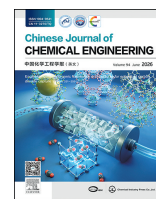




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Full Length Article

Atrazine degradation in a rotating packed bed reactor integrated with plasma: Process evaluation and optimization strategy

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ABSTRACT

Atrazine (ATZ) is a highly applicable neurogenic herbicide in crops. Due to its triazine structure, ATZ is durable in nature and difficult to degrade, posing serious environmental and health threats. In this work, a rotating packed bed reactor integrated with plasma (plasma-RPB) was employed to degrade ATZ. The effects of operating conditions and typical water matrix components were systematically evaluated. Results demonstrated that increasing rotational speed and discharge power enhanced degradation efficiency, while higher initial ATZ concentrations inhibited removal. Among common water matrix species, SO_4^{2-} and Cl^- exhibited inhibitory effects, Cu^{2+} significantly suppressed degradation, whereas CO_3^{2-} showed little impact. Ultra performance liquid chromatography–mass spectrometry analysis revealed that ATZ was mainly degraded via dealkylation and hydroxyl substitution, producing cyanuric acid and eventually undergoing ring opening. To enhance process robustness against inhibitory water matrices, peroxymonosulfate (PMS) integration was investigated as an intensification strategy. Utilizing the multiple activation pathways in the plasma environment, PMS was effectively activated to generate additional sulfate radicals. Under optimized conditions, degradation efficiency and total organic carbon removal of actual industrial wastewater reached 99% and 90% within 20 min, respectively. This study highlights plasma-RPB, particularly when synergized with PMS, as a promising technology for pesticide wastewater treatment.

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1. Introduction

The agricultural production process consumes large amounts of agricultural chemicals such as chemical fertilizer and pesticide, leading to serious environmental pollution [1,2]. Atrazine (ATZ), as a neurogenic herbicide of triazine compounds, is one of the most commonly used pesticide due to its high effectiveness [3,4]. However, extensive application of ATZ has resulted in its frequent detection in wastewater from pesticide plants [5]. In addition, ATZ is an endocrine disruptor that pose potential risks to the immune and nervous systems [6]. Due to its molecular structure of triazine, ATZ was durable in nature and difficult to decompose, making the

development of efficient treatment methods for ATZ-contaminated wastewater an urgent priority [7].

Common degradation approaches of ATZ include biological treatment, chemical oxidation, and photocatalytic degradation [8]. Zhao *et al.* [9] utilized *Pseudomonas* and *Arthrobacter* to biologically degrade ATZ, and the concentration of ATZ could be degraded below the threshold in 43 days. Ye *et al.* [10] designed an ozonation catalyst for ATZ degradation in wastewater, and the degradation efficiency of ATZ with a concentration of $10 \text{ mg} \cdot \text{L}^{-1}$ reached 93.9% in 180 min. Photocatalytic degradation using TiO_2 , ZnO, Bi-based oxides, and other catalysts has also been widely reported [11,12]. While effective, these processes often require long reaction times and may generate secondary pollution, limiting their applicability towards industrial wastewater from pesticide factories, especially with large flow rate and high concentration [13].

Compared with traditional methods, plasma technology has gained increasing attention in wastewater treatment [14,15]. A large number of active components generated by the plasma device can

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effectively degrade target pollutants without causing secondary pollution [16,17]. Various plasma configurations, such as microwave plasma systems, have been explored for contaminant degradation, demonstrating the versatility of plasma-based approaches [18,19]. In our previous study, Liang *et al.* [20] developed a novel rotating packed bed reactor integrated with plasma (plasma-RPB) that coupled plasma with a centrifugal field to enhance reactive species generation [21]. This design enables rapid degradation of high-concentration pesticide wastewater, which may reduce pollutant discharge into natural water bodies. However, existing plasma-RPB studies focused on ideal water conditions, while industrial wastewater contains complex ions such as carbonate, chloride, sulfate, and heavy metals [22–27]. Furthermore, the degradation pathways and intermediates of pesticide contaminants under plasma-RPB treatment remain insufficiently investigated.

In this work, the plasma-RPB was employed for ATZ degradation. The effects of operating parameters, including rotational speed, discharge power, and initial concentration of ATZ, on the degradation efficiency of ATZ were studied to evaluate the degradation performance of the plasma-RPB. In addition, the influences of water quality including ions, pH, and conductivity were investigated to identify the applicable fields of the plasma-RPB. Degradation pathways were analyzed using ultra performance liquid chromatography–mass spectrometry (UPLC-MS), and peroxymonosulfate (PMS) integration was evaluated as a process intensification strategy to overcome inhibitory effects. Finally, the optimized strategy was utilized for actual industrial wastewater treatment, and a comprehensive comparison with other degradation methods was carried out to evaluate its application potential.

2. Experimental

2.1. Experimental materials

Atrazine ($\geq 96\%$), Na_2SO_4 , NaCl , Na_2CO_3 , $\text{Cu}(\text{NO}_3)_2$, NaNO_3 , NaH_2PO_4 , $\text{CH}_3\text{CH}_2\text{OH}$ (for HPLC), and PMS were purchased from McLean Reagent Co., LTD., China. Oxygen (purity 99.5%) was

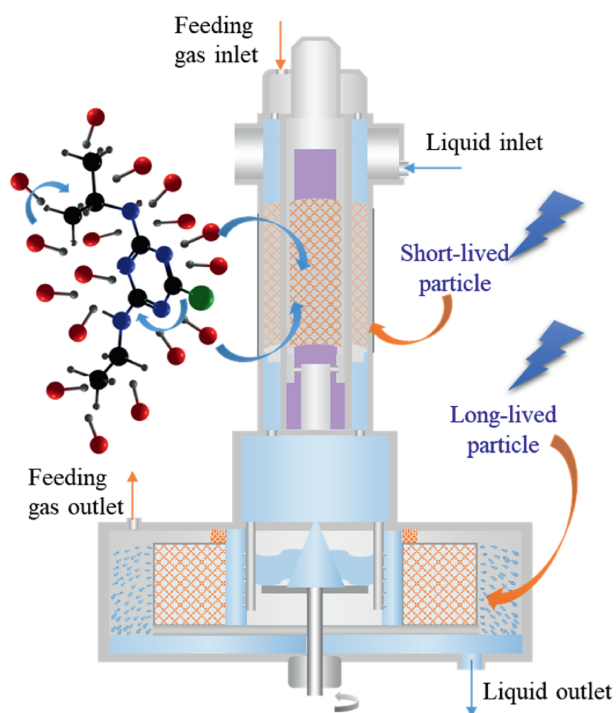


Fig. 1. Diagram of the plasma-RPB.

ordered from Beijing Shunan Qite Gas Co., LTD., China. Deionized water was used in all experiments.

2.2. Plasma-RPB

Fig. 1 shows the schematic diagram of the plasma-RPB [20]. It consists of two sections, namely a dielectric barrier discharge plasma reactor (cylindrical quartz tube with mesh electrodes powered by a plasma generator, CTP-2000KP, Nanjing Suman Electronics Co., LTD., China) and an RPB section. The plasma section enables contaminant oxidation by reactive species, while the RPB enhances oxidation through peroxone reaction of ozone and hydrogen peroxide. Detailed parameters of plasma-RPB are listed in Table 1.

