ mmol} \cdot \text{L}^{-1}$. Experiments in the absence of PS were also performed to investigate the adsorption capacity of each catalyst. Some of these experiments were performed in duplicate, evidencing a maximum deviation of 2–3%, thus being only the average values reported in this study. Once the best catalyst was found, a more specific study was carried out with different concentrations of catalyst and PS, varied according to a central composite experimental design (CCD). This experimental design consists of a 2^2 factorial design, where the catalyst and PS are varied in two levels [catalyst ($\text{g} \cdot \text{L}^{-1}$) = (0.1; 1) and PS ($\text{mmol} \cdot \text{L}^{-1}$) = (10; 50)], with four additional star points. Three replicates of the central point ($0.53 \text{ g} \cdot \text{L}^{-1}$ catalyst and $30 \text{ mmol} \cdot \text{L}^{-1}$ PS) were used for statistical validation.¹⁹ The values of catalyst dosage and PS concentration that promoted the fastest AMT degradation (analyzed through the degradation rate constant $k'_{300, \text{min}^{-1}}$) and highest AMT mineralization (analyzed through the total organic carbon removal, $\text{TOC}_{\text{removal}}\%$) were optimized following a response surface methodology.¹⁹ The response surface graphics and models were obtained by using the STATISTICA 7.0 software.

The best operating conditions obtained from the analysis of the CCD were selected to perform further experiments with a functionalized catalyst and different water matrices. In these experiments, the catalyst dosage was kept as that found under the best conditions but replaced with the original catalyst by the functionalized versions. To explore the effect of water matrices, $20 \text{ mg} \cdot \text{L}^{-1}$ of AMT was added to the mineral or groundwater, while the $[\text{PS}]_0$ and catalyst dosages were kept in those found in the best conditions of the CCD.

2.5. Analytical Methods. AMT degradation was monitored by a high-performance liquid chromatography (HPLC) system (Hitachi Elite LaChrom) equipped with a C18 column (LiChroCART Purospher STAR RP-18, $250 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) and a diode array detector. An isocratic elution consisting of 70% methanol and 30% dihydrogen phosphate solution ($65 \text{ mmol} \cdot \text{L}^{-1}$, $\text{pH} = 2.8$), at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$, was used. The injection volume was $50 \mu\text{L}$ and the wavelength for AMT detection was set at 222 nm. This analytical method gave an

AMT retention time of 5.9 min; the limits of detection and quantification were 0.07 and 0.2 mg·L⁻¹, respectively.

The TOC was measured after immediate quenching with excessive NaNO₂ in a Shimadzu L-TOC total organic carbon analyzer, coupled to an ASI-L autosampler.

3. RESULTS AND DISCUSSION

3.1. Control Experiments with Different Carbon Catalysts: GAC, GRAF, and CNT. Control experiments were carried out in the presence and absence of PS to allow the distinction between the adsorption capacity and catalytic effect of each carbon material. A fixed amount of 0.5 mg of carbon material was used in these experiments. Control experiments in the absence of PS are presented in Figure 2. AMT adsorption

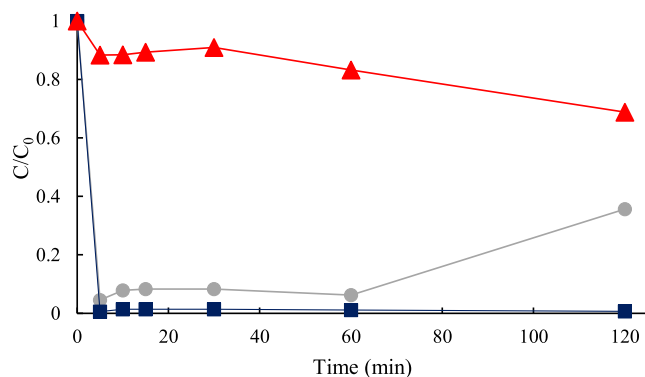


Figure 2. Adsorption experiments. [AMT]₀ = 20 mg·L⁻¹; [CNT ●] = [GRAF ■] = [GAC ▲] = 0.5 mg·L⁻¹.

profiles reveal that GRAF promotes immediate pollutant uptake, thus disabling distinguishing between adsorption and the catalytic effect of this material. CNT also reveals a similar profile up to 60 min, followed by apparent desorption of the pollutant. GAC reveals a slower and more gradual adsorption of AMT. These observations can be explained by the textural properties of the materials (Table 1). Although GRAF and

Table 1. Textural Properties of the Carbon Materials

sample	S_{BET} [m ² ·g ⁻¹] ± 5	S_{meso} [m ² ·g ⁻¹] ± 5	V_{micro} [cm ³ ·g ⁻¹]	$V_{p/p_0=0.95}$ [cm ³ ·g ⁻¹]
GRAF	427	273	0.064	0.485
CNT	250	250	0	0.500
GAC	958	117	0.367	0.480
GAC-M	585	118	0.249	0.376
GAC-U	724	195	0.214	0.383
GAC-HNO ₃	858	303	0.226	0.447

CNT present smaller specific surface areas (S_{BET}) than GAC, these present higher mesopores (S_{meso}), which is a feature that contributes more to the overall adsorption capacity. Pham et al. (2020)²⁰ also observed a similar behavior in acetaminophen adsorption when comparing CNT and GAC, and the authors justified that the larger pores of the former imply a faster adsorption rate, while the larger surface area of GAC enables adsorbing more quantity of pollutant in the long term.

