

Activation of peroxymonosulfate using biochar for the removal of trimethoprim: Effect of ball milling on catalytic efficiency, degradation pathway, and the contribution of the radical and non-radical processes

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ABSTRACT

The combination of biochar (BC) and peroxymonosulfate (PMS) is a cost-effective strategy for removing pollutants; however, optimization of BC synthesis and reaction parameters is essential. In this work, one-step pyrolysis was used for biochar production, and trimethoprim (TRIM) antibiotic degradation was investigated in the presence of PMS-containing biochar suspension. For the production of an effective biochar catalyst, grass pellets as the raw material, a pyrolysis temperature of 700 °C, and a ball-milling time of 15 min proved optimal for TRIM degradation. The effect of pyrolysis temperature highlighted that the appropriate degree of graphitization is a key factor in catalytic efficiency, while persistent free radicals (PFRs) on the surface play only a moderate role. Ball milling significantly reduced the amount of biochar ($3.0 \text{ gdm}^{-3} \rightarrow 0.5 \text{ gdm}^{-3}$) and PMS ($2.0 \text{ mM} \rightarrow 0.2 \text{ mM}$) required for TRIM degradation. In addition to the increased surface area, the enhanced density of structural defects serves as active sites, and changes in surface oxidation state also contribute to the enhanced efficiency of ball-milled biochar. The effect of radical scavengers clearly confirmed that, without ball milling, the main reactive species is $^1\text{O}_2$, and the non-radical pathway leads to the conversion of TRIM. In the case of ball-milled biochar, radical ($\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$) formation is favored, and the radical-based pathway dominates in the TRIM conversion. Although treated wastewater reduced the degradation efficiency, this effect was mitigated by higher BC and PMS doses. Furthermore, the results regarding the reusability of BC and its successful regeneration by UV/PDS underscore the potential of this process.

1. Introduction

Clean water is essential for healthy ecosystems and for various human uses and industrial purposes. The efficiency of the traditional biological water treatment process is limited in its ability to eliminate micro-pollutants, especially antibiotics, which require special attention due to the serious consequences of antibiotic resistance. Consequently, the European Parliament recently approved a new Urban Wastewater Treatment Directive (EU 2024/3019, replacing the previous Directive 91/271/EEC), which addresses environmental and health concerns related to micropollutants and their removal.

Trimethoprim ($\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$, TRIM) is among the top five antibiotics

globally detected in surface waters. It is predominantly used to treat urinary tract infections in animals and humans, and as a feed additive in the livestock industry to enhance animal growth. The residual TRIM and metabolites have been detected in the effluent of wastewater treatment plants and has also been found in municipal wastewater ($0.17\text{--}8.8 \mu\text{g L}^{-1}$), hospital wastewater ($>10 \mu\text{g L}^{-1}$), surface water ($>25 \mu\text{g L}^{-1}$), river water (up to 60 ng L^{-1}) [1] and hospital sewage wastewater ($600\text{--}760 \mu\text{g L}^{-1}$) [2]. The presence of trace amounts of TMP can pose risks to aquatic ecosystems and promote the development of antibiotic-resistant bacterial strains.

Recently, persulfate-based advanced oxidation processes (PS-AOPs), as tertiary water treatment methods, have garnered attention due to the

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generation of highly reactive sulfate ($\text{SO}_4^\bullet$) and hydroxyl radicals ($\bullet\text{OH}$). In PS-AOPs, the persulfate (PS), i.e. Peroxymonosulfate (PMS) and Peroxydisulfate (PDS) is activated via various methods. Despite their effectiveness, these PS activation techniques have some disadvantages; for example; thermal or radiation methods are expensive and energy-intensive, and transition metals result in secondary contamination due to metal leaching and sludge formation. Therefore, studies have been carried out to explore environmentally friendly catalysts that can effectively activate PS. In recent years, carbonaceous materials such as biochar, particularly those derived from waste biomasses, are conceptually beneficial because they reduce waste and can be used as catalysts in PS-AOP.

Biochar (BC) is obtained mainly by the pyrolysis of biomass in an oxygen-free environment and is suitable for H_2O_2 and PS, especially for PMS activation. In addition to the defective structures (edge defects, curvatures, and vacancies), the biochar-bound persistent free radicals (PFRs) are considered active centers for generating reactive species ($\text{SO}_4^\bullet$, $\bullet\text{OH}$, and $^1\text{O}_2$) [3,4]. Partly due to the variety of synthesis methods, the complex processes occurring on the surface of biochars, and the complex set of radicals, uncovering the mechanisms of organic compound transformation remains challenging. The structural and surface properties of biochar are determined by the biomass source, pre- and post-treatment methods, and pyrolysis conditions. The temperature and duration of pyrolysis affect the specific surface area, the degree of graphitization, and the quality and density of surface groups on the biochar. The increase of temperature accelerates the transformation of oxygen-containing groups ($\text{C}=\text{O}$, $\text{C}-\text{OH}$, $\text{C}-\text{OOH}$, $\text{C}-\text{O}-\text{C}$) and are supposed to play a role in activating PS. The oxygen-centered PFRs can be formed at relatively low temperatures (300–400 °C); however, with increased pyrolysis temperatures, the density of oxygen-containing functional groups gradually decreases, and most of them transform to carbon-centered PFRs [5,6]. The graphitic framework of biochar obtained at higher temperatures (>700 °C) manifests a better conductivity and faster electron transfer, which would accelerate pollutants remediation. The roles of various PFRs, the graphitic framework, and defective structures of BC in PMS activation are complex; to the best of our knowledge, this topic still needs further study.

Generally, biochar can donate electrons and initiate the formation of radicals ($\bullet\text{OH}$ and $\text{SO}_4^\bullet$) from H_2O_2 or PS. In addition to radical-based reactions [7], a non-radical pathway [8] for transforming organic pollutants is also possible and primarily based on $^1\text{O}_2$ formation. Nonetheless, the kinetics of these non-radical pathways are generally slower than those of $\bullet\text{OH}$ - and $\text{SO}_4^\bullet$ -based mechanisms. Although studies have provided insights into the catalytic properties of biochar, a knowledge gap remains regarding the mechanisms of the formation of the various reactive species and their contributions to pollutant transformation. The available information is sometimes fragmented, leading to contradictory interpretations. The formation of reactive species and the relative contributions of radical and non-radical processes in transforming the target compound are influenced by the quality and density of biochar's active centers [9]. The interaction between biochar and the target compound also influences transformation, primarily the charge-transfer processes; however, the structure and reactivity of the target compound toward different reactive species are also decisive for efficiency. Thus, due to the diversity of transformation pathways, the complexity of reactive species, and the interactions in the biochar/PMS system, it is difficult to distinguish individual processes and determine their relative contributions to the transformation. The efficiency of biochar-based and other AOPs in TRIM removal is compared and presented in Table S1.

Ball milling is often used to enhance specific surface area and increase the efficiency of biochar-based processes [10–14]. However, ball milling can increase the number and density of surface defects, such as edge sites, and alter the acidity and surface charge due to oxidized surface functional groups [14–17]. In biochar-activated PMS systems, edge sites provide highly reactive carbon atoms that facilitate electron transfer and boost the efficiency of PMS oxidation processes [3,15,16].

These regions often host oxygen-containing functional groups that enhance PMS activation toward radicals. Overall, ball-milling induces changes that may affect the efficiency of reactive compound formation and the rate of transformation of the organic compound in the biochar/PMS system. However, the deeper investigation of this is still incomplete.