2.3. Experimental procedure

As illustrated in Fig. 2, oxygen and wastewater were introduced co-currently into the plasma-RPB. Wastewater was distributed across the quartz wall to form a thin liquid film, then entered the RPB section via a rotating distributor. Oxygen was ionized in the plasma chamber to produce reactive species, which further reacted in the RPB. ATZ concentrations were measured every 5 min. Each experiment was repeated three times. Operating conditions are listed in Table 2.

2.4. Analytical methods

2.4.1. ATZ concentration and degradation efficiency

ATZ concentration was determined by high performance liquid chromatography (HPLC, Thermo Ferre Ultimate 3000 UPHPLC-Q

Table 1
Parameters of the plasma-RPB.

Items	Values
Electrode length/mm	12.5
Discharge gap width/mm	5
External diameter of the outer quartz tube/mm	80
Internal diameter of the inner quartz tube/mm	58
Thickness of the quartz tube/mm	3
Internal diameter of the packing/mm	90
External diameter of the packing/mm	320
Height of the packing/mm	25
Diameter of fiber/mm	0.2
Porosity of the packing	0.97
Specific surface area/ $\text{m}^2 \cdot \text{m}^{-3}$	566

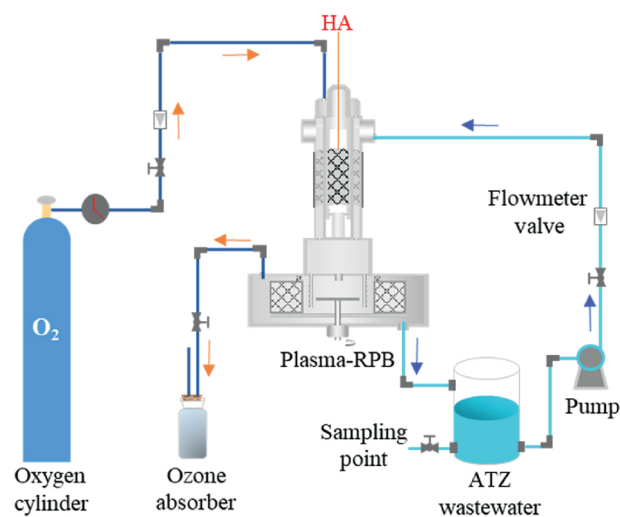


Fig. 2. Schematic diagram of experimental procedure.

Table 2

Operating conditions of experiments.

Items	Values
Liquid volume, V/L	3
Rotational speed, $N/\text{r} \cdot \text{min}^{-1}$	0–1000
Gas flow rate, $Q_G/\text{m}^3 \cdot \text{h}^{-1}$	0.5
Discharge power, P/W	20–80
Initial concentration of ATZ solution, $C_0/\text{mg} \cdot \text{L}^{-1}$	5–25
Liquid flow rate, $Q_L/\text{L} \cdot \text{h}^{-1}$	150
Anion and cation, $C_0/\text{mmol} \cdot \text{L}^{-1}$	0.5–4

Exactive, USA) using a UV detector at 225 nm. The chromatographic column was BEH C18 column (2.1 mm $\times$ 100 mm, 1.7 μm particle size), and its temperature was 35 $^{\circ}\text{C}$. The mobile phase was 60% LC-MS grade water (chromatographically pure) and 40% LC-MS grade ethanol (McLean) with flow rate of 1 $\text{mL} \cdot \text{min}^{-1}$. The degradation efficiency (η , %) was calculated as:

$$\eta = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

where C_0 and C_t are the initial and time-dependent ATZ concentrations.

2.4.2. Degradation products analysis

Degradation intermediates were identified using ultrahigh performance liquid chromatogram-tandem mass spectrometry (UPLC-MS-2020, Shimadzu 8050 triple quadrupole, Japan) and positive spray ionization (Waters-Synapt G2-Si HD mass spectrometry, USA). The chromatographic column was Shim-pack XR-ODS2.0 mm I.D. $\times$ 5 mm L, 2.2 μm . The eluents were water and acetonitrile, and their flow rate were 0.5 $\text{mL} \cdot \text{min}^{-1}$. Operating parameters included spray voltage of 400 V, heating temperature of 400 $^{\circ}\text{C}$, DL temperature of 250 $^{\circ}\text{C}$, nitrogen as atomizing/drying gas, and argon as collision gas. The sample with the injection flow rate of 0.5 $\text{mL} \cdot \text{min}^{-1}$ was measured by the gradient elution.

2.4.3. pH and TOC analysis

The pH value of solution was slowly adjusted by NaH_2PO_4 and NaOH with a pH meter (PHS-2F, Shanghai Reitz, China). The mineralization capacity was assessed by measuring total organic carbon (TOC) using a TOC analyzer (TOC-L, Shimadzu, Japan). TOC removal efficiency (η_{TOC} , %) was calculated as:

$$\eta_{\text{TOC}} = (\text{TOC}_0 - \text{TOC}_t) / \text{TOC}_0 \times 100\% \quad (2)$$

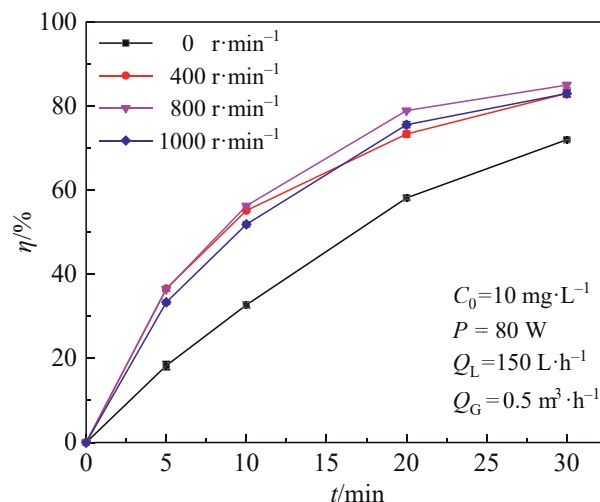
where TOC_0 and TOC_t are the TOC values at the initial time and time t , respectively.

