

Article

Thermal- and MnO_2 -Activated Peroxydisulfate for Diuron Removal from Water

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Abstract: In this work, a peroxydisulfate (PDS)-based advanced oxidation process was used for removing diuron from water. The effect of heat and MnO_2 as PDS activators was explored. It was found that diuron degradation obeyed zero-order kinetics in the presence of heat-activated PDS. The relative contribution of MnO_2 to the diuron degradation decreased with the increasing temperature. At the highest temperature investigated, $T = 55^\circ\text{C}$, complete diuron removal was achieved in less than 75 min. A kinetic model for describing the rate of diuron degradation was proposed and successfully applied to the experimental data.

Keywords: advanced oxidation processes; AOPs; persulfate; peroxydisulfate; MnO_2 ; diuron; heat activation; thermal activation; heterogeneous catalysis; homogeneous catalysis



Citation: Fenti, A.; Minò, A.; Salvestrini, S. Thermal- and MnO_2 -Activated Peroxydisulfate for Diuron Removal from Water. *Clean Technol.* **2022**, *4*, 1071–1087. <https://doi.org/10.3390/cleantechnol4040065>

Academic Editors: Mahmood Reza Karimi Estahbanati and Mohammad (Mim) Rahimi

Received: 14 September 2022

Accepted: 17 October 2022

Published: 19 October 2022

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1. Introduction

In recent years, removing toxic pollutants from impacted water has become a worldwide priority [1]. Among the emerging contaminants, herbicides are a class of compounds widely detected in various water bodies and used as selective inhibitors of plant growth in both agriculture applications and urban utility management [2–4]. Diuron [N-(3,4-dichlorophenyl)-N, N-dimethylurea] (see Figure 1) is a broad-spectrum phenyl urea herbicide widely used worldwide as an antifouling agent which can inhibit photosystem II and even lead to the photodestruction of pigments [5]. This compound is chemically stable and persistent in the environment, with a half-life that varies depending on the degradation route [6,7]. According to the contaminant candidate list 3 of the USEPA 2009 and the priority substance list in European Parliament Directive 2013/39/EU, diuron is classified as a carcinogenic and genotoxic compound for human beings, possibly causing kidney illness, anemia, and potential endocrine disorders.

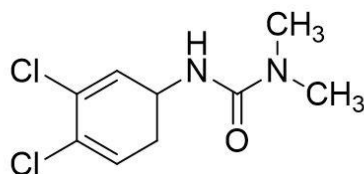


Figure 1. Diuron chemical structure.

The development of effective methods to remove diuron from water is gaining interest from the scientific community since its contamination of water bodies is currently a serious issue. Conventional treatments, such as biological processes, are generally ineffective and

not recommended for removing phenyl urea herbicides from aqueous media [8,9]. The remediation of water contaminated by diuron can be accomplished through different methods including adsorption [10–12], coagulation [13], nanofiltration [14], and reverse osmosis [15]. However, each treatment technique has advantages and drawbacks in terms of capital and operational costs, efficiency, user friendliness, pre-treatment requirements, environmental implications, production of sludge, and possible generation of toxic by-products.

Among the alternative methods, advanced oxidation processes (AOPs) are being widely investigated to remove diuron and other organic contaminants from water [16–19]. AOPs leverage the in situ generation of highly reactive oxidizing species (ROS), including hydroxyl radicals ($\text{OH}^\bullet$), sulfate radicals ($\text{SO}_4^{\bullet-}$), and ozone (O_3), which can chemically attack and destroy organic pollutants in solution [20,21]. Recently, sulfate radicals have gained rising attention as adequate oxidants in the chemical oxidation of organics due to their unique properties [22]. $\text{SO}_4^{\bullet-}$ has good stability in water, is low-cost, has a longer lifetime in solution than other oxidizing species, and is non-selective towards organic compounds [23,24], attacking both saturated and unsaturated bonds [25,26]. Moreover, $\text{SO}_4^{\bullet-}$ has proven to be very reactive with target compounds under a wide range of pH, between 2.0 and 8.0. In general, $\text{SO}_4^{\bullet-}$ can be generated by the activation of two main precursors, namely peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) [27]. The generation of $\text{SO}_4^{\bullet-}$ from PMS and PDS occurs via O-O bond cleavage, a process which requires an activator agent. PMS has a shorter O-O (1.453 Å) bond than PDS (1.497 Å), resulting in a higher bond energy (213 kJ mol⁻¹ vs. 140 kJ mol⁻¹). Consequently, PDS may be more readily broken down (by a catalyst) to generate $\text{SO}_4^{\bullet-}$ [28–30]. Moreover, PMS is less stable than PDS and may decompose to SO_5^{2-} [29]. Notably, PDS cannot directly oxidize organics, but as mentioned above, it requires an activator agent to produce sulfate radicals. Various energy-based and electron transfer-based methods are employed for PDS activation, such as light and UV radiation [31,32], transition metal-based catalysts [33–35], alkali [36], and organic acids [37]. Among them, heat activation is a solid and efficient method to activate PDS due to its high $\text{SO}_4^{\bullet-}$ formation rate and simple reaction process. In recent years, many studies have widely reported on herbicides' degradation (including diuron, simazine, thiamethoxam, and atrazine) using the thermal-activated PDS process [38–41]. The main drawback of thermal activation is its high energy demand. For this reason, the use of appropriate catalysts in combination with heat has recently attracted the attention of researchers for PDS activation, allowing to operate at lower temperatures and thus reducing the energy costs [42].

Among the different catalysts, MnO_2 is promising owing to its efficiency and low environmental impact [43]. MnO_2 [44,45] and PDS [38] alone have been investigated in the past for the oxidative removal of diuron from water. However, to our knowledge, very little is known about the combined effect of heat, MnO_2 , and PDS on diuron's reactivity.

Based on the above considerations, the aim of the present study was to explore the degradation of diuron in water by MnO_2 – and heat-activated persulfate. Diuron reactivity was monitored via HPLC and the oxidation efficiency was evaluated by TOC analysis. A kinetic model was proposed to explain the observed rate of diuron degradation.

2. Materials and Methods

2.1. Reagents

All chemicals, including diuron and MnO_2 , were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. MnO_2 Analysis

Milli-Q water dispersions of MnO_2 (0.6, 1.2, 1.8, and 2.4 g L⁻¹) were prepared and placed in an ultrasonic water bath (Ultrasons P-Selecta, Barcelona, Spain) for 1 min. Afterwards, dynamic light scattering (DLS) and electrophoretic mobility measurements were carried out to determine the average hydrodynamic diameter, the polydispersity index (PDI), and the ζ -potential values of the samples using a Malvern UK Zetasizer-Nano ZS90

commercial instrument operating with a 4 mW He-Ne laser at a wavelength of 633 nm. The average size and the PDI values were estimated with a fixed detector angle of 90° by cumulant analysis of the autocorrelation function. ζ -potential values were obtained by determining the electrophoretic mobility of the aggregates via laser Doppler velocimetry. The detection angle was 17°. All measurements were performed at 25 °C and in triplicate.

The specific surface area (SSA) of MnO₂ was determined using the methylene blue (MB) adsorption method [46]. In brief, ten milliliters of MB aqueous solution (concentration range 3–50 µM) was added to 1 mg of MnO₂ in polypropylene vessels (to avoid glass container adsorption) and agitated at 30 rpm and 25 °C until the attainment of the adsorption equilibrium. Afterwards, the samples were centrifuged at 3000 rpm for 10 min and analyzed spectrophotometrically at 665 nm for MB concentration determination. The amount of MB adsorbed at equilibrium per mass of MnO₂, $q_{MB,e}$ (mol g^{−1}), was evaluated using the following expression:

$$q_{MB,e} = \frac{C_{MB,0} - C_{MB,e}}{m} V \quad (1)$$

where $C_{MB,0}$ and $C_{MB,e}$ are the concentrations of MB before contact with the adsorbent and at equilibrium (mol L^{−1}), respectively, and m and V represent the mass of MnO₂ (g) and the volume of the liquid phase (L), respectively.