During application, several factors can reduce biochar's catalytic activity, including adsorption of intermediate products, blocking of active centers responsible for radical formation, pore clogging, and oxidation of functional groups and PFRs. Therefore, regeneration of the biochar surface is essential. Thermal regeneration (pyrolysis or combustion in a controlled atmosphere) is widely used to remove adsorbed organic intermediates, reopen pores, and restore active sites. However, high temperatures can alter biochar structure (pore collapse, changes in surface properties, and loss of oxygen-containing functional groups), thereby reducing catalytic activity and limiting regeneration efficiency [18]. Regeneration of the surface with acids, bases, or oxidants is only partially effective and often impairs catalytic activity, as PMS or H_2O_2 consume oxygen-containing functional groups and PFRs [19,20].

This work aims to investigate the effect of raw material, pyrolysis temperature and ball-milling treatment time on the catalytic activity of waste biomass-derived biochar in PMS activation and TRIM elimination. The effect of radical scavengers and EPR studies were performed to gain a deeper understanding of the formation of the radical set and the relative contribution of various reactive species to the transformation of the TRIM. In the case of all AOP methods, it is crucial to examine the effect of the matrix for the purpose of practical applicability. Matrix components can significantly change the efficiency of the method by acting as radical scavengers, internal filters in the case of photochemical methods, or by adsorbing onto the surface of the catalyst in the case of heterogeneous catalysis. To provide insights into the practical applicability of the process, the matrix effect, reusability and regeneration of biochar were also studied.

2. Materials and methods

2.1. Materials

Trimethoprim (TRIM), an antibiotic, was used as the target substance. Oxone ($2\text{KHSO}_5 \times \text{KHSO}_4 \times \text{K}_2\text{SO}_4$, containing peroxymonosulphate (KHSO_5 , PMS) as active gradient), Sodium-peroxydisulfate ($\text{Na}_2\text{S}_2\text{O}_8$; PDS), and Sodium-peroxydisulfate were used as oxidants. Ultrapure water from Merck Millipore was used to prepare the solutions. Each chemical was used without further purification. Table S2 shows the purity and manufacturer of each applied chemical and material. Table S3 shows the data of the biologically treated domestic wastewater (from the water treatment plant, Szeged, Hungary) used as a matrix.

2.2. Preparation of biochar

Three raw materials for biochar preparation were poplar wood (PW), corn-cob (CC), and grass pellet (GP). The PW was collected locally, while CC and GP were purchased from a pet food store. The raw materials were crushed in an electric shredder. Subsequently, these materials were washed with distilled water, dried at 90 °C and pyrolyzed for 3 h, under continuous nitrogen flow (50 mL min^{-1}). The initial temperature of pyrolysis was 30 °C, the heating rate was 5 °C min^{-1} up to the pyrolysis temperature (changed from 400 to 800 °C). The prepared biochar was labeled as PW-BC_x, CC-BC_x, and GP-BC_x, with X denoting the pyrolysis temperature. The biochars were further treated using physical modification through ball-milling for 15 min (Tungsten carbide grinding jar (80 mL), 25 grinding balls, 450 rpm), resulting in PW-^{BM}BC_x, CC-^{BM}BC_x, and GP-^{BM}BC_x, where BM represents ball-milling.

2.3. Experimental procedure

A batch-scale study was conducted in a 150 mL beaker at room temperature. 100 mL of TRIM solution and biochar were mixed in the beaker. The PMS was added to the suspension after achieving the adsorption equilibrium (30 min). After sampling, the PMS residual was decomposed by adding sodium thiosulfate to the sample. For analyzing TRIM transformation, samples were collected, centrifuged, and filtered with a syringe filter (PES, pore size 0.1 μm).

2.4. Characterization of biochars

Powder X-ray diffractograms (XRD) were measured in the range $2\theta = 5\text{--}80^\circ$ (the most relevant region of $10\text{--}60^\circ$ can be seen) by a Rigaku Miniflex II instrument at a scanning speed of 4°min^{-1} using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV, 30 mA. The characteristic reflections were identified with the aid of the database JCPDS-ICDD (Joint Committee of Powder Diffraction Standards- International Centre for Diffraction Data).

The specific surface area was determined via N_2 adsorption/desorption isotherms using a Quantachrome NOVA 2200 analyser, according to the BET equation. Thermogravimetric measurements were achieved using a TA Instruments Q500 TGA device in inert nitrogen flow, using a heating rate of $5^\circ \text{C min}^{-1}$. The DSC measurements were performed using a TA Instruments Q200 device in modulated mode ($0.5^\circ \text{C min}^{-1}$) with Tzero aluminum sample holders. A scanning electron microscope (SEM) (Zeiss-Sigma VP) was conducted to examine morphological features and particle size of the prepared biochars.

A Kratos XSAM 800 X-ray photoelectron spectroscope was operated using an Al $\text{K}\alpha$ source with 120 W (12 kV) power. As sample preparation, the powdered samples were pressed into double-sided carbon tapes attached to the sample holder. Survey spectra were collected with 160 eV pass energy and 1 eV step size. High-resolution spectra were collected with 40 eV pass energy and 0.1 eV step size. Charge accumulation on the sample surface was observed in the spectra during measurement. Charge compensation was achieved with an electron flood gun. Spectra were fit using CasaXPS software version 2.3.22PR1.0. All high-resolution spectra were charge corrected for the aliphatic component of the C 1s spectrum at 284.8 eV. All high-resolution spectra were background-corrected using a Shirley background. All peaks were fit with a Gauss-Lorentzian product function peak shape where the Lorentzian contribution is 0.3. The only exception to this is the $\text{sp}^2 \text{C}$ species, which have an asymmetric Lorentzian peak shape. The species present on the surface were quantified with the corresponding peak surface areas, which were corrected with relative sensitivity factors (RSF) based on Scofield photoionization cross-sections.

Raman spectra were detected using a Bruker Senterra II Raman microscope. Spectra were taken by using a light source of 532 nm wavelength and 12.5 mW laser power. For each sample, 32 spectra were collected and averaged with an exposition time of 6 s.

Hydrodynamic diameter and electrophoretic mobility measurements were performed at 25°C using a Malvern Zetasizer NanoZS instrument, equipped with a 4 mW He–Ne laser ($\lambda = 632 \text{ nm}$) at a backscattering angle of 173° . Aqueous dispersions of biochar samples were analyzed in ultrapure water at a final concentration of 0.1 mg cm^{-3} in the presence of $10^{-5} \text{ mol dm}^{-3}$ of NaCl. The pH of the particle dispersion was adjusted by diluted HCl or NaOH solutions right before the analysis. The intensity-average hydrodynamic diameter (Z_{Ave}, in nm) and polydispersity index (PDI) were obtained by cumulant analysis of the correlation function. The zeta potential (ZP, in mV) was calculated from the electrophoretic mobility values using the Smoluchowsky relationship and assuming that $Ka \gg 1$ (where K and a are the Debye–Hückel parameter and particle radius, respectively).