3. Results and Discussion

3.1. Evaluation of ATZ degradation process in the plasma-RPB

3.1.1. Effects of operating parameters

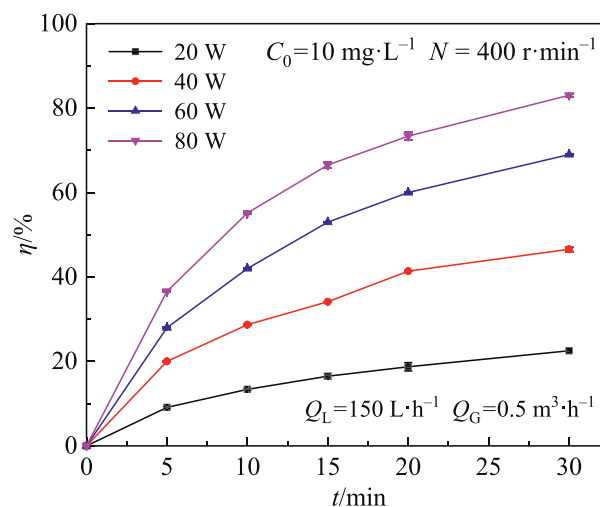
Fig. 3 shows the effect of the rotational speed (N) on the degradation efficiency (η). The η value first increased and then decreased with increasing N . When N increased from 0 to 400 $\text{r} \cdot \text{min}^{-1}$, the degradation efficiency significantly improved, reaching nearly 80% after 30 min. This enhancement is attributed to the intensified gas–liquid mass transfer and the thinner liquid film generated under higher centrifugal force [28], which increases the contact area between reactive species and ATZ molecules. The centrifugal field promotes liquid dispersion and formation of micro-scale droplets, significantly enhancing interfacial area and mass transfer coefficients. However, further increasing N resulted in nearly constant or even reduced η values. Excessive rotation

**Fig. 3.** Effects of N on η in the plasma-RPB.

reduces liquid residence time in the RPB section, limiting complete reaction between pollutants and active species [29]. Thus, 400 $\text{r} \cdot \text{min}^{-1}$ was identified as the optimal rotational speed for subsequent experiments.

Fig. 4 depicts the effect of discharge power (P) on η . The results show a positive correlation between discharge power and degradation efficiency. At 20 W, the η value of ATZ in the plasma-RPB was only 20% after 30 min of treatment, whereas at 80 W it increased to approximately 80%. The increase in discharge power enhances electron energy and density in the plasma region, promoting the generation of reactive oxygen species including $\cdot\text{OH}$, O_3 , and H_2O_2 through electron-impact reactions and energy transfer processes [30,31]. Considering the degradation efficiency, 80 W was chosen as the preferred discharge power.

Fig. 5 shows the influence of initial concentration of ATZ (C_0) on η . The increase of C_0 led to a weakened degradation effect of ATZ. When C_0 was 5 $\text{mg} \cdot \text{L}^{-1}$, the η value reached 89% after 30 min, but at 25 $\text{mg} \cdot \text{L}^{-1}$, it decreased to 58% under the same treatment time. This phenomenon can be explained by the relatively constant generation rate of reactive species at fixed discharge power. With higher pollutant concentrations, the reactive species become insufficient for complete degradation, resulting in lower η values.

**Fig. 4.** Effects of P on η in the plasma-RPB.

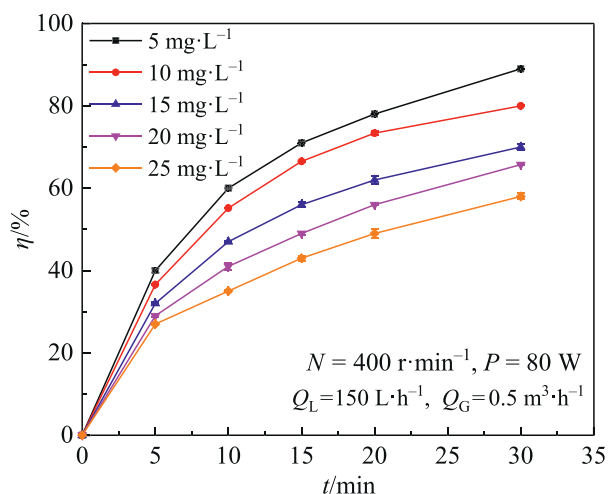


Fig. 5. Effects of C_0 on η in the plasma-RPB.

[32]. Additionally, intermediate products compete with parent ATZ for reactive species at higher concentrations.

3.1.2. Effects of water quality

In real wastewater systems, various anions and cations coexist. Therefore, it is necessary to investigate their influence on ATZ degradation in plasma-RPB. Commonly detected ions in actual wastewater include CO_3^{2-} , Cl^- , SO_4^{2-} , Cu^{2+} and so on [22,23].

Fig. 6 shows the effect of CO_3^{2-} on the η . As CO_3^{2-} concentration increased, the η value gradually decreased. When CO_3^{2-} concentration rose from 0 to 4 $\text{mmol}\cdot\text{L}^{-1}$, η decreased from 73% to 69%. This can be attributed to the scavenging of hydroxyl radicals by carbonate ions ($k = 4.0 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$), forming carbonate radicals ($\text{CO}_3^{\cdot-}$) with lower oxidation potential (1.50 V) compared to $\cdot\text{OH}$ (2.80 V) [25]. Although the reaction rate constants between CO_3^{2-} and $\cdot\text{OH}$ are relatively low, the large carbonate content can still induce the rapid consumption of $\cdot\text{OH}$ [33].

Fig. 7 presents the influence of Cl^- on η . As Cl^- concentration increased from 0 to 4 $\text{mmol}\cdot\text{L}^{-1}$, η decreased significantly from 73% to 47%. The reason was that Cl^- reacts with $\cdot\text{OH}$ to produce $\cdot\text{Cl}$, whose oxidation potential (1.36 V) was lower than that of $\cdot\text{OH}$ [25]. Additionally, Cl^- may react with ozone to produce HClO ,

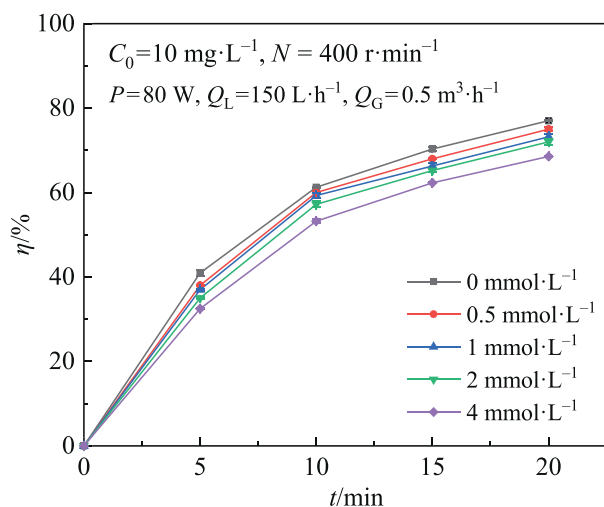


Fig. 6. Effects of CO_3^{2-} concentration on η in the plasma-RPB.

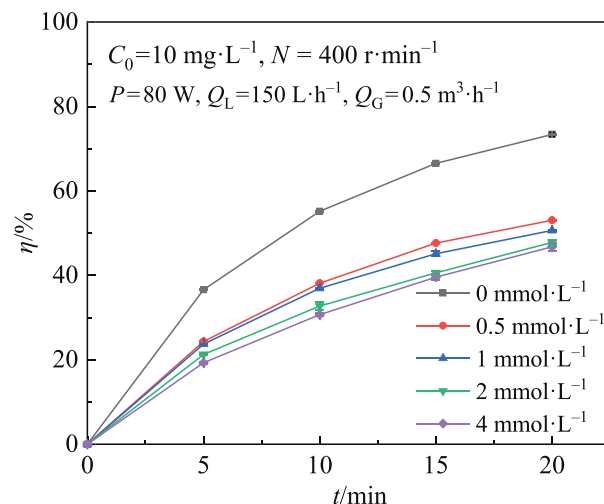


Fig. 7. Effects of Cl^- concentration on η in the plasma-RPB.