The SSA (expressed in mol g^{−1}) was obtained with the following equation:

$$SSA = q_{MB,max} N_A \quad (2)$$

where $q_{MB,max}$ is the maximum adsorption capacity of MnO₂ for MB, N_A is the Avogadro number, and A is the surface area occupied per molecule of MB (130 Å²).

2.3. Diuron Degradation Experiments

Diuron degradation experiments were conducted using the batch method (see Figure 2).

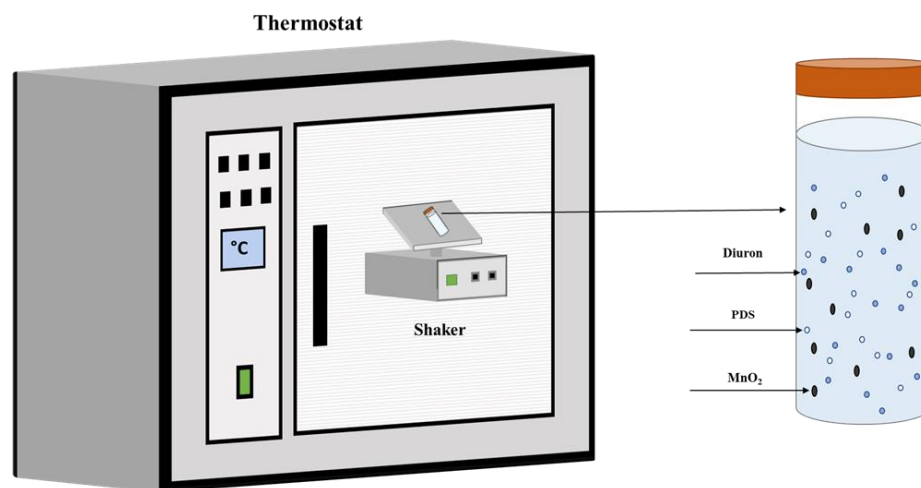


Figure 2. Diuron experiments apparatus.

Ten milliliters of Milli-Q water containing 67 µM diuron was contacted with 45 mg of PDS and/or 24 mg of MnO₂. The samples were then placed on a shaker at 30 rpm agitation speed and thermostated at 30, 37, 45, and 55 °C. At selected reaction times, a small aliquot of supernatant was collected and analyzed by HPLC-UV using a Waters instrument consisting of a 515 pump system and a 2487 dual-λ detector. Diuron was eluted on a C18 reverse-phase column, and its concentration was monitored at 248 nm with a 64% CH₃CN/36% H₂O isocratic method and a flow rate of 1 mL min^{−1}.

The residual total organic carbon (TOC) was determined at the end of the experiments using a TOC meter analyzer (3S Analyzers, Avegno (GE), Italy) equipped with a non-dispersive infrared detector for CO₂ counting.

3. Results and Discussion

3.1. MnO₂ Characterization

The results of the size distribution and ζ -potential measurements of MnO₂ samples are displayed in Figure 3. As can be seen, the average hydrodynamic diameter, the PDI, and the surface charge for MnO₂ (0.6 g L⁻¹) turned out to be 175.2 ± 4.0 nm, 0.314 ± 0.037 , and -35.3 mV, respectively. The size distribution and the PDI of MnO₂ did not vary appreciably with MnO₂ dosage, whereas the surface charge increased only slightly with increasing the metal oxide content. These results suggest that MnO₂ is stable and does not aggregate in solution.

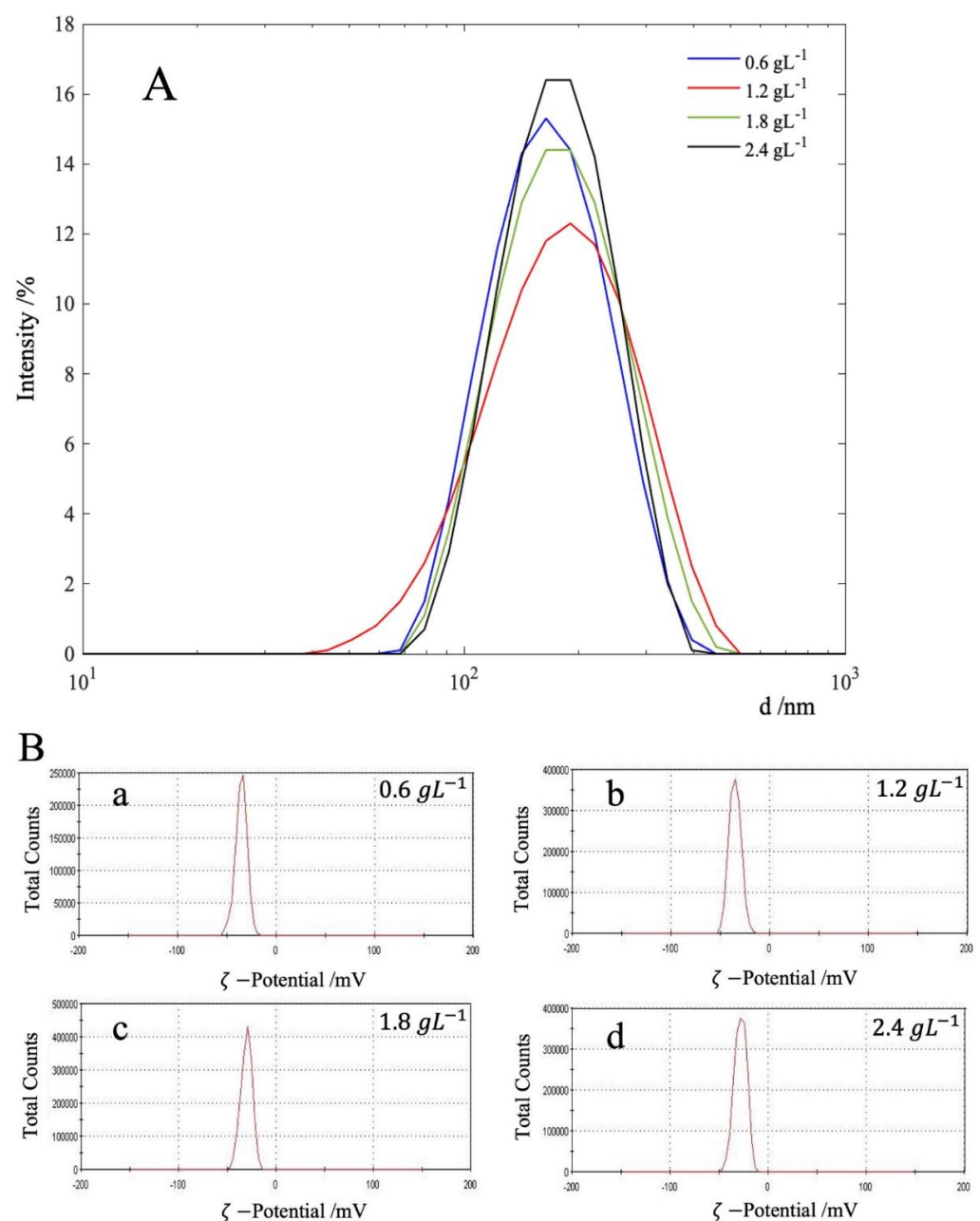


Figure 3. Cont.