EPR measurements were carried out to analyze the persistent free radicals (PFRs) on the surface of biochar, responsible for catalytic activity and reactive species formation, in an aqueous suspension of

biochar in the presence of PMS. For solid samples, 0.20 mg of biochar was loaded into a glass capillary (with an internal diameter of 1 mm). For suspensions, samples were prepared in the presence of biochar and, for the control, in its absence: 0.2 mg of biochar was suspended in 25 μL of 60 mM spin trap (DMPO, TEMP, or $\text{TEMPD} \times \text{H}_2\text{O}$) dissolved in water. All continuous-wave EPR measurements were carried out on a Bruker ELEXSYS-II E580 X-band spectrometer at room temperature, with the following instrument settings: for solid samples, a 350–6350 G scan range, 0.474 mW microwave power, and a 3.0 G modulation amplitude was used. In the case of aqueous suspensions 3255–3455 G scan range, 1.5 mW microwave power and 1.5 G modulation amplitude was used.

2.5. Analytical methods

The samples were analyzed with high-performance liquid chromatography (HPLC). The concentration of TRIM was determined using an Agilent 1100 HPLC system equipped with a diode array detector (DAD) and a C18 column, thermostated to 30°C . The mobile phase contained 20 % methanol and 80 % formic acid buffer, and the flow rate was maintained at 1.0 mL min^{-1} . The detection wavelength was 275 nm.

The formation of $\text{SO}_4^{\cdot -}$ was measured using ion chromatography (Shimadzu, Kyoto, Japan) Prominence LC-20AD, Shodex NI-424 5U for anion detection. The eluent was a mixture of phthalic acid (2.5 mM) and aminomethane (2.3 mM), the flow rate of the mobile phase was 1.0 mL min^{-1} .

The products were identified using an Agilent LC/MSD VL mass spectrometer coupled to the HPLC device. The solid phase extraction was used as a sample-pretreatment method; 10 mL of the sample was loaded onto the SPE cartridge (Stata-X 33u, Phenomenex). After washing (2.0 mL water), elution was performed using 1.5 mL methanol. The positive electrospray ionization (ESI) mode was used (3.5 kV capillary voltage, 300°C drying gas temperature, and 70 V fragmentor voltage).

2.6. Kinetic models

Generally, the catalytic oxidation of organic pollutants was frequently fitted with the pseudo-first-order kinetic model (PFO) [1]:

$$\ln \frac{C_t}{C_0} = -k_{\text{PFO}} \times t \quad (1)$$

where k_{PFO} is the pseudo-first-order rate constant (min^{-1}), C_0 and C_t are the initial and actual concentration of the TRIM, respectively. By plotting $-\ln(C_t/C_0)$ versus t , a straight line with slope k_{PFO} can be obtained.

The PFO kinetic was used in the case of TRIM degradation using biochars prepared without ball-milling, however, for ball-milled biochars, the PFO kinetic is not suitable. In these cases (Fig. S1 and Table S4), the model developed by Zhu et al. [21] was used. The proposed model is a two-stage mathematical model (TSM) consisting of a fast “reaction stage” followed by a slow “stagnant stage”, which can properly describe the two-stage degradation curve. The model equations are as follows:

$$\frac{C_t}{C_0} = 1 - \frac{t}{k_1 + k_2 t} \quad (2)$$

where k_1 (min) and k_2 (dimensionless) are two characteristic constants in reaction kinetics and oxidation capacities. By plotting $t/(1 - C_t/C_0)$ versus t , a straight line is obtained with two kinetic constants, the intercept k_1 as well as slope k_2 . The physical meaning of $1/k_1$ (min^{-1}) is the initial removal rate and $1/k_2$ represents the degradation efficiency, i. e. maximal oxidation capacity.

3. Results and discussion

3.1. Optimization of synthesis conditions and reaction parameters

3.1.1. Effect of feedstock

In the case of the first runs, the biochars were prepared at 700 °C. The pyrolysis temperature was chosen based on publications on the application of biochar for PMS activation, and on thermogravimetric analysis of the raw materials (Fig. S2). The main weight loss occurred between 200 °C and 400 °C, reflecting the devolatilization of hemicellulose and cellulose. A further increase in temperature resulted in moderate weight loss. After the 3 h pyrolysis at 700 °C, an average weight loss of 75–80 % was measured for each raw material.

Comparing the biochars synthesized from three different materials, the specific surface area is influenced by the type of feedstock, due to differences in chemical composition, lignin, cellulose, ash content, and structure. The prepared biochars have a small specific surface area, which could be attributed to dead-end pores and inorganic materials that partially fill or block them (Table 1).

2.0 mM PMS, without biochar, caused less than 10 % of TRIM (0.05 mM) transformation (not shown). As PMS was added to the biochar suspension, the degradation of TRIM became significant (Fig. 1). Adsorption capacities of biochars were quite low (Table 1, Fig. S3), and the GP-BC₇₀₀ proved the best efficiency for TRIM transformation (Fig. 1). The surface area of GP-BC₇₀₀ was found to be higher than that of

PW-BC₇₀₀ and CC-BC₇₀₀; however the adsorption capacity for TRIM was lower than that of CC-BC₇₀₀ (Table 1). Lopez et al. [22] observed that the acidity and total number of accessible surface functional groups were different and depended mainly on the original oxygen content of the raw material. However, XPS results showed no difference in the surface element distributions (C, N, and O) among the three biochars (Table S5). The outstanding activity of GP-BC₇₀₀ is attributed to its relatively larger surface area and advanced graphitization, as indicated by the atomic ratio of carbon atoms in *sp*²-hybridization states (19.8, 23.8 and 27.0 for PW-BC₇₀₀, CC-BC₇₀₀ and GP-BC₇₀₀, respectively, Table S5), as well as the combined effects of surface functional groups, the latter of which can be significantly influenced by the quality of the feedstock.

3.1.2. Effect of biochar dose and PMS concentration

The TRIM concentration, PMS, and biochar dosage were optimized for non-milled biochars (Figs. S4-S5 and Table S6). During TRIM transformation, the pH of the biochar suspension was 9.5–10.0, addition of TRIM (pK_{a1} = 3.2 and pK_{a2} = 6.7 [1]) did not change the pH, while addition of PMS decreased to 6.2–7.2. Thus, without the PMS, TRIM is in anionic form in the biochar suspension, while in the presence of PMS, TRIM is mainly in neutral form. The surface charge of biochar is negative within the pH range 3.2–10 (pH PZC is 3.2) (Fig. S6). Consequently, the adsorption of TRIM on the negatively charged biochar surface in the pH range of 3–10 can occur primarily due to non-electrostatic interactions (e.g., π - π electron donor-acceptor interactions, hydrophobic

Table 1

The effect of raw material, ball milling and pyrolysis temperature on the surface area (SSA), adsorption capacity (q_m^*) and K_L values determined from Langmuir isotherm (Fig. S3) ($c^{BC} = 3 \text{ g L}^{-1}$, $c^{BMBC} = 0.5 \text{ g L}^{-1}$, $c^{TMP} = 0.05 \text{ mM}$ for BC and $c^{TMP} = 0.1 \text{ mM}$ for ^{BM}BC).