When 10 mmol·L⁻¹ of PS is added to the AMT solution in the presence of these carbon materials, the AMT removal profile remains similar to that observed for GRAF and CNT in the adsorption experiments, except that in the latter, the removal stagnates right after 5 min until the end of the

experiment (120 min) at around 90% (Figure 3). Since the concentration did not change over time after 5 min for these

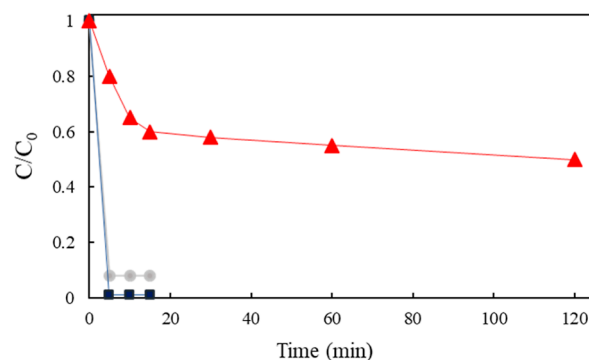


Figure 3. AMT removal in the presence of PS and CNT, GRAF, or GAC. [AMT]₀ = 20 mg·L⁻¹; [PS]₀ = 10 mmol·L⁻¹; [CNT ●] = [GRAF ■] = [GAC ▲] = 0.5 mg·L⁻¹.

experiments, subsequent measurements did not show any significant changes, not shown in the graph. This is not verified with GAC, since a faster degradation was observed, which can be attributed to the synergistic effect of the adsorption promoted by the material, the degradation promoted by PS alone, and the activation of PS promoted by GAC.²⁰ A graph comparing these three reactions can be found in the Supporting Information (Figure S1). Based on these observations, GAC was elected as the most appropriate material to perform further experiments regarding the study of reaction parameters for AMT degradation mediated by PS activation.

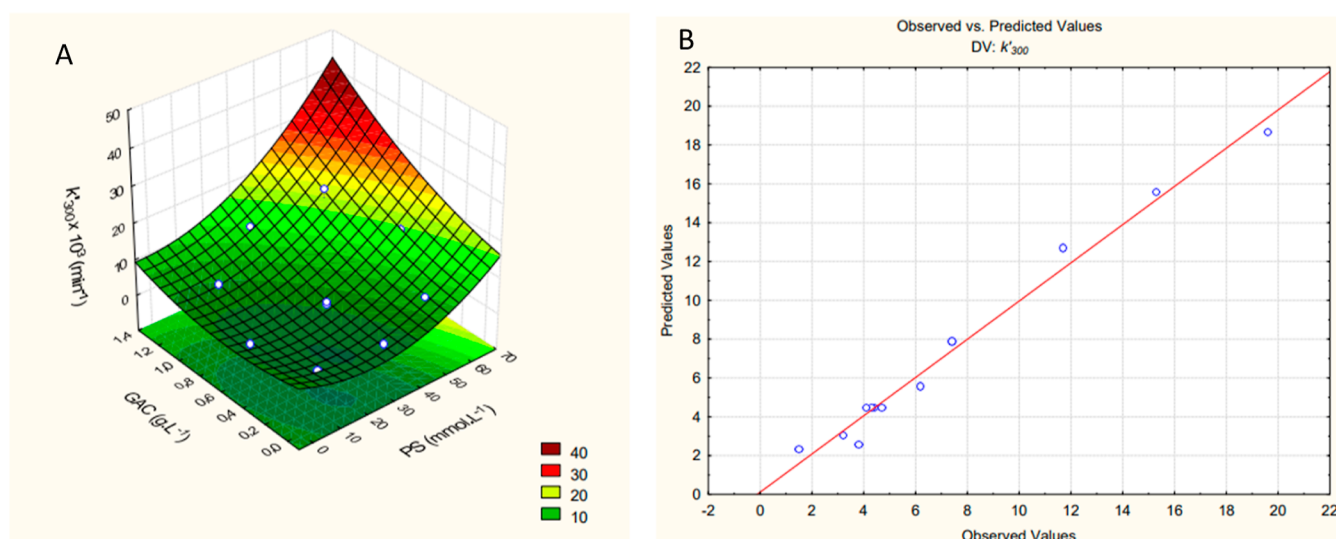
3.2. Characterization Results. Since GAC was selected as the carbon material to be employed in further experiments, modifications to GAC surface chemistry were performed with the aim of improving catalytic properties. Melamine (GAC-M) and urea (GAC-U) were the nitrogen precursors adopted for this purpose and nitric acid (GAC-HNO₃) for oxygen-containing groups since there is evidence in the literature that these are capable of introducing new active sites and improving the electron-transfer properties of carbon materials.^{17,18,21}