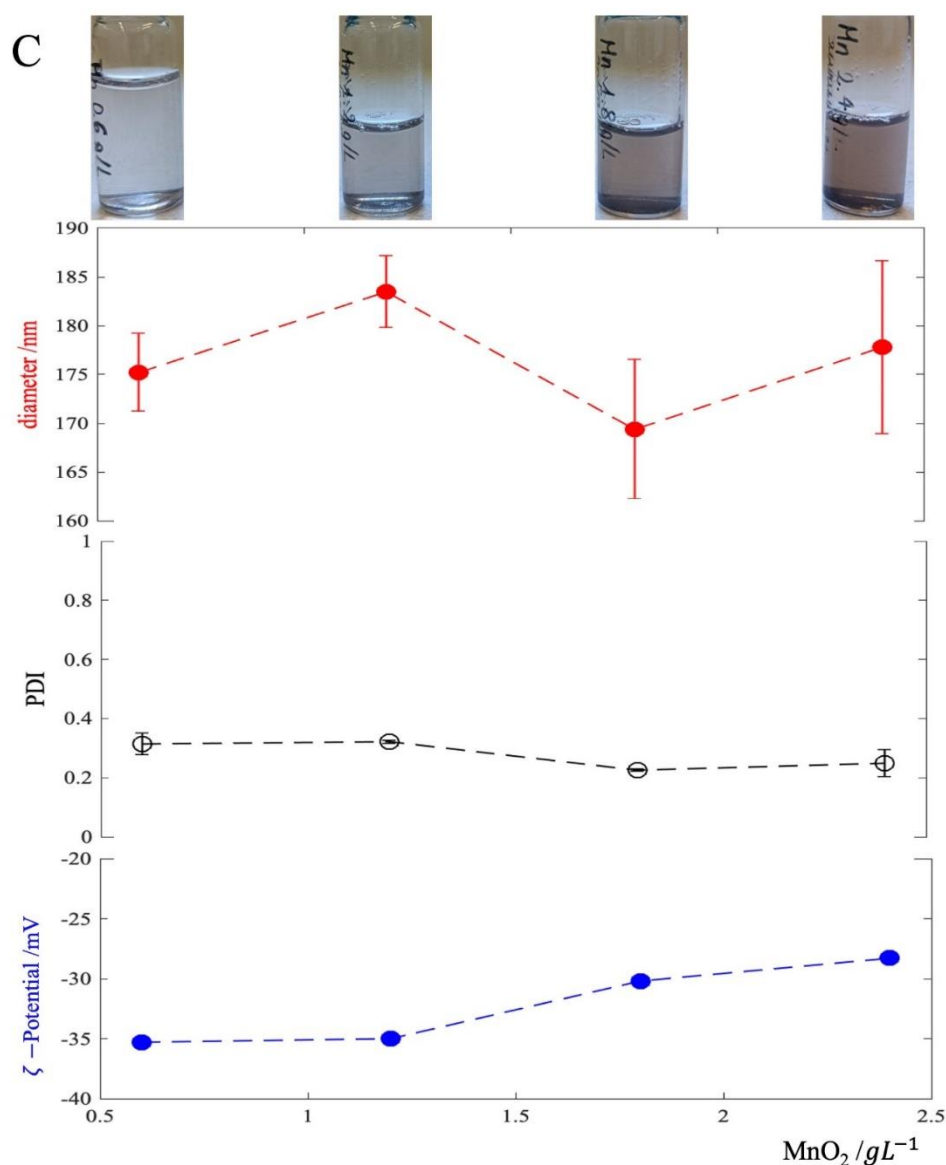


Figure 3. (A) Size distributions and (B) ζ -potential values of MnO₂ samples at different concentrations: 0.6 (a), 1.2 (b), 1.8 (c), and 2.4 (d) g L⁻¹. (C) Average hydrodynamic diameter (red full dots), PDI (empty black dots), and ζ -potential values (blue full dots) of MnO₂ samples at different MnO₂/water dosages.

The MB adsorption isotherm onto MnO₂ is shown in Figure 4. In order to obtain information on the maximum adsorption capacity of MnO₂ for MB ($q_{MB,max}$), the data in the figure were modeled by using the Langmuir model [47]:

$$q_{MB,e} = q_{MB,max} \frac{K_L C_{MB,e}}{1 + K_L C_{MB,e}} \quad (3)$$

where K_L represents the Langmuir equilibrium constant. The obtained $q_{MB,max}$ value was $23 \pm 1 \mu\text{mol g}^{-1}$. As a result, the specific surface area (SSA) of MnO₂ turned out to be $18 \pm 1 \text{ m}^2 \text{ g}^{-1}$.

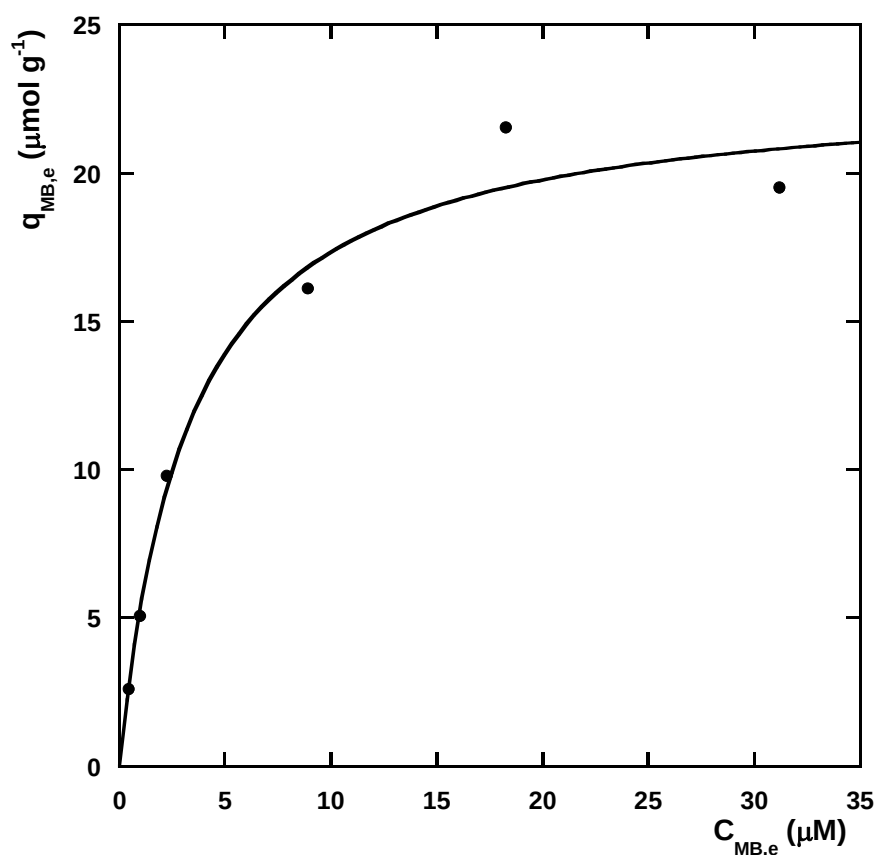


Figure 4. Adsorption isotherm of MB onto MnO_2 .

3.2. Diuron Degradation Kinetics

3.2.1. Effect of the Presence of MnO_2

Figure 5 shows the effect of MnO_2 on the diuron degradation kinetics at different temperatures. Control experiments without MnO_2 and PDS revealed that diuron was stable in solution at all the temperatures investigated (data not shown). Conversely, in the presence of MnO_2 , a moderate decrease in the diuron liquid phase concentration was observed. Interestingly, the effect of the temperature was negligible, and all the kinetic profiles approached the same limit value in about 50 min. In addition, the reacted diuron did not undergo mineralization since the organic carbon content at the end of the experiments was, within the experimental errors, the same as that of the initial reaction time, as determined by TOC analysis. The low reactivity of diuron found in the present work contrasts with the results of Jing et al. [45], according to which MnO_2 , in similar experimental conditions, promoted an almost complete degradation of diuron in less than 250 min.

3.2.2. Effect of the Presence of PDS

Figure 6 shows the effect of the presence of PDS on the diuron degradation kinetics. The diuron concentration apparently decreased by following a linear trend. A significant effect of temperature on the diuron degradation rate was observed. At the highest temperature investigated, $T = 55^\circ\text{C}$, complete diuron degradation, with a mineralization degree of $\approx 83\%$ (TOC analysis), was achieved in less than 75 min. The residual organic content in the reacted mixture might be ascribed to the presence of oxidation intermediates such as 2-chloro-4-((((3,4-dichlorophenyl)amino)oxy)(dimethylamino)methyl)amino)phenol, 2-((((3-chloro-4-hydroxyphenyl) amino) (((3,4-dichlorophenyl)amino)oxy)methyl)(methyl)amino) acetic acid, and 2,2'-((((3-chloro-4-hydroxyphenyl)amino) (((3,4-dichlorophenyl)amino)oxy)methyl)azanediyl)diacetic acid [38].