Biochar	SSA (m ² g ⁻¹)	q_m^* (mg.g ⁻¹)	K_L^*	R ²
<i>Effect of temperature and feedstock</i>				
GP-BC ₈₀₀	50	n.d.		
GP- ^{BM} BC ₈₀₀	161	5.68	1.48	0.47
GP-BC₇₀₀	49	1.00	0.72	0.99
GP-^{BM}BC₇₀₀	167	4.76	57.2	0.99
CC-BC₇₀₀	<10	1.62	1.39	0.99
CC-^{BM}BC₇₀₀	228	7.56	17.7	0.98
PW-BC₇₀₀	<10	0.59	0.21	0.90
PW-^{BM}BC₇₀₀	236	9.40	7.88	0.96
GP-BC ₆₀₀	101	n.d.		
GP- ^{BM} BC ₆₀₀	170	8.06	0.41	0.97
GP-BC ₅₀₀	132	n.d.		
GP- ^{BM} BC ₅₀₀	190	11.93	2.03	0.94
GP-BC ₄₀₀	160	n.d.		
GP- ^{BM} BC ₄₀₀	210	48.46	0.35	0.94
<i>Effect of ball milling treatment time (GP-BC₇₀₀)</i>				
Milling time (min)				
3.75	118	2.05	0.32	0.87
7.5	157	2.68	1.45	0.96
15	167	5.19	0.24	0.84
30	189	6.53	0.72	0.98
60	211	8.18	0.32	0.99

(Samples prepared at 700 °C were used to compare the effect of the raw material (highlighted in bold)).

*Determined from Langmuir isotherm (Fig. S2).

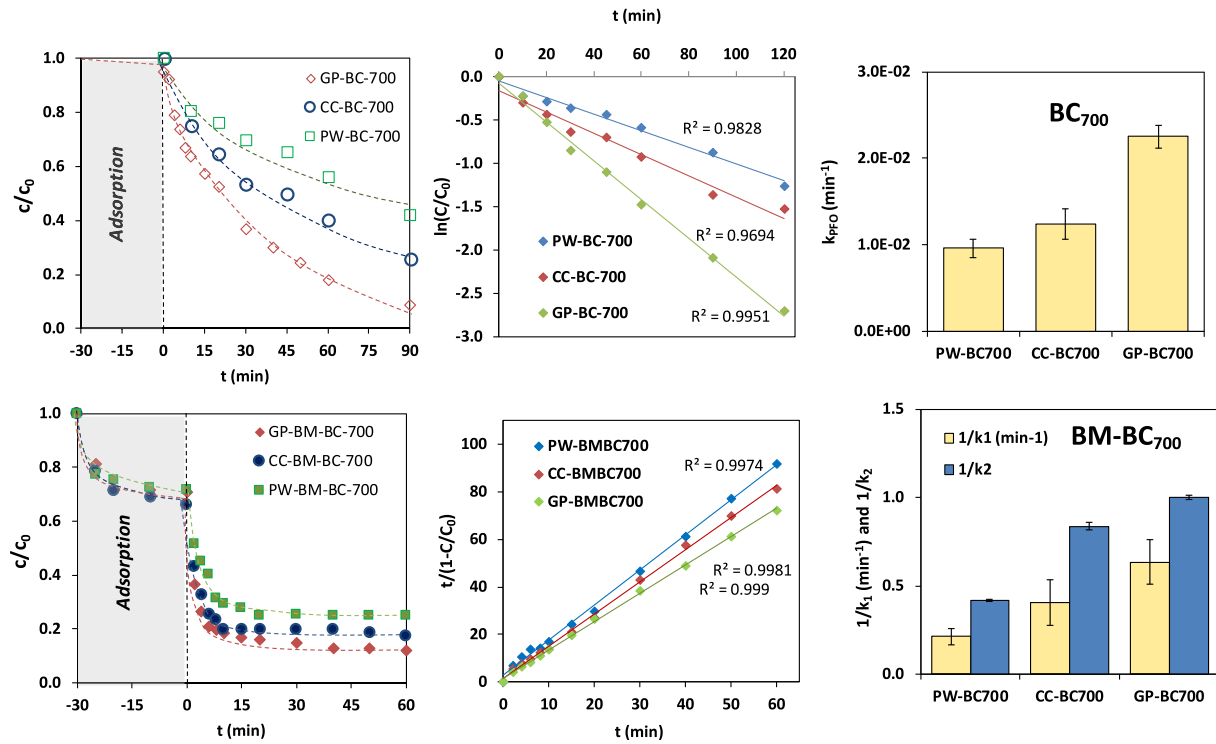


Fig. 1. The effect of feedstock GP (grass pellet), CC (corn cob), and PW (poplar wood) on the efficiency in TRIM transformation in the case of non-milled (A-C: 2.0 mM PMS, 3.0 g dm⁻³ BC) and ball-milled (D-F: 0.2 mM PMS, 0.5 g dm⁻³ BMBC) biochar samples, prepared under 700 °C. (B and C show the kinetic parameters derived from the pseudo-first-order model (PFO); E-F shows the kinetic parameters derived from the two-stage mathematical model (TSM).

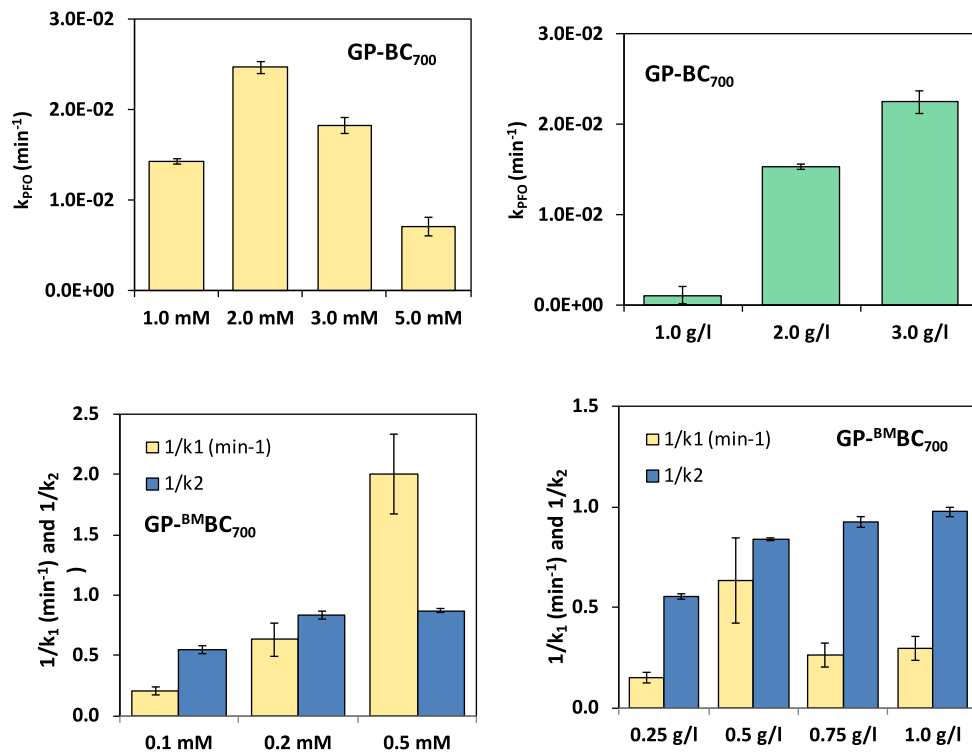
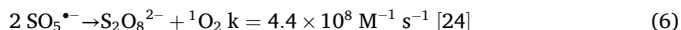
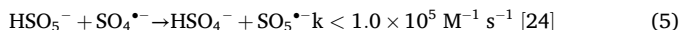
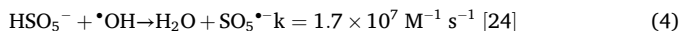
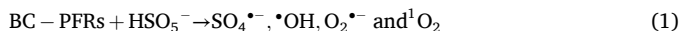


Fig. 2. The effect of PMS (A, C) and biochar (B, D) dose on the kinetic parameters of TRIM transformation in the case of GP-BC₇₀₀ and GP-BMBC₇₀₀ (A: 3.0 g dm⁻³ BC B: 2.0 mM PMS, D: 0.5 g dm⁻³ BMBC; E: 0.2 mM PMS).