Table 1 shows the textural data of all the materials tested in this study, obtained from the N₂ adsorption–desorption isotherms at −196 °C. From the isotherms obtained, it can be concluded that the functionalized materials present characteristics of micro-mesoporous carbons.²² Also, it is clear that the treatments performed with the N-containing precursors lead to some changes in the textural properties of GAC. The specific surface area of the treated samples is lower than that of the original samples, which can be attributed to the new surface groups that may be blocking some pores of the material, thus impacting the penetration of N₂ during the measurement of the surface area. Similar observations were reported in other studies in which GAC was studied as the catalyst and modified with the same N-precursors.²³ However, the treatment with HNO₃ resulted in a material with a much larger area of mesopores (S_{meso}) (~3 times higher), which can be attributed to some unclogging action that the acid exerts during the oxidation treatment.

3.3. Insights into the Main Effects Influencing AMT Degradation through GAC-Mediated PS Activation: An Experimental Design Approach. A CCD is a useful

Table 2. Central Composite Design and Variable Levels Used to Study the Influence of $[\text{PS}]_0$ and GAC Dosage on the Degradation Rate Constant (k'_{300} , min^{-1}) and $\text{TOC}_{\text{removal}}$ (%)

run	codified levels		real variable levels		response variables	
	X_1	X_2	$[\text{PS}]_0$ ($\text{mmol}\cdot\text{L}^{-1}$)	GAC ($\text{g}\cdot\text{L}^{-1}$)	k'_{300} (min^{-1}) $\times 10^3$	$\text{TOC}_{\text{removal}}$ (%)
1	−1.41	0	1.8	0.5	3.20	38
2	0	0	30.0	0.5	4.40	32
3	0	0	30.0	0.5	4.30	23
4	−1	1	10.0	1.0	6.20	75
5	0	1.41	30.0	1.2	11.7	72
6	−1	−1	10.0	0.05	1.50	37
7	0	0	30.0	0.5	4.10	31
8	1	1	50.0	1.0	19.6	57
9	0	−1.41	30.0	0.0	3.80	0
10	1	−1	50.0	0.05	7.40	8
11	1.41	0	58.2	0.5	15.3	21
12	0	0	30.0	0.5	4.70	34

**Figure 4.** (A) Response surface and (B) observed vs predicted values for the k'_{300} (min^{-1}).

experimental design for evaluating the influence of the reaction parameters. This tool was then selected to study the influence of PS initial concentration ($\text{mmol}\cdot\text{L}^{-1}$) and GAC dosage ($\text{g}\cdot\text{L}^{-1}$) on AMT degradation, which corresponds to the codified factors X_1 and X_2 in Table 2, respectively. These two factors were first varied between a maximum (codified level “1” in Table 2) and a minimum level (codified level “−1” in Table 2), which corresponds to 10 and 50 $\text{mmol}\cdot\text{L}^{-1}$ for PS and 0.05 and 1 $\text{g}\cdot\text{L}^{-1}$ for GAC, respectively. It is important to bear in mind that the PS concentration range explored in this study was selected to allow a measurable pollutant abatement within the experiment period (300 min), but caution has to be made when working with such solutions. According to a recent study, the remaining PS can convert into sulfate and H_2S , which is a highly toxic gas and poses a threat to human health.²⁴ Therefore, it is of great importance to follow proper disposal protocols for solutions containing PS residues.

CCD also involves conducting experiments at the vertices and center of a multidimensional response surface (illustrative representation can be found in Supporting Information, Figure S2) to allow the evaluation of both linear and quadratic effects of the factors on the response, as well as the interactions between variables. The vertices or axial points are equidistant from the central point and are nominated as α , which can be

calculated as $\alpha = \pm \sqrt{k}$, where k represents the number of factors. Hence, in the present study, as there are two factors, the value of α is $\pm\sqrt{\pm 2} = \pm 1.41$. The combination of the highest and lowest levels of each variable, plus the axial points and four replicates at the central point for statistical validation, gives a total of 12 experiments. The codified levels were converted into real variable levels, according to the following expressions²⁵

$$\text{real level} = b \times \text{codified level} + a \quad (1)$$

where

$$a = \frac{\text{maximum real level} + \text{minimum real level}}{2} \quad (2)$$

and

$$b = \frac{\text{maximum real level} - \text{minimum real level}}{2} \quad (3)$$