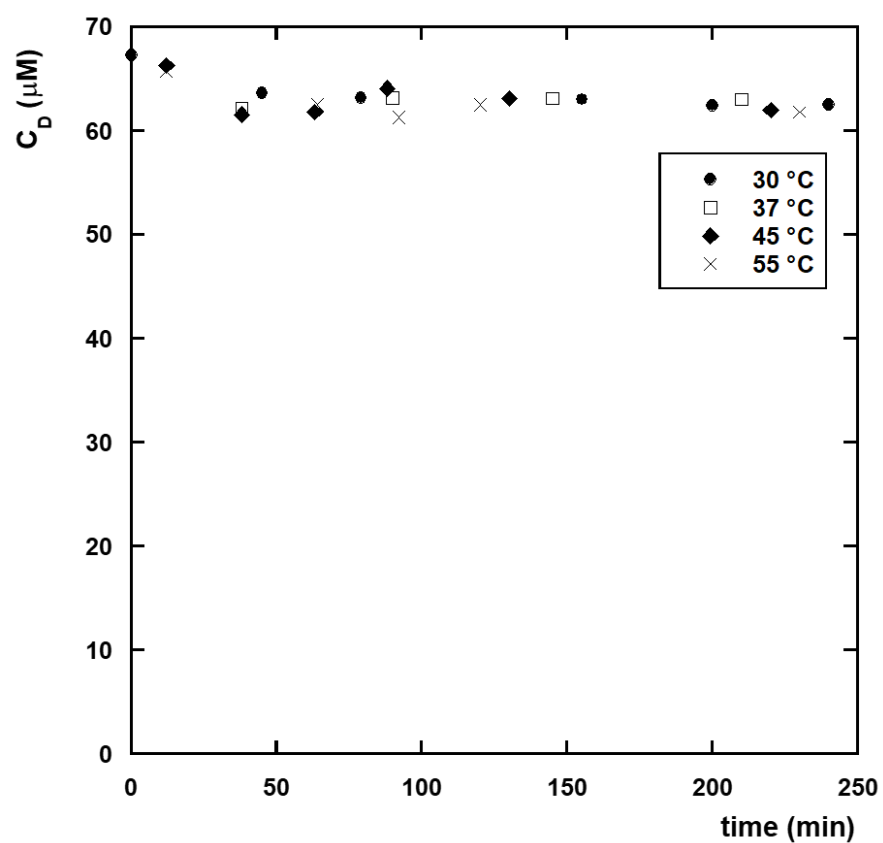


Figure 5. Diuron degradation kinetics profiles in the presence of MnO_2 (2.4 g L⁻¹) at different temperatures; initial pH = 4.3.

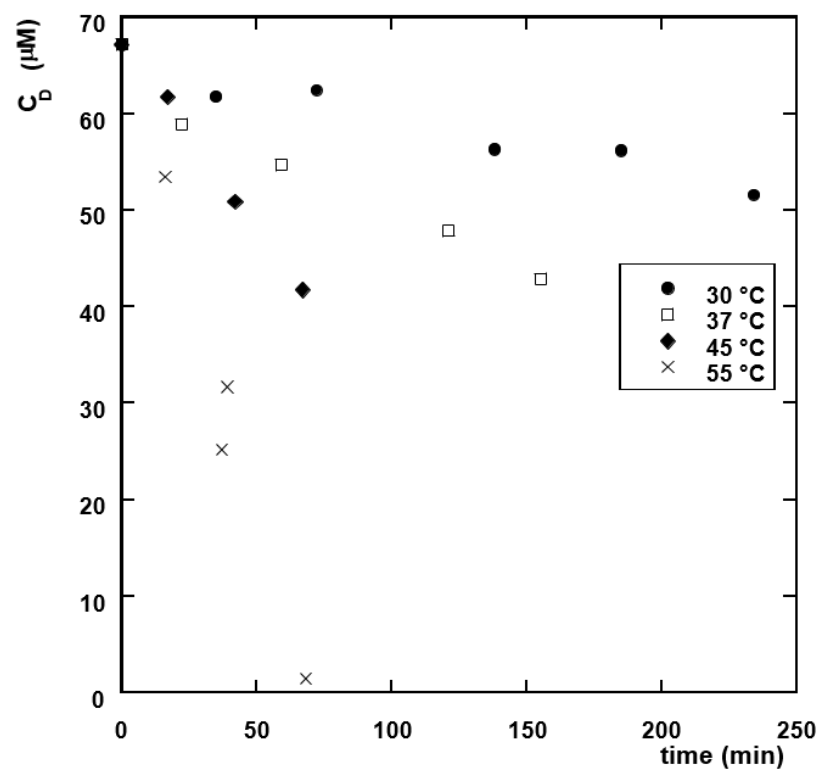


Figure 6. Diuron degradation kinetics profiles in the presence of PDS (4.5 g L⁻¹) at different temperatures; initial pH = 3.8.

3.2.3. Effect of the Co-Presence of MnO₂ and PDS

The diuron degradation kinetics in the co-presence of MnO₂ and PDS at various temperatures are reported in Figure 7. For comparison purposes, Figure 8 shows the diuron degradation kinetics at 30 °C in the co-presence of MnO₂ and PDS and in the presence of MnO₂ and PDS alone. A significant effect of the co-presence of MnO₂ and PDS on diuron degradation was observed at the lowest temperature (T = 30 °C), whereas at higher temperatures, the effect was almost negligible. In line with the latter result, the mineralization degree in the PDS+MnO₂ samples at the end of the experiments at 55 °C was virtually the same (83%) as that of the samples containing PDS only.

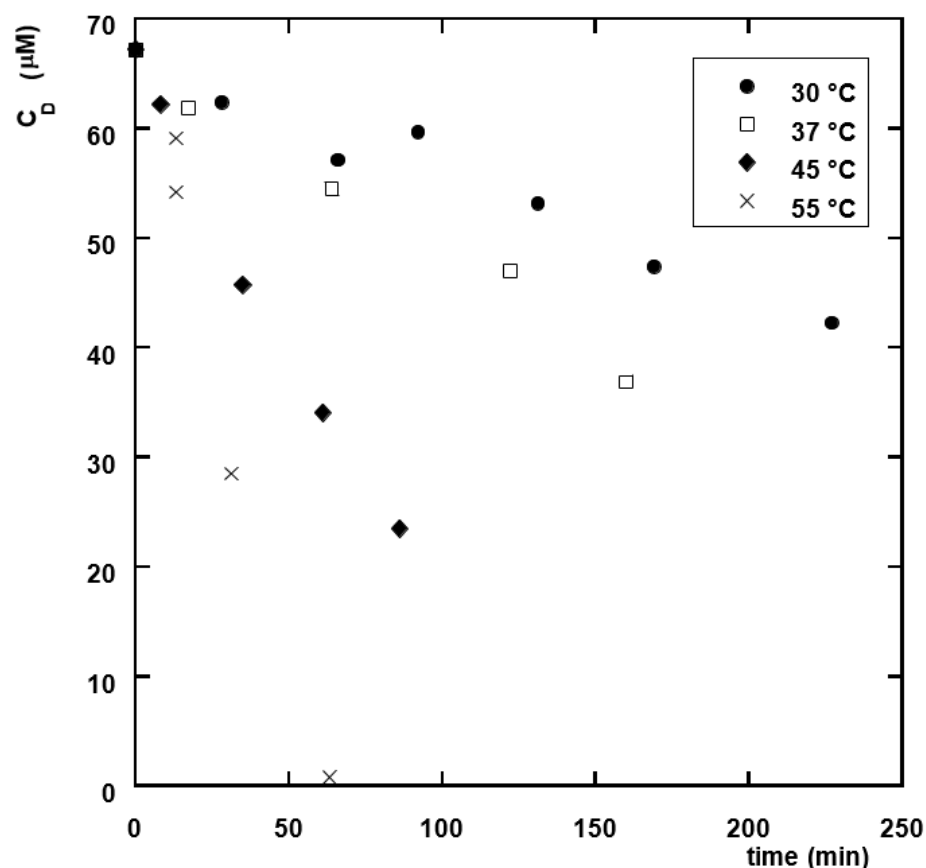


Figure 7. Diuron degradation kinetics profiles in the co-presence of MnO₂ (2.4 g L^{−1}) and PDS (4.5 g L^{−1}) at different temperatures; initial pH = 3.6.