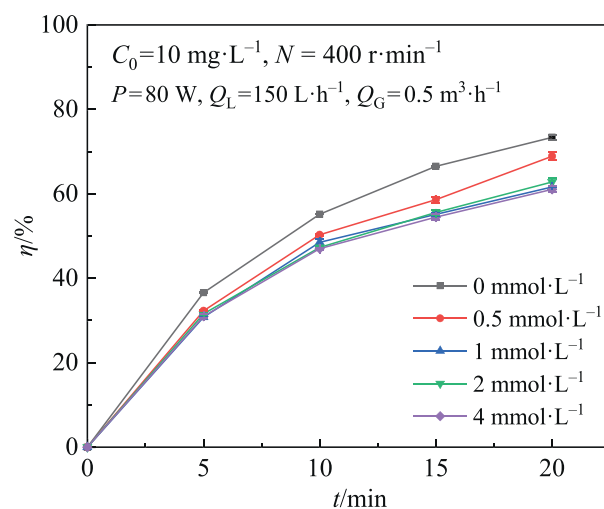


Fig. 8. Effects of SO_4^{2-} concentration on η in the plasma-RPB.

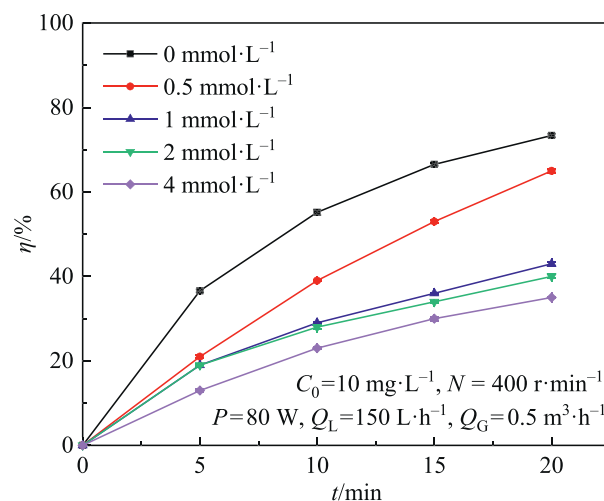


Fig. 9. Effects of Cu^{2+} concentration on η in the plasma-RPB.

which also exhibits lower oxidation capability [34]. These processes collectively reduced ATZ degradation. At higher Cl^- concentrations, however, the accumulation of Cl^- and HClO may promote ATZ degradation to some extent through alternative reaction pathways.

Fig. 8 shows the impact of SO_4^{2-} on ATZ degradation. When SO_4^{2-} concentration was increased from 0 to $1 \text{ mmol} \cdot \text{L}^{-1}$, the η value decreased by nearly 11%. Further increase in SO_4^{2-} concentration did not cause significant changes. This can be explained by the generation of sulfate radicals, which have a high oxidation potential and can supplement $\cdot\text{OH}$ consumed during the reaction [35,36]. As a result, the inhibitory effect was mitigated at higher SO_4^{2-} levels [25].

Fig. 9 illustrates the effect of Cu^{2+} on degradation efficiency. The results showed that Cu^{2+} strongly inhibited ATZ degradation. Although Cu^{2+} can undergo Fenton-like reactions with H_2O_2

produced by plasma discharge, which theoretically enhances degradation [37,38], in practice, η decreased steadily with increasing Cu^{2+} concentration. This inhibition is due to complex formation between ATZ and Cu^{2+} through nitrogen atom electron donation, making the complexes more resistant to degradation compared with free ATZ molecules [39].

3.2. Strategy optimization for ATZ wastewater treatment

3.2.1. Analysis of degradation products and pathways

To optimize degradation strategies, it is crucial to identify the degradation products and pathways of ATZ. First-order mass spectrometry scans were conducted on samples collected at 5, 10, 15, 20 min. Total ion chromatograms and extracted ion flow diagrams were analyzed to determine intermediate products, which are summarized in Table S1 (in Supplementary Material).