(Panels A and B show the kinetic parameters derived from the pseudo-first-order model (PFO) applied in the case of non-milled biochars; panels C and E show the kinetic parameters derived from the two-stage mathematical model (TSM) applied in the case of ball-milled biochars).

interaction, and H-bonding).

The density of active sites of the biochar for PMS activation, as in the case of each catalyst, limits the transformation efficiency. The degradation rate of 0.05 mM TRIM increased with increasing BC dose due to more available active sites for PMS activation, especially when 1.0 g dm⁻³ dosage was doubled. The further increase up to 3.0 g dm⁻³ just slightly enhanced the efficiency for GP-BC₇₀₀; however, it has a significant positive effect for PW-BC₇₀₀ (Fig. 2, Table S6 and Figs. S4-S5). However, the elevated biochar dosages can result in particle aggregation, which reduces the accessible surface area. The increase of PMS dose from 1.0 mM to 2.0 mM results in a higher efficiency; however, further increase slightly reduces that (Fig. 2, Table S6 and Figs. S4-S5). Due to the PMS transformation on the biochar surface, SO₄^{•-}, [•]OH, O₂^{•-} and ¹O₂ can form (1–3). At elevated PMS dose, competition can occur between the reaction of radicals with PMS (4–5) and with the organic target substance, as TRIM; $k(\text{TRIM} + ^\bullet\text{OH}) = 8.66 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k(\text{TRIM} + \text{SO}_4^{\bullet-}) = 3.88 \pm 0.07 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{TRIM} + ^1\text{O}_2) = 3.2 \pm 0.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [23]. The reaction of radicals with PMS (4, 5) results in SO₅^{•-} having lower oxidative ability and reactivity than SO₄^{•-}. Thus, its formation cannot compensate for the decrease in SO₄^{•-} (5) and [•]OH (4) concentration available for TRIM to transform [24]



3.1.3. Effect of ball-milling time

Ball-milling enhanced the specific surface area (SSA), adsorption capacity (Fig. 3, Table 1 and Fig. S3), and catalytic activity of each BC (Figs. 1, 2 and S7, S8 and Table S7). The catalyst and PMS dose required for the transformation of TRIM decreased, highlighting the connection between SSA value and catalytic performance. Without ball-milling 3.0 g dm⁻³ BC₇₀₀ and 2.0 mM PMS dose resulted in 40–80 % transformation of 0.05 mM TRIM during 60 min, depending on the feedstock. However, 0.5 g dm⁻³ BMBC₇₀₀ dose was able to remove more than 70 % of 0.1 mM TRIM, with 0.2 mM PMS, within 10 min (Figs. 1 and S4, S7).

The effect of ball-milling on the SSA value (Table 1) is attributed to the reduction in particle size. Besides, the opening of dead-end pores makes the internal pore surface of the biochar accessible. The decrease in particle size was confirmed by changes in hydrodynamic diameter values (Fig. S6) and supported by the SEM images (Figs. S9, S10). The increase in SSA value enhanced the adsorption capacity (Fig. S3). The surface oxidation changes the surface functional groups, thereby modifying the surface charge, adsorption capacity and catalytic efficiency [16,25,26]. Ball-milling can intensify the oxidation of the functional groups on the surface due to the energy release, and increase the oxygen content, and the acidity of biochar [8,22,27,28]. The decrease in the Zeta potential also suggests that milling may have altered the surface functional groups (Fig. S6). The XPS spectra showed that 15 min of ball-milling increased the oxygen atomic concentration from 11.2 to 19.8 (Table S5), which also contributed to the change in catalytic activity. Both the graphitic C-OH (i.e., the hydroxyl group) and C=O can interact with PMS, reducing the activation energy required for PMS transformation and the production of reactive species [3]. The enhanced defect density is reflected in the increased intensity of the EPR signal (Fig. 3D and E).

In the case of ball-milled biochar 0.5 g dm⁻³ biochar dose adsorbed 30 % of 0.1 mM TRIM. The kinetic analysis of adsorption (Fig. S11,

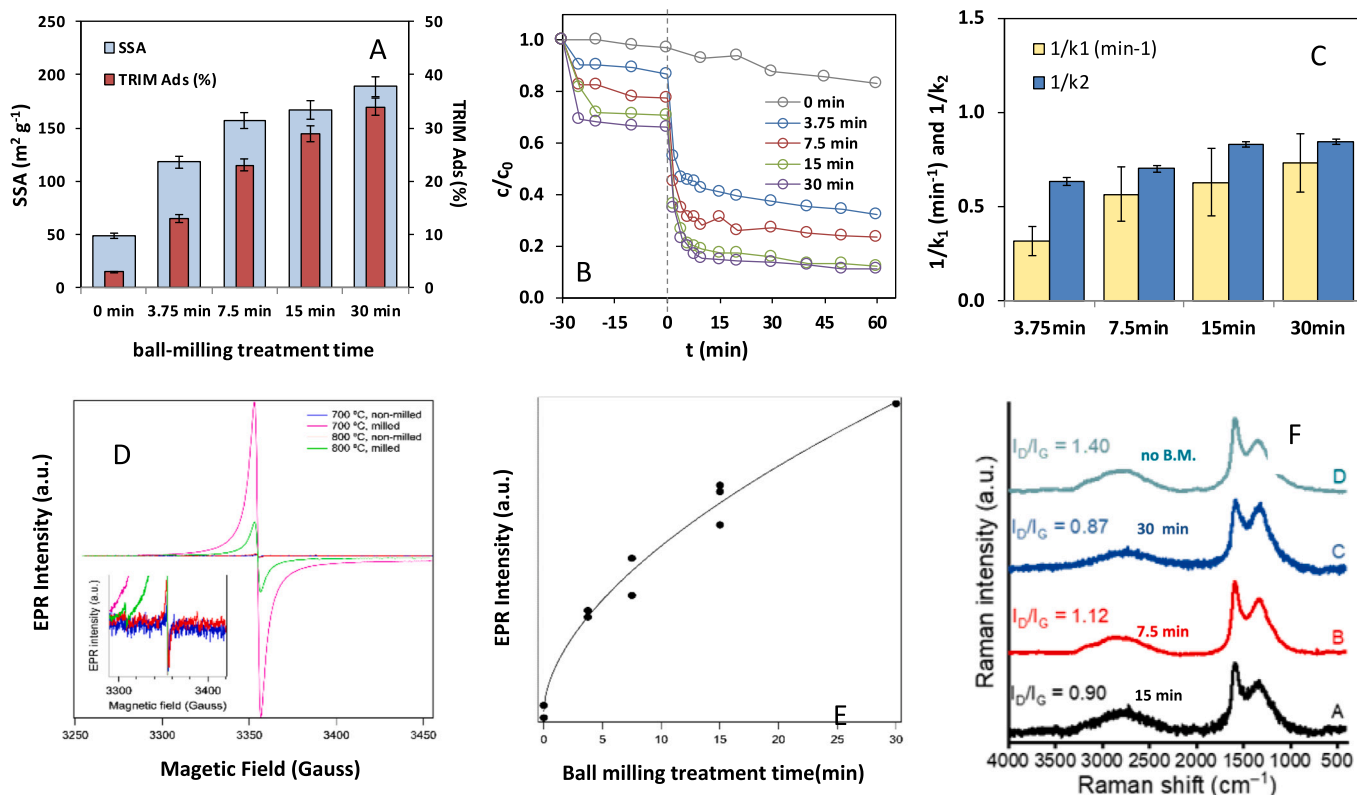


Fig. 3. The effect of ball-milling treatment time on the specific surface area (SSA) and TRM adsorption (A) and degradation efficiency (B and C $1/k_1$ refers to the initial transformation rate, $1/k_2$ refers to the maximum oxidation efficiency) ($c^{\text{BMBC}} = 0.5 \text{ gL}^{-1}$, $c^{\text{TMP}} = 0.1 \text{ mM}$ and $c^{\text{PMS}} = 0.2 \text{ mM}$), the EPR signal intensity (D and E) and Raman spectra (F) in the case of GP-BMBC₇₀₀.