3.2.4. Kinetic Modeling

As has been shown in Figure 6, the diuron concentration linearly decreased over time, thus suggesting that the reaction obeys zero-order kinetics. This result is in contrast with the findings of Tan et al. [38], who claimed that diuron decomposition exhibited pseudo-first-order kinetics. Zero-order kinetics behavior can be explained by considering that the active radicals generated by heat activation of PDS have a very short life and that their concentration in steady state is very low, resulting in a constant consumption of diuron over time [48].

Based on the above considerations, the rate (v_P) of diuron degradation mediated by heat-activated PDS can be expressed as follows:

$$v_P = \frac{dC_D}{dt} = -k_P \quad (4)$$

where k_p is the kinetic rate constant. By integrating Equation (4), we obtain the following:

$$C_D = -k_p t + C_{D,0} \quad (5)$$

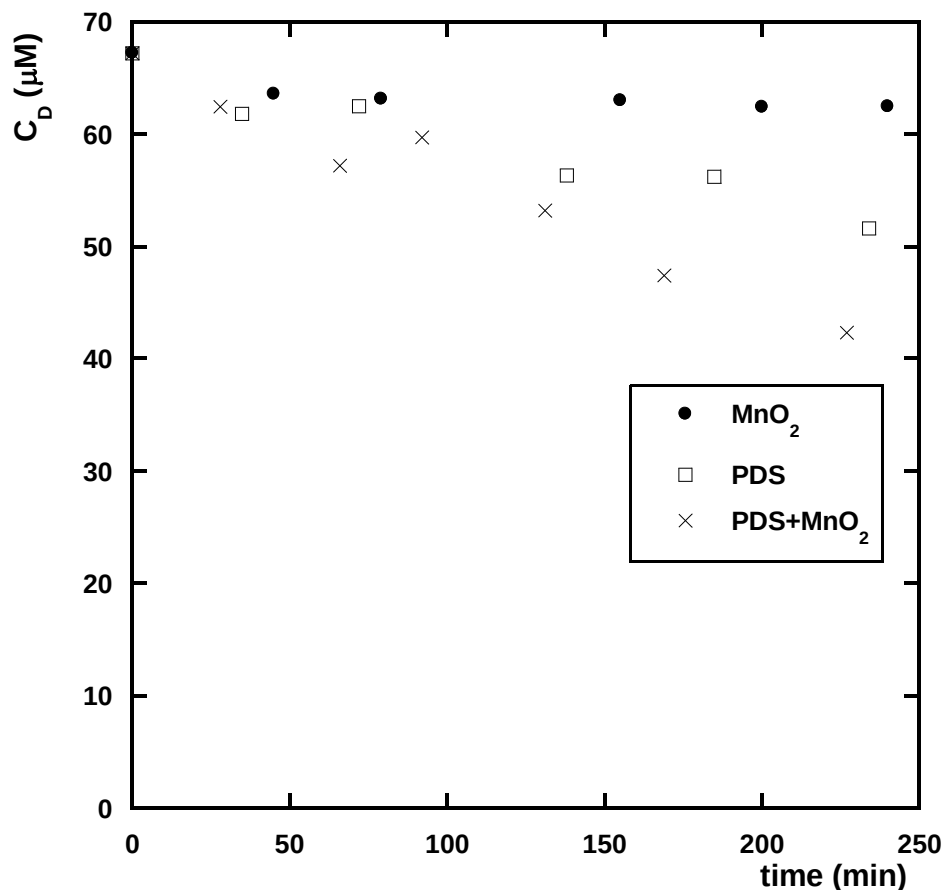


Figure 8. Diuron degradation kinetics profiles in the presence of MnO_2 (2.4 g L^{-1}), in the presence of PDS (4.5 g L^{-1}), and in their co-presence; $T = 30^\circ \text{C}$.

Figure 9 and Table 1 show the results of the application of Equation (5) to the kinetic data of diuron degradation by heat-activated PDS. As can be seen, Equation (5) adequately describes the kinetic data trend. The estimated values of k_p were used in the Arrhenius equation (Equation (6)) to determine the activation energy (E_a) of the process by using a non-linear weighted least squares method [49]:

$$k_p = A e^{-\frac{E_a}{RT}} \quad (6)$$

where A ($\mu\text{M min}^{-1}$) is the pre-exponential Arrhenius constant and T (K) is the absolute temperature.

Table 1. Kinetic parameters of diuron degradation.

T (K)	k_M ($\mu\text{M}^{-1} \text{ min}^{-1}$)	k_p ($\mu\text{M min}^{-1}$)	k_p' ($\mu\text{M min}^{-1}$)
303.15	$(7.9 \pm 3.9) \times 10^{-4}$	$(5.98 \pm 0.79) \times 10^{-2}$	$(7.20 \pm 0.17) \times 10^{-2}$
310.15	$(7.9 \pm 3.9) \times 10^{-4}$	$(14.1 \pm 1.8) \times 10^{-2}$	$(13.6 \pm 0.1) \times 10^{-2}$
318.15	$(7.9 \pm 3.9) \times 10^{-4}$	$(38.7 \pm 1.3) \times 10^{-2}$	$(48.9 \pm 12.4) \times 10^{-2}$
328.15	$(7.9 \pm 3.9) \times 10^{-4}$	$(103 \pm 14) \times 10^{-2}$	$(109 \pm 14) \times 10^{-2}$