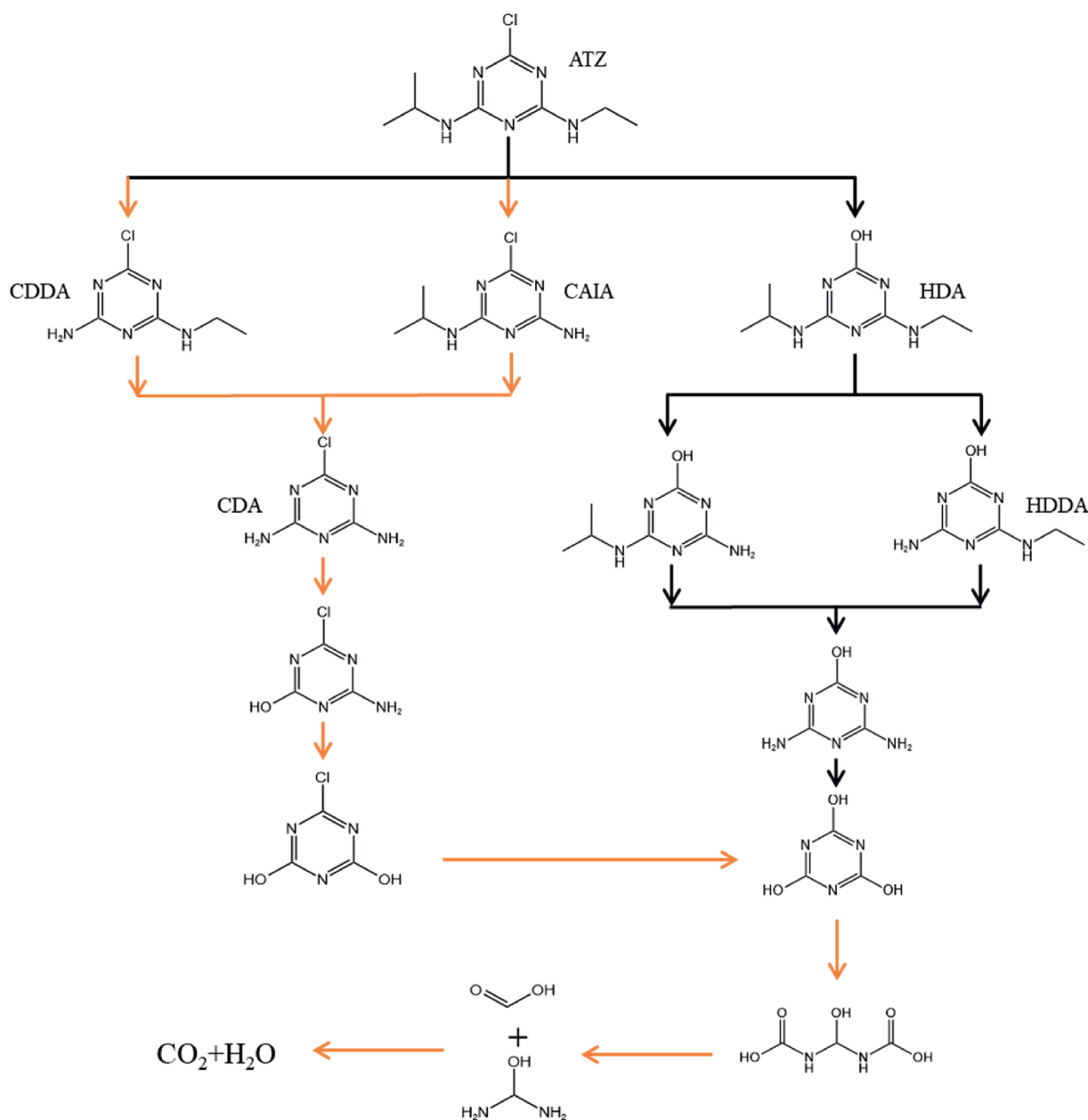


Fig. 10. Degradation pathway of ATZ in the plasma-RPB.

Based on detected intermediates, ATZ degradation in plasma-RPB followed two main pathways: (i) hydroxyl substitution of chlorine atoms, and (ii) oxidation of isopropylamino groups. These pathways were not mutually exclusive and converged to cyanuric acid in later stages. Cyanuric acid is highly stable and often accumulates in many degradation processes, making its further degradation essential [40]. Fig. 10 illustrates the proposed degradation pathways. Most intermediates resulted from oxidation of isopropylamino groups (e.g. CAIA, CDDA, CDA), whereas intermediates from hydroxyl substitution (e.g. HDDA, HDA) were less abundant. Although not quantitatively measured, the formation of hydroxylated intermediates provides strong evidence for $\cdot\text{OH}$ involvement. It was hypothesized that ATZ initially underwent oxidation of isopropylamino groups to form CDA, which then underwent amino hydroxylation and chlorine substitution to form cyanuric acid. A parallel route involved hydroxyl substitution of chlorine to form HAD, followed by amino hydroxylation to produce cyanuric acid. Ultimately, cyanuric acid underwent ring-opening oxidation, generating CO_2 and H_2O , thereby completing mineralization while minimizing accumulation of intermediates. The proposed pathways are consistent with previous studies, where cyanuric acid is a common intermediate that eventually mineralizes to CO_2 and H_2O , reducing overall toxicity.

3.2.2. Process intensification with peroxymonosulfate

The results indicated that degradation efficiency was inhibited under complex water matrices. To enhance process robustness and oxidative capacity, we investigated the integration of PMS as an intensification strategy. The plasma environment, characterized by multiple activation pathways including UV radiation, high-energy electrons, and localized heating, provides efficient activation of PMS to generate sulfate radicals ($\text{SO}_4\cdot^-$) with high oxidation potential [26,41].

Fig. 11(a) shows that increasing PMS concentration from 0 to $2\text{ mmol}\cdot\text{L}^{-1}$ enhanced ATZ degradation, owing to the elevated generation of active radicals. The optimal PMS dosage should be carefully tuned depending on pollutant concentration and discharge power to avoid self-scavenging effects at excessive concentrations. Fig. 11(b) illustrates the effect of pH when PMS concentration was $1\text{ mmol}\cdot\text{L}^{-1}$. As pH increased from 6 to 8, degradation efficiency improved markedly, reaching nearly 100% within 15 min at pH value of 8. This suggests that slightly alkaline conditions favor PMS activation through base activation pathways and reduce $\text{SO}_4\cdot^-$ scavenging by H^+ . Although temperature was not monitored in this study, the improved degradation efficiency with PMS is consistent with activation mechanisms reported in the literature [26]. The enhanced degradation and mineralization with PMS suggest the generation of sulfate radicals ($\text{SO}_4\cdot^-$), which possess higher oxidation potentials and longer lifetimes than hydroxyl radicals [36,41], creating a synergistic oxidation environment.

3.2.3. Application to industrial wastewater

To verify the practical applicability of the plasma-RPB system, industrial ATZ wastewater was obtained from a pesticide production process at Zhongshan Industry Group Co., Ltd., China. The wastewater was used without any pretreatment to evaluate the system's performance under realistic and challenging conditions. It contained an initial ATZ concentration of approximately $15\text{ mg}\cdot\text{L}^{-1}$ with a pH of ~ 8 . Critically, qualitative analysis confirmed the presence of a complex water matrix, inducing the common inhibitory ions specifically investigated in this study, namely CO_3^{2-} , Cl^- , and Cu^{2+} . The degradation performance achieved in this real wastewater (Fig. 12) qualitatively aligns with the inhibition trends observed in the controlled experiments

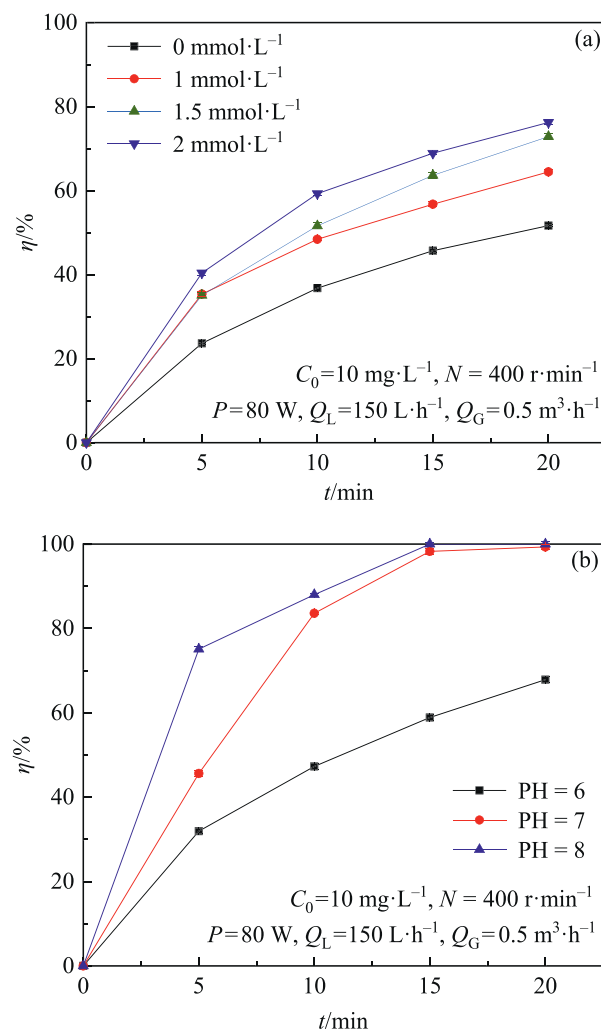


Fig. 11. Effects of (a) PMS concentration and (b) PH on η .