Table S8) proved that adsorption is predominantly controlled by physisorption and chemisorption, with very limited influence from intra-particle pore diffusion. The active adsorption sites are mostly located on the external surface or in very large mesopores/macropores, which might have allowed rapid access of TRIM.

At 700 °C, amorphous to moderately crystalline graphite structures is formed. The sp^2 carbon atoms dominate in the Raman spectra (in the range of 1300–1600 cm^{-1}) (Fig. 3/F). The co-existence of the first-order G band ($\sim 1585 \text{ cm}^{-1}$) with the highest intensity, originating from the stretching modes of sp^2 carbon atoms in pairs, and the doubly-resonant second order D band ($\sim 1345 \text{ cm}^{-1}$), originating from the breathing modes of sp^2 carbon atoms in six-membered aromatic ring configurations, refers to the defect-containing graphite-like crystal structure [29]. If there were no defect sites in the structures, the D band would have disappeared, as it only becomes Raman active in the presence of crystal defects. The slight shift of the D-band (1339–1349 cm^{-1}) emphasizes the change of the structure from amorphous to graphitic. The intensity ratio of the in-plane bands (I_D/I_G) indicates the degree of structural disorder of graphitic materials and defect density [30]. The I_D/I_G value for GP-BC₇₀₀, decreased from 1.4 to 0.9 due to the 15 min ball-milling, which is attributed to the fragmentation of the biochar, providing more edges and/or surfaces, evidenced by the increase in SSA value (Table 1) and supported by the SEM images (Fig. SX). The effect of ball milling of the intensity of EPR signal (Fig. 3) is support that, the formed edges contributes to the radical formation. The edge sites facilitate electron transfer and boost the efficiency of PMS transformation and radical formation. Thus, in addition to the higher SSA value, the enhanced defect density most likely contributes to the improved catalytic activity. The I_D/I_G value was only slightly changed by ball milling for more than 15 min (Fig. 3/F), consistent with the effect of milling time on catalytic activity (Fig. 3C). Henceforth, 15 min of ball-milling was used for each sample.

3.1.4. Effect of pyrolysis temperature

The pyrolysis temperature is a crucial factor in determining the structure, surface properties, and activity of biochar. [25,31–35]. GP-

BC, as the most efficient catalyst, was selected to investigate the effect of pyrolysis temperature (Figs. 4, S8, S12 and S13). The SSA of GP-BC declined ($160 \rightarrow 50 \text{ m}^2 \text{ g}^{-1}$) with the temperature rise (Table 1), possibly because of the “ablation”, which causes pore interpenetration. Most likely, higher temperatures can lead to the collapse of the carbon skeleton structure, thereby diminishing the surface area. For the ball-milled samples, the SSA value decreased from 210 to $170 \text{ m}^2 \text{ g}^{-1}$ as temperature increased from 400 to 600 °C, but further increase in temperature did not cause any significant change (Table 1 and Fig. 4). The $^{BM}SSA:SSA$ ratio changed from 1.3 (400 °C) to 3.2 (800 °C), reflecting the formation of a more rigid and breakable structure at higher temperature. The effect of temperature on particle size and morphology is illustrated by scanning electron microscopy (SEM) images, supporting the conclusion that milling is more effective at reducing particle size for samples prepared at high temperatures (Fig. S13). The adsorption efficiency decreased ($67 \rightarrow 29 \%$), while degradation efficiency increased ($23 \rightarrow 59 \%$) as the pyrolysis temperature changed from 400 °C to 700 °C and a moderate decline was observed in the case of the sample prepared at 800 °C (Figs. 4 and S8 and S12).

To understand the most influential structural differences among the BCs, a combined XRD (Fig. 5/A), Raman (Fig. 5/B), EPR study (Fig. 5/C) and XP spectroscopy (Fig. 5/D–F) studies were performed (Fig. 4). Up to 500 °C, the devolatilization and decomposition of hemicelluloses and cellulose resulted a significant weight loss (Fig. S2) and formation of oxygen containing functional groups on the surface. The change in adsorption capacity up to 600 °C (Fig. 4) is mainly determined by the qualitative change in the surface groups; the slight decrease in SSA only partially influences it. Most likely, the sample prepared at 400 °C retains some cellulose and hemicellulose, which benefit the adsorption; however, the GP- $^{BM}BC_{400}$ does not have the necessary properties for PMS activation. Furthermore, TRIM adsorption may inhibit PMS activation by occupying active sites.

Pyrolysis at 500 °C leads to a significant change in activity, despite a 10 % decrease in specific surface area. The XRD studies (Fig. 5/A) show that amorphous to moderately crystalline graphite structures were formed and the crystallinity of the biochar-derived graphite structures