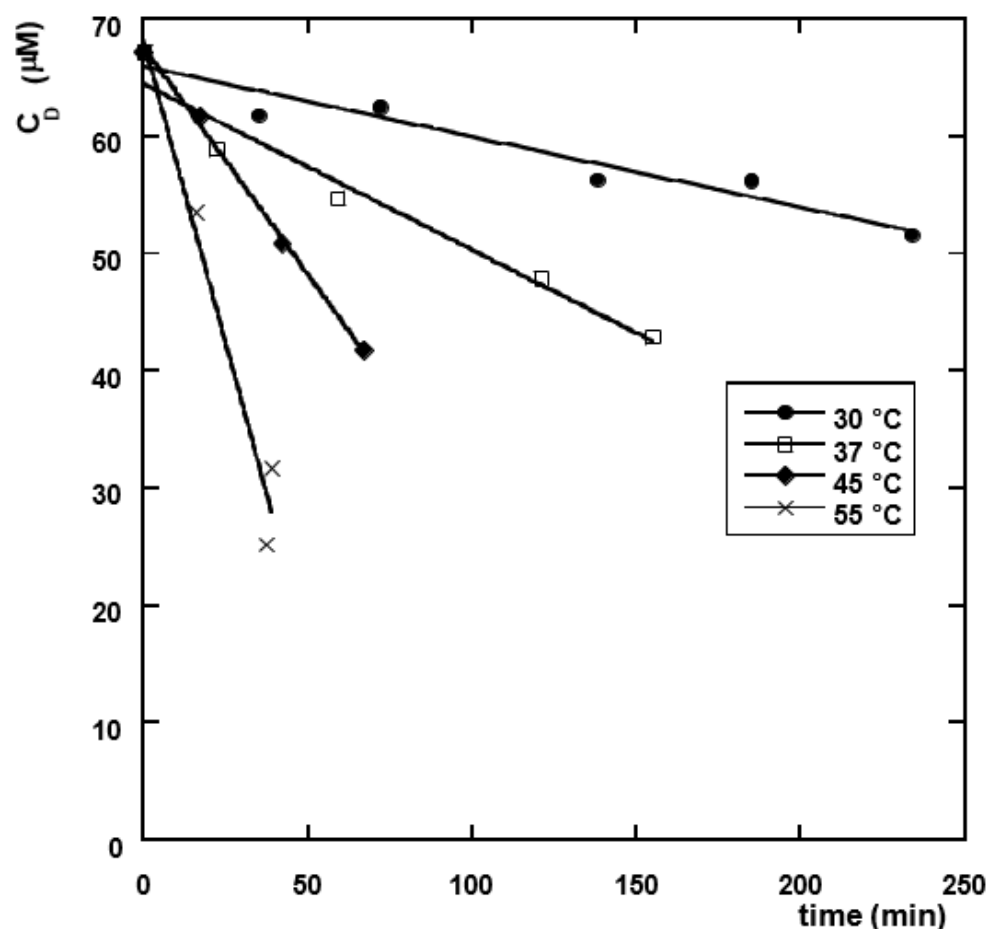


Figure 9. Diuron degradation kinetics profiles in the presence of PDS (4.5 g L^{-1}) at different temperatures modeled by using a zero-order kinetics equation (Equation (5)).

The results of the application of the Arrhenius law are displayed in Figure 10.

The calculated E_a turned out to be $82 \pm 5 \text{ kJ mol}^{-1}$. This value is approximately half of the value obtained by Tan et al. in their work [38].

In the presence of MnO_2 , the rate of diuron degradation was expected to be negatively affected by pore diffusion inside the metal oxide domain [50]. For this reason, kinetic models accounting for the diffusion phenomenon [47,51] were preliminary tested on the experimental data. The results (data not shown) revealed that the effect of diffusion on the degradation rate was negligible, thus suggesting that surface reaction might play a leading role in the oxidation kinetics. Based on the above considerations, the rate of diuron degradation in the presence of MnO_2 (v_M) can be assumed to be proportional to the concentration of diuron in the solution (C_D) and of MnO_2 (C_{MnO_2}):

$$v_M = \frac{dC_D}{dt} = -k_M C_D C_{\text{MnO}_2} \quad (7)$$

where k_M is the kinetic rate constant in the presence of MnO_2 .

As stated before, only a very small decrease in C_D was observed during the reaction (see Figure 5), which allows us to reasonably assume v_M to be independent of the diuron concentration (i.e., $C_D \approx C_{D,0}$). Under this assumption, Equation (7) reduces to pseudo-first-order kinetics in C_{MnO_2} :

$$v_M = \frac{dC_D}{dt} = -k_M C_{D,0} C_{\text{MnO}_2} \quad (8)$$

where $C_{D,0}$ is the initial diuron concentration in the liquid phase.

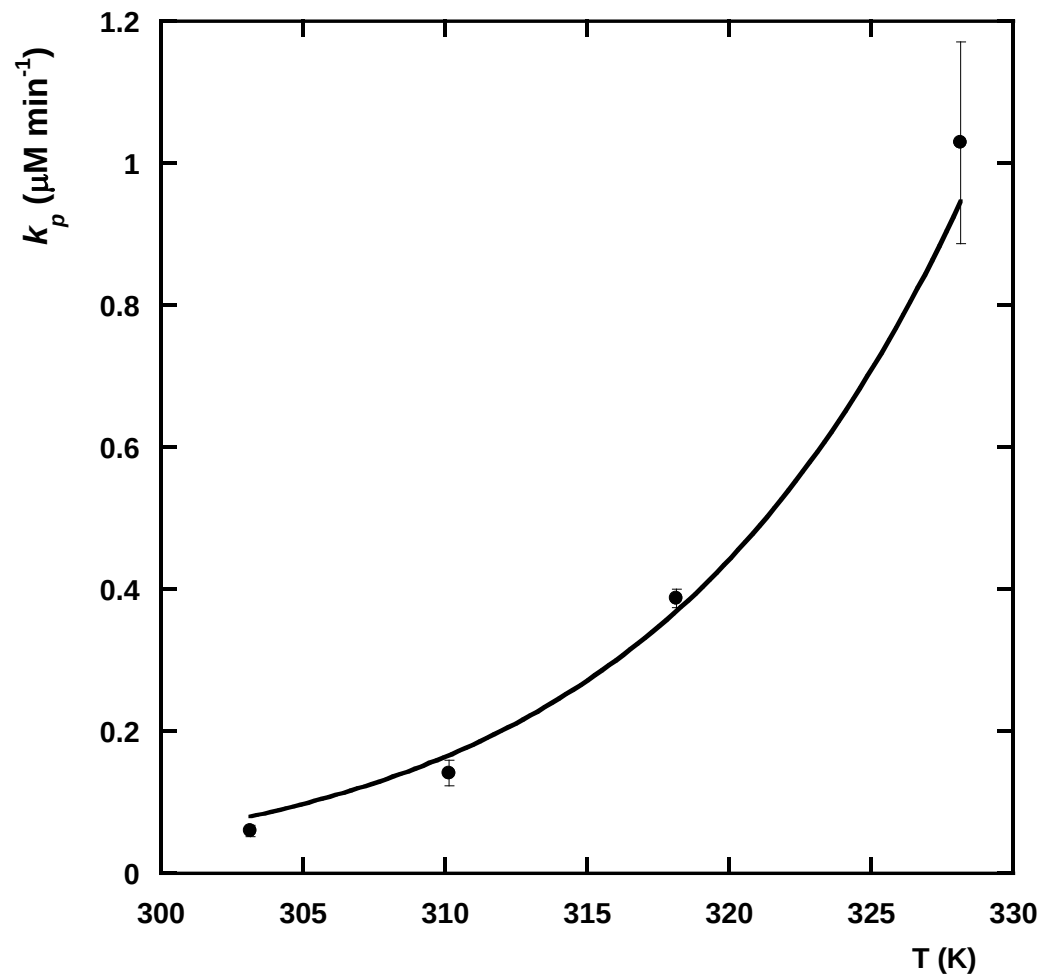


Figure 10. Arrhenius plot for the diuron degradation kinetics in the presence of heat-activated PDS.

Moreover, C_{MnO_2} corresponds to the amount of diuron that can be oxidized per unit of liquid volume, that is:

$$C_{MnO_2} = C_D - C_{D,f} \quad (9)$$

where $C_{D,f}$ is the final diuron concentration in the solution. It follows that Equation (7) can be re-written as follows:

$$v_M = \frac{dC_D}{dt} = -k_M C_{D,0} (C_D - C_{D,f}) \quad (10)$$

Integration of Equation (10) into the boundary conditions $t = 0, C_D = C_{D,0}$ and $t = t, C_D = C_D$ yields the following:

$$C_D = (C_{D,0} - C_{D,f}) e^{-k_M C_{D,0} t} + C_{D,f} \quad (11)$$

Equation (11) was used to fit the kinetics of diuron degradation in the presence of MnO_2 , and the results are shown in Figure 11 and Table 1. The kinetic rate constant, k_M , and the maximum oxidation capacity of MnO_2 , $C_{D,f}$, resulted equal to $(7.9 \pm 3.9) \times 10^{-4} \mu M^{-1} \text{ min}^{-1}$ and $62.4 \pm 0.5 \mu M$, respectively.