(Figs. 6–9), thereby validating the system's effectiveness in a complex, non-ideal environment representative of actual industrial scenarios. Additionally, Fig. 12 shows that the plasma-RPB with PMS integration achieved 99% degradation efficiency,

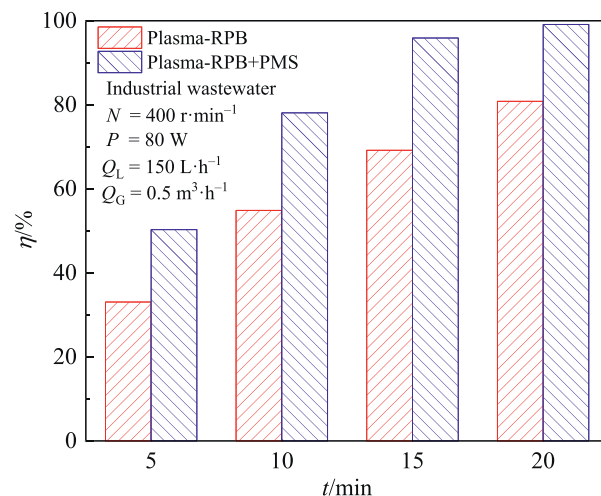


Fig. 12. Comparisons of ATZ degradation efficiency.

Table 3

Comparison of ATZ degradation performance of different methods.

Methods	Conditions	$\eta/\%$	$\eta_{\text{TOC}}/\%$	Reference
US/PMS	$C_{\text{ATZ}} = 2.5 \mu\text{mol}\cdot\text{L}^{-1}$, $C_{\text{PMS}} = 400 \mu\text{mol}\cdot\text{L}^{-1}$ US intensity = $0.88 \text{ W}\cdot\text{mL}^{-1}$, 150 kHz	62% within 60 min	—	[26]
Photocatalytic degradation	$C_{\text{ATZ}} = 20 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{ZnIn}_2\text{S}_4} = 0.5 \text{ g}\cdot\text{L}^{-1}$ 450 W, $1000 \text{ W}\cdot\text{m}^{-2}$ solar simulator	90% within 1 h	—	[42]
Photocatalytic degradation	$C_{\text{ATZ}} = 10 \text{ mg}\cdot\text{L}^{-1}$, $m_{\text{photocatalyst}} = 20 \text{ mg}$ Light intensity = $46.5 \text{ mW}\cdot\text{cm}^{-2}$	95% within 30 min	90% within 30 min	[43]
Electro-fenton	$C_{\text{ATZ}} = 10 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{Fe}^{2+}} = 2.0 \text{ mmol}\cdot\text{L}^{-1}$, pH = 2.0, potential = -0.4 V	93% within 30 min	75% within 30 min	[44]
Persulfate oxidation	$C_{\text{ATZ}} = 10 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{PS}} = 0.5 \text{ mmol}\cdot\text{L}^{-1}$ $N = 150 \text{ r}\cdot\text{min}^{-1}$, $V = 100 \text{ mL}$	90% within 30 min	40% within 30 min	[45]
Persulfate oxidation	$C_{\text{ATZ}} = 20 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{Fe}_2\text{SO}_4} = 4.2 \text{ mmol}\cdot\text{L}^{-1}$ $C_{\text{FeS}_2} = 4.2 \text{ mmol}\cdot\text{L}^{-1}$, $C_{\text{PS}} = 3.0 \text{ mmol}\cdot\text{L}^{-1}$ $V = 20 \text{ mL}$	90% within 40 min	32% within 15 min	[46]
Plasma + PI	$C_{\text{ATZ}} = 10 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{PI}} = 0.02 \text{ mmol}\cdot\text{L}^{-1}$ $P = 68 \text{ W}$, $V = 35 \text{ mL}$	82% within 10 min	22% within 10 min	[47]
Plasma-RPB + PMS	$C_{\text{ATZ}} = 15 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{PMS}} = 1 \text{ mmol}\cdot\text{L}^{-1}$, $P = 80 \text{ W}$, $N = 400 \text{ r}\cdot\text{min}^{-1}$, $V = 3 \text{ L}$	99% within 20 min	90% within 20 min	This work

superior to that of using plasma-RPB only. The TOC removal efficiency was 90% within 20 min (Table S1), highlighting the enhanced mineralization capacity through PMS-integration strategy.

3.2.4. Comparison of ATZ degradation technologies

Table 3 compares the performance of plasma-RPB with other advanced oxidation processes, including ultraviolet photocatalytic degradation [26,42,43], electrochemical oxidation [44], persulfate oxidation [45,46], and plasma technology [47]. Key performance indicators such as degradation efficiency, TOC removal, and treatment time are summarized. Additionally, the energy yield was evaluated as shown in Table S1. Among these methods, the plasma-RPB with PMS demonstrated excellent degradation efficiency and energy yield within short treatment time. This highlights its superiority for treating ATZ-containing wastewater at industrial scale.

4. Conclusions

This work employed a plasma-RPB for efficient degradation of ATZ. The effects of operating conditions on degradation efficiency were illustrated first. Rotational speed ($400 \text{ r}\cdot\text{min}^{-1}$) and discharge power (80 W) significantly enhanced degradation efficiency, whereas higher initial ATZ concentrations reduced removal efficiency. Then, the effects of water quality on degradation process were investigated. SO_4^{2-} , Cl^- , and Cu^{2+} inhibited ATZ degradation, with Cu^{2+} showing the strongest suppression, while CO_3^{2-} had minimal effect. UPLC-MS analysis revealed that ATZ was mainly degraded via dealkylation and hydroxyl substitution, leading to the generation of cyanuric acid, which subsequently underwent ring opening to CO_2 and H_2O . To overcome water matrix inhibition, PMS integration was utilized as an effective intensification strategy, achieving nearly complete ATZ removal and 90% TOC reduction in real industrial wastewater. These results demonstrate that plasma-RPB, particularly when integrated with PMS, offers significant potential for scalable and sustainable pesticide wastewater treatment.

CRedit Authorship Contribution Statement

Hanzhuo Xu: Writing – original draft, Methodology, Investigation. Tao Ding: Writing – review & editing, Methodology, Conceptualization. Chuang Liang: Writing – review & editing, Data curation. Yanbin Li: Writing – review & editing, Conceptualization. Guangwen Chu: Writing – review & editing, Supervision, Project administration. Jianfeng Chen: Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2025.12.042>.