Considering k'_{300} as the response variable, it can be verified in Table 2 that the values of this variable increase as both $[\text{PS}]_0$ and GAC increase, reaching their highest value on run 8, where PS and GAC are on high levels (codified as “1”), 50 $\text{mmol}\cdot\text{L}^{-1}$ and 1 $\text{g}\cdot\text{L}^{-1}$, respectively. Effects of variables with p -values higher than 0.05 are considered significant; thus, from the

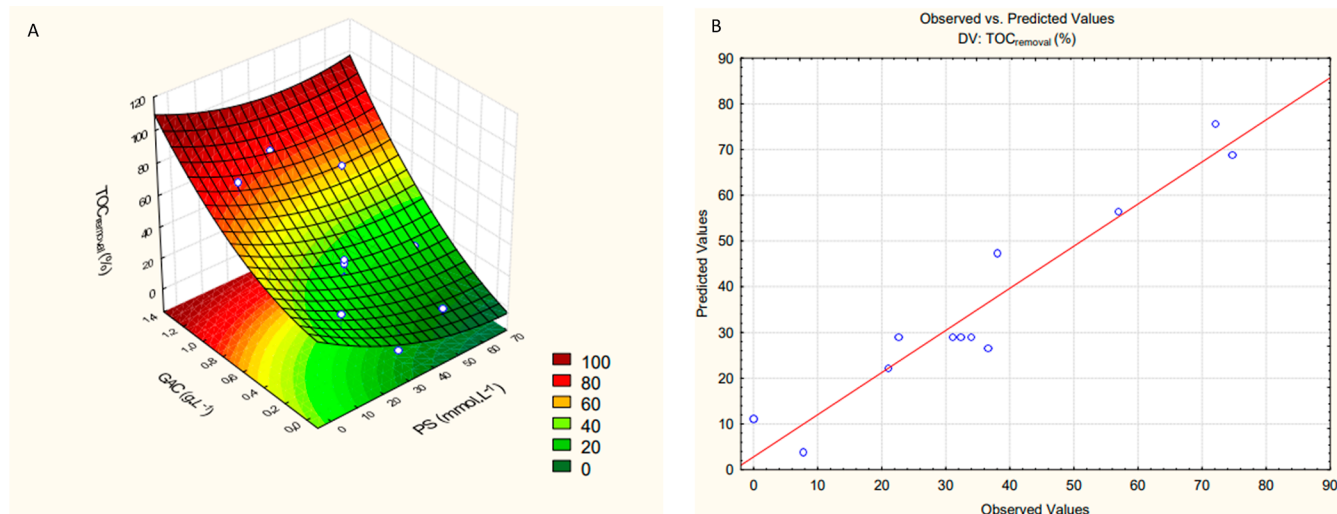


Figure 5. (A) Response surface and (B) observed vs predicted values for the $\text{TOC}_{\text{removal}}$ (%).

Pareto chart (Supporting Information, Figure S3) generated from the analysis of variance (ANOVA, Table S1 of the Supporting Information), it can be stated that all the effects are significant, especially the linear effects of $[\text{PS}]_0$ and GAC, since these present higher coefficients. All of the effects have positive coefficient values, indicating that their increment implies an increase of k'_{300} . The quadratic model that describes the behavior of k'_{300} as a function of $[\text{PS}]_0$ and GAC is presented in eq 3 and the corresponding response surface is in Figure 4A. Figure 4B shows the correlation between the observed and predicted values of the model, and as can be verified, these are very close, indicating an accurate fitting of the model to the experimental data. The accuracy is also confirmed by the model determination coefficient, R^2 , which is 0.984. The model adequacy can be evaluated using the Fisher test, following the methodology described in Souza et al. (2019).¹⁹ According to these authors, the model is considered statistically significant if the regression F -value is greater than the tabulated F -value. The first can be obtained by the analysis of variance (ANOVA) of the model, and the latter can be consulted in the F distribution table for a significance level of 0.05, knowing the degrees of freedom of the regression and residual sum of squares (ANOVA, Table S1, Supporting Information). Based on this, it can be concluded that the model described by eq 4 for the response variable k'_{300} is statistically significant. From this model, a minimum value (inflection point of the response surface, Figure 4A), which has coordinates $[\text{PS}]_0 = 17.3 \text{ mmol}\cdot\text{L}^{-1}$ and $\text{GAC} = 0.14 \text{ g}\cdot\text{L}^{-1}$. A maximum or optimal response cannot be determined, since k'_{300} always increases with increasing $[\text{PS}]_0$ and GAC.

$$k'_{300} (\text{min}^{-1}) = 4.5 - 0.24 \cdot \text{PS} + 0.006 \cdot \text{PS}^2 - 5.82 \cdot \text{GAC} + 6.63 \cdot \text{GAC}^2 + 0.21 \cdot \text{GAC} \cdot \text{PS} \quad (4)$$