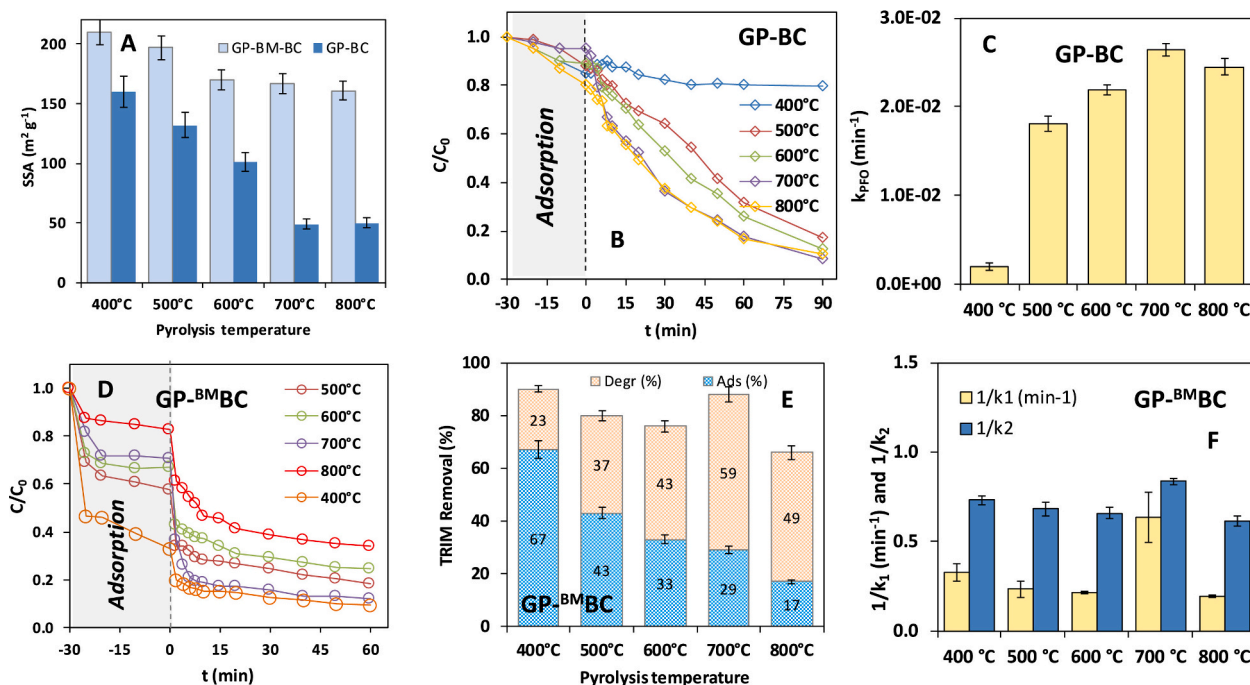


Fig. 4. Effect of pyrolysis temperature on the SSA value, and the TRIM adsorption and transformation efficiency in the case of GP- ^{BM}BC (A: SSA value of the GP-BC and GP- ^{BM}BC ; B,D,E: kinetic curves and efficiency of TRIM adsorption and degradation; C and F: kinetic parameters of TRIM transformation (B and C: $c^{BMBC} = 3.0 \text{ g L}^{-1}$, $c^{TMP} = 0.1 \text{ mM}$ and $c^{PMS} = 2.0 \text{ mM}$; D,E,F: $c^{BMBC} = 0.5 \text{ g L}^{-1}$, $c^{TMP} = 0.1 \text{ mM}$ and $c^{PMS} = 0.2 \text{ mM}$); C: adsorption and degradation efficiency of TRIM (60 min treatment)).

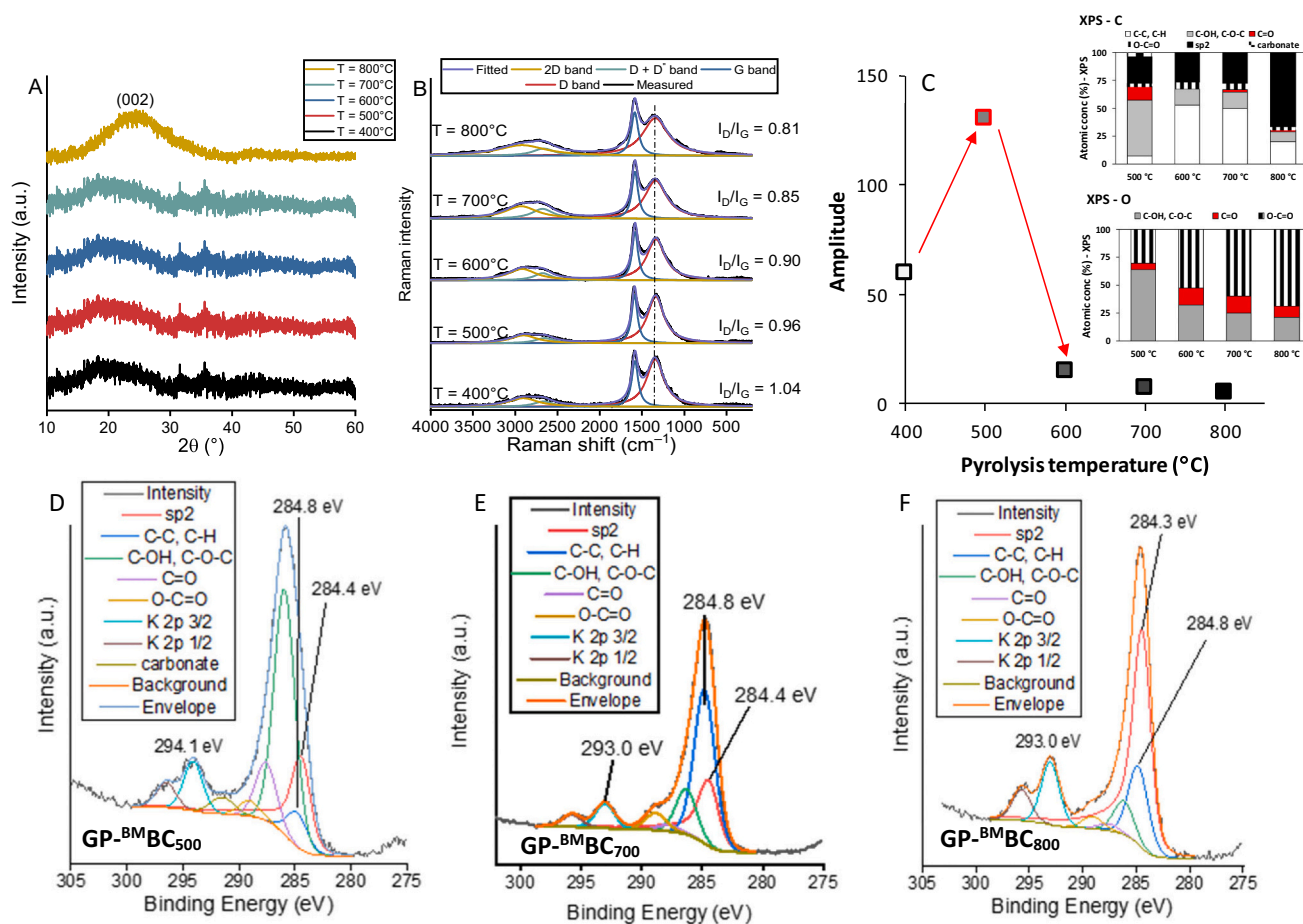


Fig. 5. The effect of pyrolysis temperature on the structure and properties of GP-BMBC (A: XRD; B: Raman spectra; C: EPR signal intensity (inserted: atomic concentration, calculated from XPS spectra of carbon and oxygen); D: XPS spectra of GP-BMBC₅₀₀; E: XPS spectra of GP-BMBC₇₀₀; F: XPS spectra of GP-BMBC₈₀₀).

increases with temperatures. For GP-BMBC₅₀₀, the increase of the EPR signal intensity (Fig. 5/C) indicates the change of PFRs density and the TRIM transformation can be interpreted by the interaction between PMS and PFRs [36,37]. The transformation of O-centered to C-centered PFRs occurs above 400 °C and the formed graphitic C=O groups can be decisive for PMS activation [38]. At this point, it is essential to note that the XPS study also revealed the absence of metals or other components that could alter the catalytic capabilities of the biochars. Increasing pyrolysis temperature changed the atomic concentration of carbon and oxygen atoms; and the carbon concentration shows a minimum, while oxygen shows a maximum value at 700 °C (Fig. S14). The results reflect the conversion of a saturated hydrocarbon chain to an unsaturated aromatic structure at 600 °C. Moreover, Tan et al. [39] observed that when the temperature changed from 500 to 600 °C, a significant loss of surface negative charge can occur, which can facilitate the accessibility of the BC surface for the negatively charged PMS, thereby enhancing the catalytic efficiency. At 700 °C, the coke on the biochar surface can undergo additional cracking reactions with CO₂ ($C + CO_2 \rightarrow 2CO\uparrow$), resulting in a lower carbon content. In contrast, at 800 °C, enhanced graphitization increases the carbon content. The XRD studies (Fig. 5A) confirmed that the crystallinity of the biochar-derived graphite structures increases with temperature, particularly when the temperature is changed from 700 °C to 800 °C. The concentration of carbon atoms in the sp² hybridization state increases moderately (23.8 → 27.8) when the temperature increases from 500 °C to 700 °C, but doubles (27.8 → 66.57) when the temperature increases to 800 °C (Fig. 5/C inserted). A significant decrease in PFR density was observed above 500 °C, and at 700 °C, PFRs are generally eliminated (Fig. 5/C) due to the breakdown and reorganization of organic structures [28,40]. For GP-BMBC₆₀₀ and

GP-BMBC₇₀₀, the defect density of the graphite structure became a crucial factor in determining catalytic activity.