Nomenclatures

C_{ATZ}	initial ATZ concentration, $\text{mg}\cdot\text{L}^{-1}$
C_t	ATZ concentration at t , $\text{mg}\cdot\text{L}^{-1}$
C_0	initial concentration of ATZ solution at $t = 0$, $\text{mg}\cdot\text{L}^{-1}$
H	degradation efficiency of ATZ, %
N	rotational speed of RPB, $\text{r}\cdot\text{min}^{-1}$
P	discharge power, W
Q_G	gas flow rate, $\text{L}\cdot\text{h}^{-1}$
Q_L	liquid flow rate, $\text{L}\cdot\text{h}^{-1}$
TOC	total organic carbon, $\text{mg}\cdot\text{L}^{-1}$
T	reaction time, min
V	liquid volume, L
η_{TOC}	TOC removal efficiency

References

- [1] J.T. Sun, L.L. Pan, Y. Zhan, D.C.W. Tsang, L.Z. Zhu, X.D. Li, Atrazine contamination in agricultural soils from the Yangtze River Delta of China and associated health risks, *Environ. Geochem. Health* 39 (2) (2017) 369–378.
- [2] S. Singh, V. Kumar, A. Chauhan, S. Datta, A.B. Wani, N. Singh, J. Singh, Toxicity, degradation and analysis of the herbicide atrazine, *Environ. Chem. Lett.* 16 (1) (2018) 211–237.
- [3] J.T. Liu, J.H. Zhou, Q.N. Guo, L.Y. Ma, H. Yang, Physiochemical assessment of environmental behaviors of herbicide atrazine in soils associated with its degradation and bioavailability to weeds, *Chemosphere* 262 (2021) 127830.
- [4] L. Yue, C.J. Ge, D. Feng, H.M. Yu, H. Deng, B.M. Fu, Adsorption-desorption behavior of atrazine on agricultural soils in China, *J. Environ. Sci.* 57 (2017) 180–189.