Considering the $\text{TOC}_{\text{removal}}$ (%) as the response variable, only the linear effects of PS and GAC are significant (p -value > 0.05), with a positive coefficient for GAC, as can be verified in the Pareto chart depicted in Figure S2 of the Supporting Information. Analyzing the data from Table 2, it can be stated that higher TOC removals were obtained in runs using high levels of GAC, namely, runs 4, 5, and 8, which can be justified by the higher pollutant uptake promoted by increasing loads of sorbent. In run 9, no TOC removal was observed, which

corresponds to a run in the absence of GAC. This indicates that $30 \text{ mmol}\cdot\text{L}^{-1}$ of PS alone, although promoting a slow decomposition of AMT, is not capable of mineralizing the pollutant in 300 min, which was predictable since usually the oxidant needs to be activated in order to obtain significant mineralization results.²⁶ Fixing a GAC dosage and increasing the PS concentration, the TOC removal always decreases, as can be verified from runs 4 to 8, or 6 to 10, and justifies the negative coefficient of the linear effect of PS. The faster AMT degradations observed in these cases are indicative of a higher generation of $\text{SO}_4^{\bullet-}$, but this is not necessarily followed by a TOC decrease because the strong oxidizing power of the $\text{SO}_4^{\bullet-}$ can break down the carbon–carbon bonds in the GAC, resulting in the release of smaller organic molecules and thus contributing to the overall TOC value. Therefore, the best operating conditions are those that enable a fast AMT degradation with a simultaneous considerable TOC removal, which can be accomplished in the conditions of run 8. Notwithstanding, the predicted values of $\text{TOC}_{\text{removal}}$ (%) from the model computed by STATISTICA (Figure 5B) can be considered close to the experimental data and also its accuracy can be confirmed by the R^2 , which is equal to 0.92. The expression that describes this model is shown in eq 5. From this and also by the analysis of the response surface (Figure 5A), a minimum value but not a maximum can be verified, similar to what was verified for k'_{300} . The evaluation of the model adequacy by the Fisher test shows that the model can be considered both statistically significant and predictive (Table S2 of Supporting Information). Given these observations together with what was verified for k'_{300} , the conditions of run 8 were selected as the most adequate and therefore adopted to continue the investigation with modified GAC.

$$\text{TOC}_{\text{removal}} (\%) = 35.04 - 1.01 \cdot \text{PS} + 0.007 \cdot \text{PS}^2 + 14.73 \cdot \text{GAC} + 25.7 \cdot \text{GAC}^2 + 0.27 \cdot \text{PS} \cdot \text{GAC} \quad (5)$$

3.4. Experiments with Modified GAC. The commercially obtained GAC was functionalized with N- and O-precursors as an attempt to improve the catalytic activity, namely, with urea (GAC-U), melamine (GAC-M), and HNO_3 (GAC- HNO_3), according to the procedure detailed in Section 2.2.1. AMT degradation experiments employing these new materials were carried out in the conditions of run 8, i.e., using $50 \text{ mmol}\cdot\text{L}^{-1}$

of $[PS]_0$ and $1 \text{ g}\cdot\text{L}^{-1}$ of catalyst. Results of k'_{300} and $\text{TOC}_{\text{removal}}$ obtained for these experiments are presented in Table 3. An

Table 3. First-Order Reaction Kinetic Constants (k'_{300}) and TOC Removal (%) for AMT Degradation Reactions Using Modified GAC for PS Activation

material	$k'_{300} (\text{min}^{-1}) \times 10^3$	$\text{TOC}_{\text{removal}} (\%)$
GAC-M	6.5	28
GAC-HNO ₃	19.0	66
GAC-U	8.7	43
none (only PS)	5.5	5

experiment in the absence of a catalyst (only $50 \text{ mm}\cdot\text{L}^{-1}$ of PS) was performed for control purposes, and compared to run 9 of the CCD (Table 2), an increment on k'_{300} and TOC removal is observed. This indicates that above a certain PS concentration, the oxidant alone can oxidize AMT within the duration of the experiments. The direct oxidation of pollutants with PS, i.e., without involving radicals, was already reported in the literature, which occurs mainly by hydroxylation mechanisms.²⁷ Comparing the k'_{300} and TOC removal values of modified GACs with those of neat GAC (run 8, Table 2), it can be verified that GAC-M and GAC-U revealed poorer performances, while the performance of GAC-HNO₃ can be considered quite close in terms of k'_{300} , but superior in terms of $\text{TOC}_{\text{removal}}$ (9% superior). Adsorption experiments using $1 \text{ g}\cdot\text{L}^{-1}$ of each catalyst reveal that the TOC removal after 300 min is higher than that observed in the presence of PS (Table S3 of Supporting Information), except for GAC-HNO₃. This means that neat GAC, GAC-M, and GAC-U release organic carbon in the presence of PS; otherwise, the TOC removal would be higher when both compounds are mixed. In the case of GAC-HNO₃, the higher TOC removal indicates a symbiotic effect when this catalyst is mixed with PS, confirming that this modification on GAC really improved its capacity to activate PS. The textural property of GAC-HNO₃ that stands out is the S_{meso} , indicating that the acid treatment created more pores, and consequently, increased the reactive area. This means that GAC-HNO₃ is likely to have more active sites for interactions with PS and AMT, which justifies the greater oxidative efficiency. The surface chemistry of this material can also be a key feature behind these results, since GAC-HNO₃ is expected to present a higher content in oxygen-containing surface groups than raw GAC and GAC modified with N-precursors,^{17,21} which are known to be active sites for sulfate radicals generation.^{26–29}