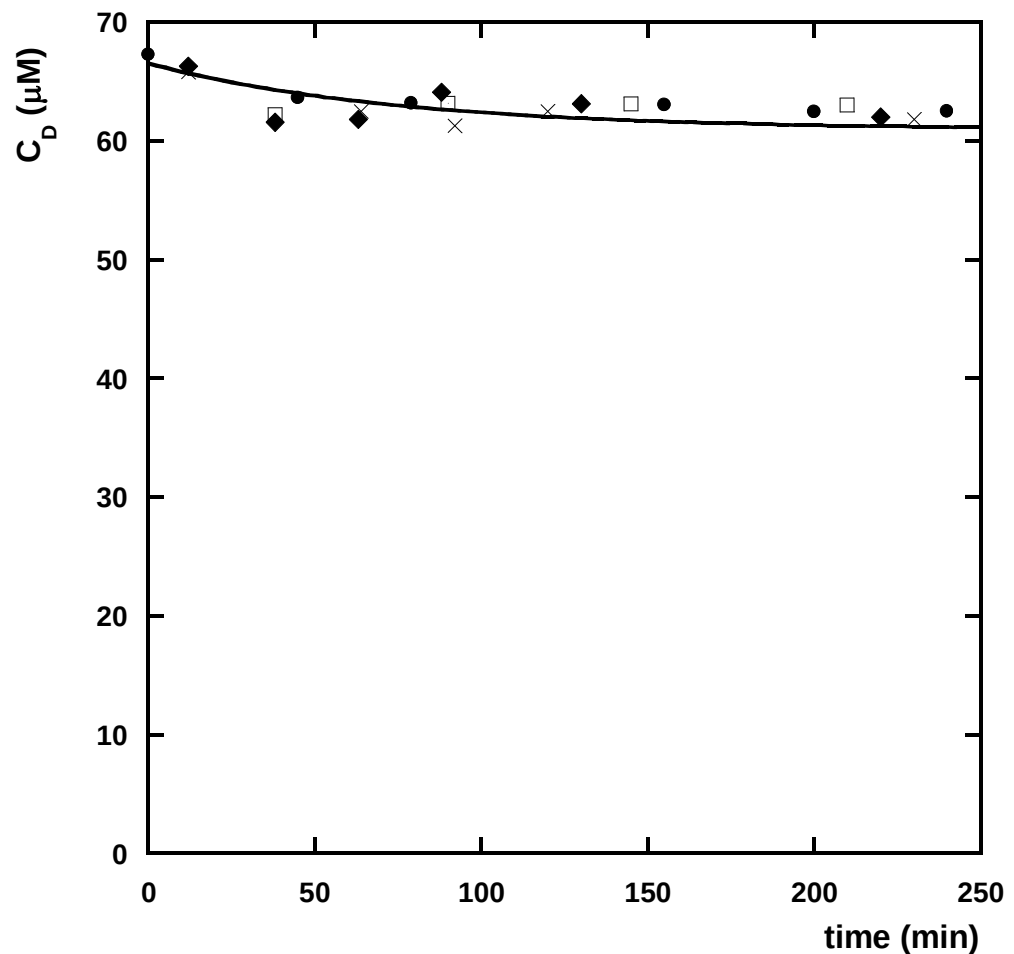
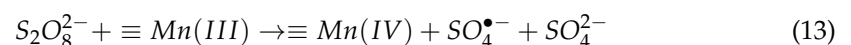
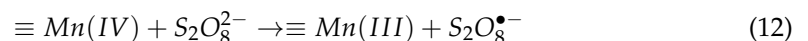


Figure 11. Diuron degradation kinetics profiles in the presence of MnO_2 at different temperatures, modeled by using Equation (11).

When both PDS and MnO_2 are present in the reactant system, the two compounds act synergistically to oxidize diuron. The large excess of PDS (PDS/diuron molar ratio $\cong 250$) reasonably induces an almost instantaneous full regeneration of the oxidation capability of MnO_2 during the process [52] (i.e., $(C_D - C_{D,f}) \cong (C_{D,0} - C_{D,f})$), and parallelly, MnO_2 acts as a catalyst for PDS activation [52]:



Under these experimental conditions, the oxidation rate of diuron (v_{Tot}) can be obtained by summing up the reaction rate corresponding to each diuron degradation route:

$$v_{\text{Tot}} = v_M + v'_P = \frac{dC_D}{dt} = -k_M C_D (C_{D,0} - C_{D,f}) - k_{P'} \quad (14)$$

where v'_P and $k_{P'}$ represent the reaction rate and the kinetic rate constant of diuron degradation, respectively, promoted by both heat- and MnO_2 -activated PDS. After integration of Equation (14), we finally obtain the following:

$$C_D = (C_{D,0} - \beta) e^{-k_M(C_{D,0} - C_{D,f})t} + \beta \quad (15)$$

$$\beta = -\frac{k_{P'}}{k_M(C_{D,0} - C_{D,f})} \quad (16)$$

Figure 12 and Table 1 show the results of the diuron kinetic data modeling in the co-presence of MnO_2 and PDS by using Equation (15).

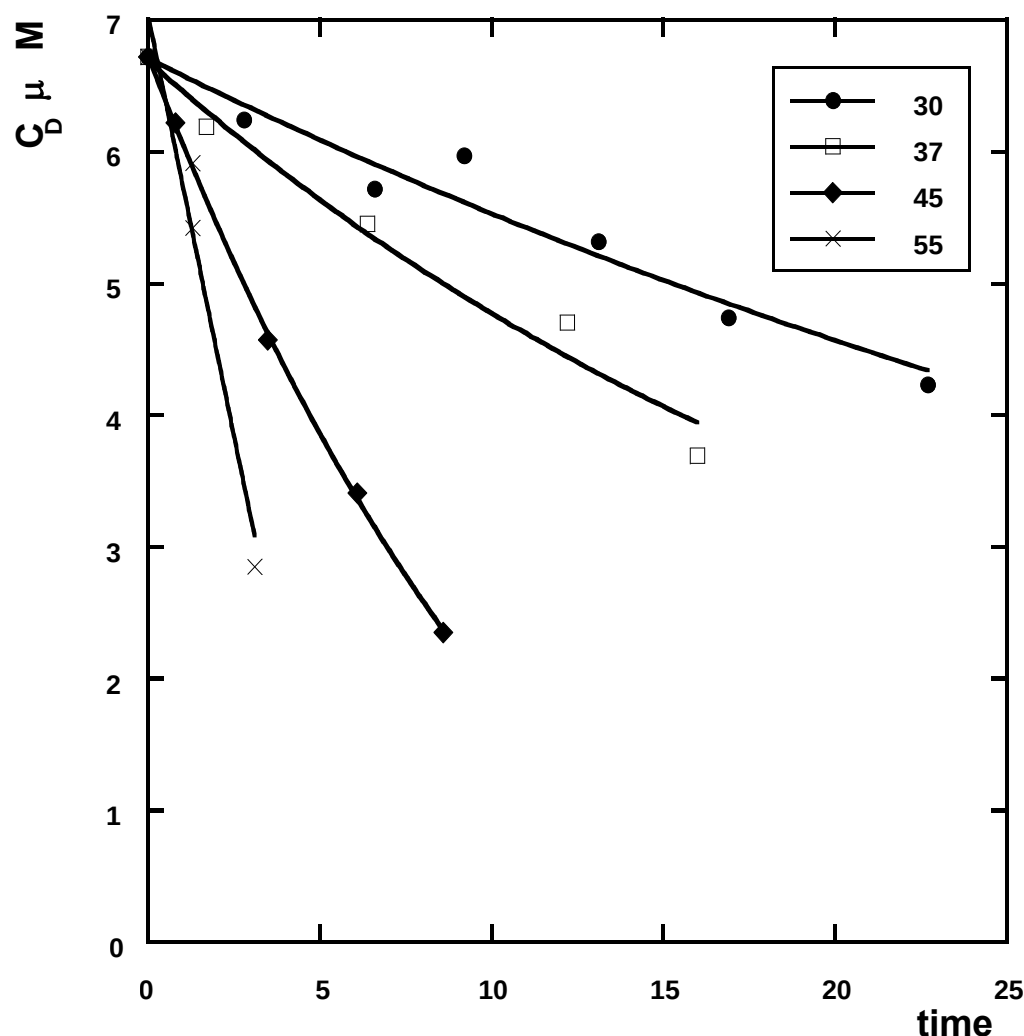


Figure 12. Diuron degradation kinetics profiles in the co-presence of PDS and MnO_2 at different temperatures, modeled by using Equation (15).