- [5] Q. Li, Y. Luo, J. Song, L. Wu, Risk assessment of atrazine polluted farmland and drinking water: a case study, *Bull. Environ. Contam. Toxicol.* 78 (3–4) (2007) 187–190.
- [6] X.C. Wang, Q.L. Liu, Spatial and temporal distribution characteristics of triazine herbicides in typical agricultural regions of Liaoning, China, *Bull. Environ. Contam. Toxicol.* 105 (6) (2020) 899–905.
- [7] Y.S. Mok, J.O. Jo, J.C. Whitehead, Degradation of an azo dye Orange II using a gas phase dielectric barrier discharge reactor submerged in water, *Chem. Eng. J.* 142 (1) (2008) 56–64.
- [8] K. Poonia, V. Hasija, P. Singh, A.A. Parwaz Khan, S. Thakur, V.K. Thakur, S. Mukherjee, T. Ahamad, S.M. Alshehri, P. Raizada, Photocatalytic degradation aspects of atrazine in water: enhancement strategies and mechanistic insights, *J. Clean. Prod.* 367 (2022) 133087.
- [9] X.Y. Zhao, S.W. Bai, C.Y. Li, J.X. Yang, F. Ma, Bioaugmentation of atrazine removal in constructed wetland: performance, microbial dynamics, and environmental impacts, *Bioresour. Technol.* 289 (2019) 121618.
- [10] G.J. Ye, P. Luo, Y.S. Zhao, G.L. Qiu, Y. Hu, S. Preis, C.H. Wei, Three-dimensional Co/Ni bimetallic organic frameworks for high-efficient catalytic ozonation of atrazine: mechanism, effect parameters, and degradation pathways analysis, *Chemosphere* 253 (2020) 126767.
- [11] M. Shekofteh-Gohari, A. Habibi-Yangjeh, M. Abitorabi, A. Rouhi, Magnetically separable nanocomposites based on ZnO and their applications in photocatalytic processes: a review, *Crit. Rev. Environ. Sci. Technol.* 48 (10–12) (2018) 806–857.
- [12] K. Sharma, V. Dutta, S. Sharma, P. Raizada, A. Hosseini-Bandegharai, P. Thakur, P. Singh, Recent advances in enhanced photocatalytic activity of bismuth oxyhalides for efficient photocatalysis of organic pollutants in water: a review, *J. Ind. Eng. Chem.* 78 (2019) 1–20.
- [13] Y.S. Mok, J.O. Jo, H.J. Lee, H.T. Ahn, J.T. Kim, Application of dielectric barrier discharge reactor immersed in wastewater to the oxidative degradation of organic contaminant, *Plasma Chem. Plasma Process.* 27 (1) (2007) 51–64.
- [14] E.S.M. Mouele, J.O. Tijani, K.O. Badmus, O. Pereao, O. Babajide, O.O. Fatoba, C. Zhang, T. Shao, E. Sosnin, V. Tarasenko, K. Laatikainen, L.F. Petrik, A critical review on ozone and co-species, generation and reaction mechanisms in plasma induced by dielectric barrier discharge technologies for wastewater remediation, *J. Environ. Chem. Eng.* 9 (5) (2021) 105758.
- [15] P. Bruggeman, C. Leys, Non-thermal plasmas in and in contact with liquids, *J. Phys. D Appl. Phys.* 42 (5) (2009) 053001.
- [16] B. Wang, W. Shi, H. Zhang, H.Y. Ren, M.Y. Xiong, Promoting the ozone-liquid mass transfer through external physical fields and their applications in wastewater treatment: a review, *J. Environ. Chem. Eng.* 9 (5) (2021) 106115.
- [17] M. Rahimpour, H. Taghvaei, M.R. Rahimpour, Degradation of crystal violet in water solution using post discharge DBD plasma treatment: factorial design experiment and modeling, *Chemosphere* 232 (2019) 213–223.
- [18] A.J. Moreira, A.C. Borges, B.B. de Souza, L.R. Barbosa, V.R. de Mendonça, C.D. Freschi, G.P.G. Freschi, Microwave discharge electrodeless mercury lamp (Hg-MDEL): an energetic, mechanistic and kinetic approach to the degradation of Prozac®, *J. Environ. Chem. Eng.* 7 (2) (2019) 102916.
- [19] J.O.D. Malafatti, A.J. Moreira, C.R. Sciena, T.E.M. Silva, G.P.G. Freschi, E.C. Pereira, E.C. Paris, Prozac® removal promoted by HAP: Nb₂O₅ nanoparticles system: by-products, mechanism, and cytotoxicity assessment, *J. Environ. Chem. Eng.* 9 (2) (2021) 104820.
- [20] C. Liang, Z.H. Liu, B.C. Sun, H.K. Zou, G.W. Chu, Improvement in discharge characteristics and energy yield of ozone generation via configuration optimization of a coaxial dielectric barrier discharge reactor, *Chin. J. Chem. Eng.* 60 (2023) 61–68.
- [21] Y. Cai, G.W. Chu, Y. Luo, M.J. Su, B.J. Wang, B.C. Sun, J.F. Chen, An evaluation of metronidazole degradation in a plasma-assisted rotating disk reactor coupled with TiO₂ in aqueous solution, *Engineering* 7 (11) (2021) 1603–1610.
- [22] A.R. Lado Ribeiro, N.F.F. Moreira, G. Li Puma, A.M.T. Silva, Impact of water matrix on the removal of micropollutants by advanced oxidation technologies, *Chem. Eng. J.* 363 (2019) 155–173.
- [23] M. Aliste, C.M. Martínez, I. Garrido, P. Hellín, P. Flores, J. Fenoll, Multivariate effect of inorganic wastewater matrix on the removal of pesticides by solar photo-Fenton, *J. Environ. Manag.* 345 (2023) 118699.
- [24] P. Soriano-Molina, P. Plaza-Bolaños, A. Lorenzo, A. Agüera, J.L. García Sánchez, S. Malato, J.A. Sánchez Pérez, Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circum-neutral pH from very different municipal wastewater effluents, *Chem. Eng. J.* 366 (2019) 141–149.
- [25] Q.R. Zhang, G.Z. Qu, T.C. Wang, C.G. Li, H. Qiang, Q.H. Sun, D.L. Liang, S.B. Hu, Humic acid removal from micro-polluted source water in the presence of inorganic salts in a gas-phase surface discharge plasma system, *Sep. Purif. Technol.* 187 (2017) 334–342.
- [26] Y.X. Lu, W.L. Xu, H.S. Nie, Y. Zhang, N. Deng, J.Q. Zhang, Mechanism and kinetic analysis of degradation of atrazine by US/PMS, *Int. J. Environ. Res. Publ. Health* 16 (10) (2019) 1781.
- [27] Q.Z. Dai, J.Z. Zhou, X.Y. Meng, D.L. Feng, C.Q. Wu, J.M. Chen, Electrochemical oxidation of cinnamic acid with Mo modified PbO₂ electrode: electrode characterization, kinetics and degradation pathway, *Chem. Eng. J.* 289 (2016) 239–246.
- [28] Z.N. Wen, Y.B. Li, W. Liu, Y. Luo, L.L. Zhang, G.W. Chu, Flow behavior in a rotating packed bed reactor with single-layer mesh: effect of fiber cross-sectional shape, *Chem. Eng. Sci.* 248 (2022) 117147.
- [29] T.Y. Guo, K.P. Cheng, L.X. Wen, R. Andersson, J.F. Chen, Three-dimensional simulation on liquid flow in a rotating packed bed reactor, *Ind. Eng. Chem. Res.* 56 (28) (2017) 8169–8179.
- [30] C. Liang, Y. Cai, K. Li, Y. Luo, Z. Qian, G.W. Chu, J.F. Chen, Using dielectric barrier discharge and rotating packed bed reactor for NO_x removal, *Sep. Purif. Technol.* 235 (2020) 116141.
- [31] R. Mosteo, N. Miguel, S. Martín-Muniesa, M.P. Ormad, J.L. Ovelheiro, Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process, *J. Hazard. Mater.* 172 (2–3) (2009) 661–666.
- [32] F.M. Huang, L. Chen, H.L. Wang, Z.C. Yan, Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma, *Chem. Eng. J.* 162 (1) (2010) 250–256.
- [33] Y.N. Liu, S.F. Zhu, H. Tian, M. Zhou, J. Miao, Effect of inorganic ions on the oxidation of methyl violet with gliding arc discharge of arcs plasma discharge, *Plasma Process.* 33 (4) (2013) 737–749.
- [34] D.R. Merouani, F. Abdelmalek, F. Taleb, M. Martel, A. Semmoud, A. Addou, Plasma treatment by gliding arc discharge of dyes/dye mixtures in the presence of inorganic salts, *Arab. J. Chem.* 8 (2) (2015) 155–163.
- [35] H.V. Lutze, S. Bircher, I. Rapp, N. Kerlin, R. Bakkour, M. Geisler, C. von Sonntag, T.C. Schmidt, Degradation of chlorotriazine pesticides by sulfate radicals and the influence of organic matter, *Environ. Sci. Technol.* 49 (3) (2015) 1673–1680.
- [36] Y. Yang, J. Jiang, X.L. Lu, J. Ma, Y.Z. Liu, Production of sulfate radical and hydroxyl radical by reaction of ozone with peroxymonosulfate: a novel advanced oxidation process, *Environ. Sci. Technol.* 49 (12) (2015) 7330–7339.
- [37] J.B. Zhang, Z. Zheng, Y.N. Zhang, J.W. Feng, J.H. Li, Low-temperature plasma-induced degradation of aqueous 2,4-dinitrophenol, *J. Hazard. Mater.* 154 (1–3) (2008) 506–512.
- [38] M.M. Sein, A. Golloch, T.C. Schmidt, C. von Sonntag, No marked kinetic isotope effect in the peroxone (H₂O₂/D₂O²⁺+O₃) reaction: mechanistic consequences, *ChemPhysChem* 8 (14) (2007) 2065–2067.
- [39] T. Zhang, J.P. Croué, Catalytic ozonation not relying on hydroxyl radical oxidation: a selective and competitive reaction process related to metal–carboxylate complexes, *Appl. Catal. B Environ.* 144 (2014) 831–839.
- [40] J.A. Khan, X.X. He, N.S. Shah, H.M. Khan, E. Hapeshi, D. Fatta-Kassinos, D.D. Dionysiou, Kinetic and mechanism investigation on the photochemical degradation of atrazine with activated H₂O₂, S₂O₈²⁻ and HSO₅⁻, *Chem. Eng. J.* 252 (2014) 393–403.
- [41] Y.F. Ji, C.X. Dong, D.Y. Kong, J.H. Lu, Q.S. Zhou, Heat-activated persulfate oxidation of atrazine: implications for remediation of groundwater contaminated by herbicides, *Chem. Eng. J.* 263 (2015) 45–54.
- [42] L.L. Bo, H.D. Kiriarachchi, J.A. Bobb, A.A. Ibrahim, M.S. El-shall, Preparation, activity, and mechanism of ZnIn₂S₄-based catalysts for photocatalytic degradation of atrazine in aqueous solution, *J. Water Process Eng.* 36 (2020) 101334.
- [43] D. Majhi, K. Das, A. Mishra, R. Dhiman, B.G. Mishra, One pot synthesis of CdS/BiOBr/Bi₂O₂CO₃: a novel ternary double Z-scheme heterostructure photocatalyst for efficient degradation of atrazine, *Appl. Catal. B Environ.* 260 (2020) 118222.
- [44] K. Zhao, X. Quan, S. Chen, H.T. Yu, Y.B. Zhang, H.M. Zhao, Enhanced electro-Fenton performance by fluorine-doped porous carbon for removal of organic pollutants in wastewater, *Chem. Eng. J.* 354 (2018) 606–615.
- [45] S.H. Wu, H.J. He, X. Li, C.P. Yang, G.M. Zeng, B. Wu, S.Y. He, L. Lu, Insights into atrazine degradation by persulfate activation using composite of nanoscale zero-valent iron and graphene: performances and mechanisms, *Chem. Eng. J.* 341 (2018) 126–136.
- [46] X.B. Wang, Y.Y. Wang, N. Chen, Y.B. Shi, L.Z. Zhang, Pyrite enables persulfate activation for efficient atrazine degradation, *Chemosphere* 244 (2020) 125568.
- [47] H. Zhang, J.P. Duan, P.C. Luo, L.X. Zhu, Y.N. Liu, Degradation of atrazine in water by dielectric barrier discharge combined with periodate oxidation: enhanced performance, degradation pathways, and toxicity assessment, *Toxics* 12 (10) (2024) 746.