Given that, GAC-HNO₃ can be an interesting material to explore in further studies, evolving PS activation for water remediation.

3.5. Effect of Water Matrix. Different water matrices were tested in order to verify the influence of constituents of real matrices in the removal of AMT promoted by the PS activation with neat GAC. Results of k'_{300} (min^{-1}) and $\text{TOC}_{\text{removal}}$ (%) for these experiments are depicted in Figure 6. It is possible to observe a more pronounced difference between k'_{300} (min^{-1}) than between $\text{TOC}_{\text{removal}}$ (%). Mineral water used in these experiments is mostly rich in HCO_3^- , which is a well-known radical scavenger²⁸ and justifies the performance loss observed in this matrix for the AMT degradation rate (from $19.6 \times 10^{-3} \text{ min}^{-1}$ in Milli-Q water to $14.1 \times 10^{-3} \text{ min}^{-1}$ in mineral water). Another study dealing with heterogeneous PS activation with different carbon-based catalysts also observed a great

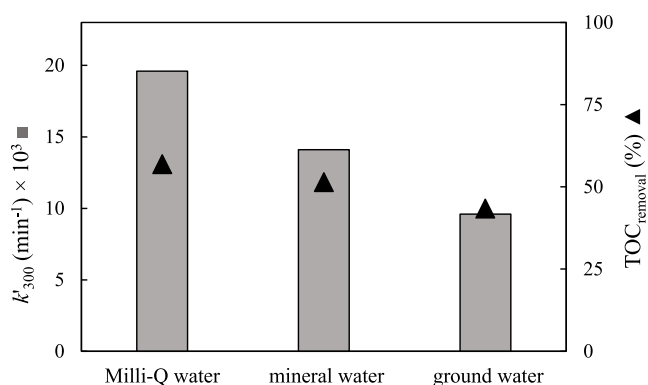


Figure 6. k'_{300} (min^{-1}) (gray column, left axis) and $\text{TOC}_{\text{removal}}$ (%) (black triangle, right axis) values for experiments in different water matrices. $[\text{AMT}] = 20 \text{ mg}\cdot\text{L}^{-1}$; $[\text{PS}]_0 = 50 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{GAC}] = 1 \text{ g}\cdot\text{L}^{-1}$, with free pH.

quenching effect of HCO_3^- in the degradation rate of the target pollutant, independently of the origin of the catalyst.³⁰ Similarly, groundwater presents a high value of conductivity, which indicates a significant presence of salts, justifying the decrease in the k'_{300} for the same reason indicated for mineral water. Moreover, this water matrix also presents some dissolved organic matter ($1.4 \text{ mg}\cdot\text{L}^{-1}$) and a significant amount of nitrate ($33 \text{ mg NO}_3^-\cdot\text{L}^{-1}$), that are known to compete with the target pollutant for sulfate radicals.^{31,32} Regarding the TOC removal, this is not so affected by the other water constituents that are mostly inorganic matter since the greatest part of the TOC that is removed is due to adsorption; thus, the other contribution from AMT degradation does not significantly affect the overall TOC decrease. Notwithstanding, these results indicate that it is possible to apply this process in AMT-contaminated waters with a high content of salts, bearing in mind a slower degradation of the contaminant, requiring adjustment of the reaction parameters.

4. CONCLUSIONS

In this study, carbon materials were explored as metal-free alternatives for PS activation in the degradation of AMT. Among GAC, CNT, and GRAF, the former was revealed to be more suitable for a more detailed study to investigate the influence of reaction parameters on the degradation (k'_{300} , min^{-1}) and mineralization ($\text{TOC}_{\text{removal, \%}}$) of AMT through a CCD approach. Results indicated that although $[\text{PS}]_0$ and GAC dosages are variables with significant impact in both k'_{300} (min^{-1}) and $\text{TOC}_{\text{removal}}$ (%), their increase does not always benefit both responses, since above a certain concentration of PS, the GAC surface starts releasing carbon, which is an undesired feature. Thus, the selection of the most appropriate operation conditions relied on those that simultaneously enabled a high k'_{300} (min^{-1}) and considerable $\text{TOC}_{\text{removal}}$ (%), which were considered those of the run using $50 \text{ mmol}\cdot\text{L}^{-1}$ of $[\text{PS}]_0$ and $1 \text{ g}\cdot\text{L}^{-1}$ of GAC with 0.02 min^{-1} and 57%, respectively. These conditions were selected to perform further investigations using modified GAC and real water matrices. GAC was modified using N- and O-precursors, such as urea, melamine, and nitric acid, the latter being the only one that promoted an increase in the GAC performance, especially in the capacity to mineralize the pollutant, reaching up to 66% organic carbon abatement. Regarding the experiments with real water matrices, it can be concluded that the system reveals the