As can be seen from Table 1, the estimated value of k_p' at 30 °C was statistically higher than that of k_p obtained with heat-activated PDS. This indicates that MnO_2 has an important catalytic role in PDS activation, at least at 30 °C. The presence of MnO_2 at 30 °C determined a decrease in the predicted diuron half-life from 560 min (PDS alone) to 320 min (PDS + MnO_2). On the contrary, at the higher temperatures investigated, the effect of the presence of MnO_2 was much less significant, suggesting that in such experimental conditions, the activation of PDS by heat is the only effective source of diuron degradation.

3.3. Diuron Degradation Mechanism

The exact mechanism through which diuron is oxidized by MnO_2 remains unclear [44]. It can be considered that under acidic conditions (as in the case of the present study, $\text{pH} \approx 4$), MnO_2 promotes the formation of hydroxyl radicals which are likely responsible for the diuron degradation [44]. According to Jiang et al. [45], the reaction might proceed through the formation of diuron radicals, followed by dechlorination or hydroxylation and C-N bond cleavage.

Tan et al. [38] proposed that in the presence of PDS, both sulfate and hydroxyl radicals play a role in diuron degradation. The formation of two intermediates, namely 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea and 3,4-dichloroaniline, is expected. These

compounds react together to form high molecular weight products such as 2-chloro-4-((((3,4-dichlorophenyl)amino)oxy)(dimethylamino)methyl)amino)phenol, 2-((((3-chloro-4-hydroxyphenyl) amino) (((3,4-dichlorophenyl)amino)oxy)methyl)(methyl)amino)acetic acid, and 2,2'-((((3-chloro-4-hydroxyphenyl)amino) (((3,4-dichlorophenyl)amino)oxy)methyl) azanediyl)diacetic acid.

When both MnO_2 and PDS are present in the reaction mixture, they act synergistically (according to Equations (12) and (13)) to accelerate the reactions discussed above.

3.4. Reusability of MnO_2

To test the reusability of the solid material (MnO_2), after the end of the experiments, the samples were allowed to settle for MnO_2 recovery. The recovered MnO_2 was then used for four further degradation cycles, each time using a fresh PDS–diuron solution. The results of the reusability tests (Figure 13) revealed that MnO_2 preserves its activity at least up to the third cycle. The subsequent decrease in the degradation efficiency could be at least partially ascribed to the MnO_2 mass loss during the recovery procedure.

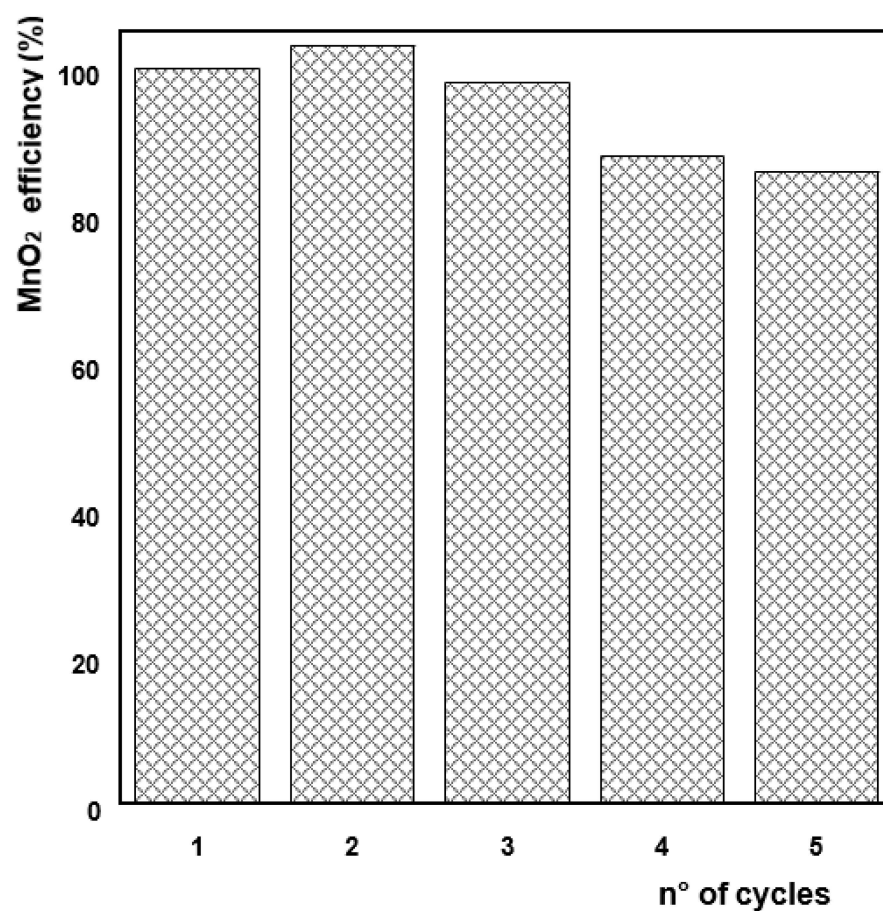


Figure 13. MnO_2 efficiency (%) in five consecutive cycles.

3.5. Operational Cost

To assess the applicability of the MnO_2 -activated-PDS system in industrial scale, we determined the overall operational cost (OOC) of the process, expressed in € per m^3 of treated water, by the sum of the electrical energy cost (EC) and the reagents cost (RC) per m^3 :

$$\text{OOC} = \text{EC} + \text{RC} \quad (17)$$

EC is the product of the electrical energy per order (EE/O) figure-of-merit with the electricity price; EE/O represents the electrical energy (kWh) required to degrade 90% of the target compound in 1 m³ of water [53]:

$$EE/O = \frac{P \cdot t}{V} \quad (18)$$

where P , t , and V are the power consumption (kW), the 90% degradation time (h), and the volume of treated water (m³), respectively.

The performance of the MnO₂-activated PDS system for diuron degradation was compared with that of the ultrasound-activated PDS process employed by Lee et al. for ibuprofen removal from water [54]. The diuron OOC was calculated at 30 °C to minimize the electrical energy consumption ($P = 300$ kW per m³). The dosages of PDS and MnO₂ were 4.5 and 24 g L⁻¹, respectively. Moreover, for a more correct comparison of the results, the same values of initial molar concentration (0.024 mM), electrical energy cost (0.1319 USD kWh⁻¹), and PDS cost (1.00 USD kg⁻¹) were used for diuron as reported for ibuprofen [54]. A cost of 3.00 USD kg⁻¹ was estimated for MnO₂, which was divided by three to take into account the number of degradation cycles with full MnO₂ efficiency. Based on the above considerations, the OOC for diuron degradation by MnO₂-activated PDS was found to be 82.5 USD m⁻³, which is only slightly higher than the cost of ibuprofen degradation by ultrasound-activated PDS [54]. These results coupled with the advantages of ease of use and simple engineering design make the MnO₂-PDS system a valid alternative to the ultrasound activation of PDS (and to the other AOPs) for pollution remediation.

4. Conclusions

In this work, the effect of heat and MnO₂ for promoting diuron degradation by activated PDS was investigated. It was found that MnO₂ alone has a low degradation capacity for diuron, whereas PDS alone exhibits an increasing oxidation efficiency with increasing temperature. Complete removal of diuron was obtained during the first hours at the highest temperature investigated (55 °C) for both the experiments conducted with PDS alone and those in the co-presence of PDS and MnO₂. The combined use of PDS and MnO₂ has a positive effect on diuron degradation, and this is particularly evident at lower temperatures. The estimated overall cost of the diuron degradation process is of the same order of magnitude of other AOPs, thus rendering PDS-MnO₂ an alternative efficient low energy demand system for water decontamination purposes.

Author Contributions: Conceptualization, S.S.; investigation, A.M. and S.S.; data curation, S.S.; writing—original draft preparation, A.F. and S.S.; writing—review and editing, S.S.; supervision, S.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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