capacity to degrade AMT both in mineral and groundwater, although at a slower rate due to the impact of other water constituents, especially the inorganic content. Given that, this research demonstrates that neat GAC and its modified version with HNO_3 can be promising alternatives to activate PS for the remediation of AMT-contaminated waters.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07479>.

Additional experimental data including the AMT degradation profile promoted by GAC and PS separately and together, schematic representation of the experimental design, Pareto charts for k'_{300} (min^{-1}) and TOC, ANOVA table for k'_{300} (min^{-1}) and TOC responses, and table comparing the AMT adsorption promoted by each GAC catalyst alone (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) UNICA. Sugarcane Industry Overview, 2023. Retrieved from <https://unica.com.br/>.
- (2) Burman, L.; Albertsson, A.-C.; Höglund, A. Solid-phase microextraction for qualitative and quantitative determination of migrated degradation products of antioxidants in an organic aqueous solution. *J. Chromatogr. A* **2005**, *1080* (2), 107–116.
- (3) Babut, M.; Mieg, C.; Villeneuve, B.; Abarnou, A.; Duchemin, J.; Marchand, P.; Narbonne, J. F. Correlations between dioxin-like and indicators PCBs: Potential consequences for environmental studies involving fish or sediment. *Environ. Pollut.* **2009**, *157* (12), 3451–3456.
- (4) Salvatierra-Stamp, V. d. C.; Ceballos-Magaña, S. G.; Gonzalez, J.; Jurado, J. M.; Muñoz-Valencia, R. Emerging contaminant determination in water samples by liquid chromatography using a monolithic column coupled with a photodiode array detector. *Anal. Bioanal. Chem.* **2015**, *407*, 4661–4670.
- (5) Albuquerque, A. F. A.; Mozeto, A. A.; Ferreira, F. Occurrence and spatial distribution of pesticides in surface water of the Northeast of São Paulo State, Brazil. *Environ. Sci. Pollut. Res.* **2016**, *23* (19), 19559–19568.
- (6) Shurvell, T.; Keir, G.; Jegatheesan, V.; Shu, L.; Farago, L. Removal of ametryn through nanofiltration and reverse osmosis. *Desalin. Water Treat.* **2014**, *52* (4–6), 643–649.
- (7) Ma, R.; Xie, Y.; Xia, S.; Xu, B.; Dong, B.; Gao, N. Ametryn removal with nanofiltration membranes. *Desalin. Water Treat.* **2011**, *29* (1–3), 331–335.
- (8) Farre, M. J.; Mas, M. C.; Santos, F. J.; Barcelo, D. Removal of triazine pesticides from aqueous samples by activated carbon. *Anal. Chim. Acta* **2002**, *466* (2), 279–289.
- (9) Zhu, J.; Fu, L.; Jin, C.; Meng, Z.; Yang, N. Study on the Isolation of Two Atrazine-Degrading Bacteria and the Development of a Microbial Agent. *Microorganisms* **2019**, *7* (3), 80.
- (10) Gao, N.-Y.; Deng, Y.; Zhao, D. Ametryn degradation in the ultraviolet (UV) irradiation/hydrogen peroxide (H_2O_2) treatment. *J. Hazard. Mater.* **2009**, *164* (2–3), 640–645.
- (11) Cavalcante, R. P.; Oliveira, D. M.; Silva, L. M.; Giménez, J.; Esplugas, S.; Oliveira, S. C.; Dantas, R. F.; Sans, C.; Machulek, A. Evaluation of the main active species involved in the TiO_2 photocatalytic degradation of ametryn herbicide and its by-products. *J. Environ. Chem. Eng.* **2021**, *9* (2), 105109.
- (12) Zhang, D.; An, Z.; Zhang, Y.; Hu, Y.; Zhan, J.; Zhou, H.; Wu, M. $\text{MoS}_2/\text{SiO}_2$ enhanced persulfate oxidation for the degradation of triazine herbicides in fixed-bed reactor. *J. Water Proc. Eng.* **2023**, *52*, 103523.
- (13) Farré, M. J.; Domènech, X.; Peral, J.; Domènech, X.; Peral, J. Pesticide elimination from water by advanced oxidation processes (AOPs). *J. Hazard. Mater.* **2006**, *129* (1–3), 80–87.
- (14) Haobo, T.; Mingfu, C.; Qi, F. An analysis of aerosol liquid water content and related impact factors in Pearl River Delta. *Sci. Total Environ.* **2017**, *579*, 1822–1830.
- (15) Joe, J.; Bae, C.; Kim, E.; Ho, T. A.; Yang, H.; Park, J. H.; Shin, H. Mixed-Phase (2H and 1T) MoS_2 Catalyst for a Highly Efficient and Stable Si Photocathode. *Catalysts* **2018**, *8* (12), 580.
- (16) Huang, W.; Xiao, S.; Zhong, H.; Yan, M.; Yang, X. Activation of persulfates by carbonaceous materials: A review. *Chem. Eng. J.* **2021**, *418*, 129297.
- (17) Ramalho, P. S. F.; Soares, O. S. G. P.; Figueiredo, J. L.; Pereira, M. F. R. Catalytic reduction of NO over copper supported on activated carbon. *Catal. Today* **2023**, *418*, 114044.
- (18) Sousa, J. P. S.; Pereira, M. F. R.; Figueiredo, J. L. Catalytic oxidation of NO to NO_2 on N-doped activated carbons. *Catal. Today* **2011**, *176* (1), 383–387.
- (19) Souza, L. P.; Graça, C. A. L.; Taqueda, M. E. S.; Teixeira, A. C. S. C.; Chiavone-Filho, O. Insights into the reactivity of zero-valent-copper-containing materials as reducing agents of 2,4,6-trichlorophenol in a recirculating packed-column system: Degradation mechanism and toxicity evaluation. *Process Saf. Environ. Prot.* **2019**, *127*, 348–358.

- (20) Pham, V. L.; Kim, D.; Ko, S. Advanced oxidative degradation of acetaminophen by carbon catalysts: Radical vs non-radical pathways. *Environ. Res.* **2020**, *188*, 109767.
- (21) Ternero-Hidalgo, J. J.; Rosas, J. M.; Palomo, J.; Valero-Romero, M. J.; Rodríguez-Mirasol, J.; Cordero, T. Functionalization of activated carbons by HNO₃ treatment: Influence of phosphorus surface groups. *Carbon* **2016**, *101*, 409–419.
- (22) Thommes, M.; Kaneko, K.; Neimark, A.; Olivier, J.; Rodríguez-Reinos, F.; Rouquerol, J.; Sing, K. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (9–10), 1051–1069.
- (23) Graça, C.; Zema, R.; Orge, C. A.; Restivo, J.; Sousa, J.; Pereira, M. F. R.; Soares, O. S. G. P. Temperature and nitrogen-induced modification of activated carbons for efficient catalytic ozonation of salicylic acid as a model emerging pollutant. *J. Environ. Manage.* **2023**, *344*, 118639.
- (24) Long, Y.; Wu, Z.; Ding, X.; Chen, J.; Shen, D.; Shentu, J.; Hui, C. Potential risks of organic contaminated soil after persulfate remediation: Harmful gaseous sulfur release. *Environ. Sci.* **2024**, *135*, 1–9.
- (25) Bhattacharya, S. Central Composite Design for Response Surface Methodology and Its Application in Pharmacy. *Response Surface Methodology in Engineering Science*; IntechOpen, 2021.
- (26) Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517.
- (27) Lee, J.; von Gunten, U.; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* **2020**, *54* (6), 3064–3081.
- (28) Rodrigues, C. S. D.; Aziz, S. N. A.; Pereira, M. F. R.; Soares, O. S. G. P.; Madeira, L. M. Degradation of p-Nitrophenol by activated persulfate with carbon-based materials. *J. Environ. Manage.* **2023**, *343*, 118140.
- (29) Forouzesh, M.; Ebadi, A.; Aghaeinejad-Meybodi, A. Degradation of metronidazole antibiotic in aqueous medium using activated carbon as a persulfate activator. *Sep. Purif. Technol.* **2019**, *210*, 145–151.
- (30) Ribeiro, R. S.; Frontistis, Z.; Mantzavinos, D.; T Silva, A. M.; Faria, J. L.; Gomes, H. T. Screening of heterogeneous catalysts for the activated persulfate oxidation of sulfamethoxazole in aqueous matrices. Does the matrix affect the selection of catalyst? *J. Chem. Technol. Biotechnol.* **2019**, *94*, 2425–2432.
- (31) Lutze, H. V.; Kerlin, N.; Schmidt, T. C. Sulfate radical-based water treatment in presence of chloride: formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and influence of bicarbonate. *Water Res.* **2015**, *72*, 349–360.
- (32) Behnami, A.; Aghayani, E.; Benis, K. Z.; Sattari, M.; Pourakbar, M. Comparing the efficacy of various methods for sulfate radical generation for antibiotics degradation in synthetic wastewater: degradation mechanism, kinetics study, and toxicity assessment. *RSC Adv.* **2022**, *12* (23), 14945–14956.