The results of the Raman spectroscopy measurement showed a decrease in the I_D/I_G ratio with increasing temperature, which can be associated with the rearrangement leading to a more ordered structure. In the overtone region (2400–2900 cm⁻¹), a similar reordering can be followed; however, the much lower intensities make the correct explanation difficult. Comparing the Raman, XRD, and XPS results, we can conclude that the development of graphitization is beneficial to the catalytic activity to a certain extent. However, in the case of the sample prepared at 800 °C, the substantial increase in the degree of graphitization clearly moderated the catalytic activity (Fig. 4). Although defect density of graphitized structures is necessary to induce direct electron transfer to PMS [38], the enhanced conductivity due to the structural ordering at 800 °C, reduces the effectiveness of electron transfer processes. This finding can readily be related to the well-known phenomenon that the completion of a catalytic cycle is unfavorable in highly ordered structures compared to those with irregular structures containing defect sites.

3.2. Reactive species – contribution of radical and non-radical-based processes

Radical quenchers such as methanol (MeOH), *tert*-butyl alcohol (*t*-BuOH), and furfuryl alcohol (FFA) were used to identify the contributions of various reactive species. MeOH is known to be a moderately effective SO₄^{•-} ($2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [41] and effective [•]OH scavenger ($9.70 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [24], whereas *t*-BuOH scavenges [•]OH ($3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [24] and has a reactivity for SO₄^{•-} ($(4.0\text{--}9) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)

[42]. FFA ($1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [43] is widely used as a $^1\text{O}_2$ scavenger [24] and also reacts with $\text{SO}_4^\bullet$ (2.5×10^9 and $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [26]), and $^\bullet\text{OH}$ (7.1×10^9 and $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [24]. The reaction of FFA with radicals is often neglected when assessing the role of $^1\text{O}_2$, which might lead to potentially overestimation of $^1\text{O}_2$'s importance.

The negligible effect of *t*-BuOH and MeOH on TRIM degradation, indicated that there is no significant radical formation on the surface of non-milled BC_{700} . FFA exhibited an inhibition, highlighting that, the non-radical processes are mainly responsible for the relatively slow transformation in this case (Fig. 6A, B).

However, in the case of ball-milled biochar, radical scavenger MeOH and *t*-BuOH reduced the transformation efficiency (Fig. 6C and D). It is likely that ball mill modification induced reactive sites in the biochar structure, which are responsible for radical formation; consequently, radical pathways also contribute to TRIM degradation. The relative contributions of radical-based and non-radical pathways to TRIM transformation became comparable, as shown by the inhibitory effect of different scavengers (Fig. 5C and D).

The involvement of various reactive species ($\text{SO}_4^\bullet$, $^\bullet\text{OH}$ and $^1\text{O}_2$) was confirmed through EPR analysis, implemented in the $\text{GP}^\text{BM}\text{BC}_{700}$ suspensions (Fig. 5E). The presence of PMS in biochar suspension resulted in a seven-peak EPR spectrum, with intensity increasing with time (not shown). Highly oxidative conditions – as the presence of PMS or H_2O_2 – support the formation of DMPOX radical (5,5-di-methylpyrroline-(2-oxyl)-(1)) [44–46]. Our splitting constants (Table S9) agree with the results [5,47,48]. According to their proposed mechanism, in a highly oxidative medium, the formation of the DMPOX radical occurs via spin trapping of an oxidative radical, such as $\text{SO}_4^\bullet$ [38] or $^\bullet\text{OH}$ [47] by DMPO, followed by an intramolecular displacement. It should be noted that although the above publications assign the observed spectrum to DMPOX; a detailed explanation of the hyperfine line positions and relative intensities with respect to the molecular structure and nuclear spins is not provided. The DMPO-adduct of $\text{SO}_4^\bullet$ or $^\bullet\text{OH}$ cannot be detected simultaneously beside DMPOX, indicating their instability under this condition [3,47,49,50], where the affinity of DMPO for oxidation was much higher than keeping the trapped radicals. This is the reason why there are no separate symbols, relating to the $\text{SO}_4^\bullet$ or $^\bullet\text{OH}$ in

Fig. 6E/1. However, the formation of DMPOX obviously confirms the formation of these highly oxidative radicals.

TEMP and TEMPD- H_2O were used for trapping $^1\text{O}_2$ specifically, with the formation of TEMPO and TEMPN, respectively (Fig. 6E/2 and E/3) (Table S9 shows the hyperfine splitting values) [51]. In the presence of biochar, the amount of generated TEMPO and TEMPN was 4–5 times higher than in a pure PMS solution. The EPR results support the formation of $^1\text{O}_2$ and oxidative radicals simultaneously in the PMS-containing suspension of ball-milled biochar, in line with the conclusions drawn from the effect of radical scavengers.

The identification of the products formed during the treatment supported the formation of $^1\text{O}_2$ and radicals. It is worth noting that reactions of $^\bullet\text{OH}$ and $\text{SO}_4^\bullet$ often yield similar hydroxylated products. The products of TRIM were analyzed using HPLC–MS and possible degradation pathways are illustrated in Fig. 7. The P1 product ($m/z = 323.1$) is generally observed when $^1\text{O}_2$ attacks the DMP moiety via a cycloaddition-like process [52]. Based on relevant literature, the reactive site on the TRIM molecule is specific to ROS and multiple shifts and intermediary formations may occur within the trimethoxybenzene moiety [53–55]. Hydroxylation (P5, P4, P9), demethylation, and carbonylation have been observed during the transformation. Carbonylation primarily occurred on a methylene bridge (P3) and a pyrimidine ring (P4) in which the reactive methylene group of TRIM was attacked, resulting in the formation of a carbonylation product (α -keto-trimethoprim, P3). Carbonylation (P4) also affected the pyrimidine ring, which was subsequently targeted by $^\bullet\text{OH}$, yielding in hydroxylation products P9. Additionally, the P4 product indicates the concurrent hydroxylation and carbonylation. During hydroxylation, $^\bullet\text{OH}$ can target the rings or methylene bridge in the TRIM molecule, resulting in intermediates with P5 and P6 [56]. Demethylation occurs when the $^\bullet\text{OH}$ non-selectively attacks the methoxy position in TRIM or its intermediates. This leads to the formation of P4, P2, and P7 through the replacement of the methoxy group in TRIM. Additionally, P7 undergoes further demethylation to yield P8. The antibacterial effect of trimethoprim is primarily due to the 2,4-diamino-pyrimidine group. This molecular moiety remained unchanged during the treatment, which raises the question of whether the products formed have an antibacterial

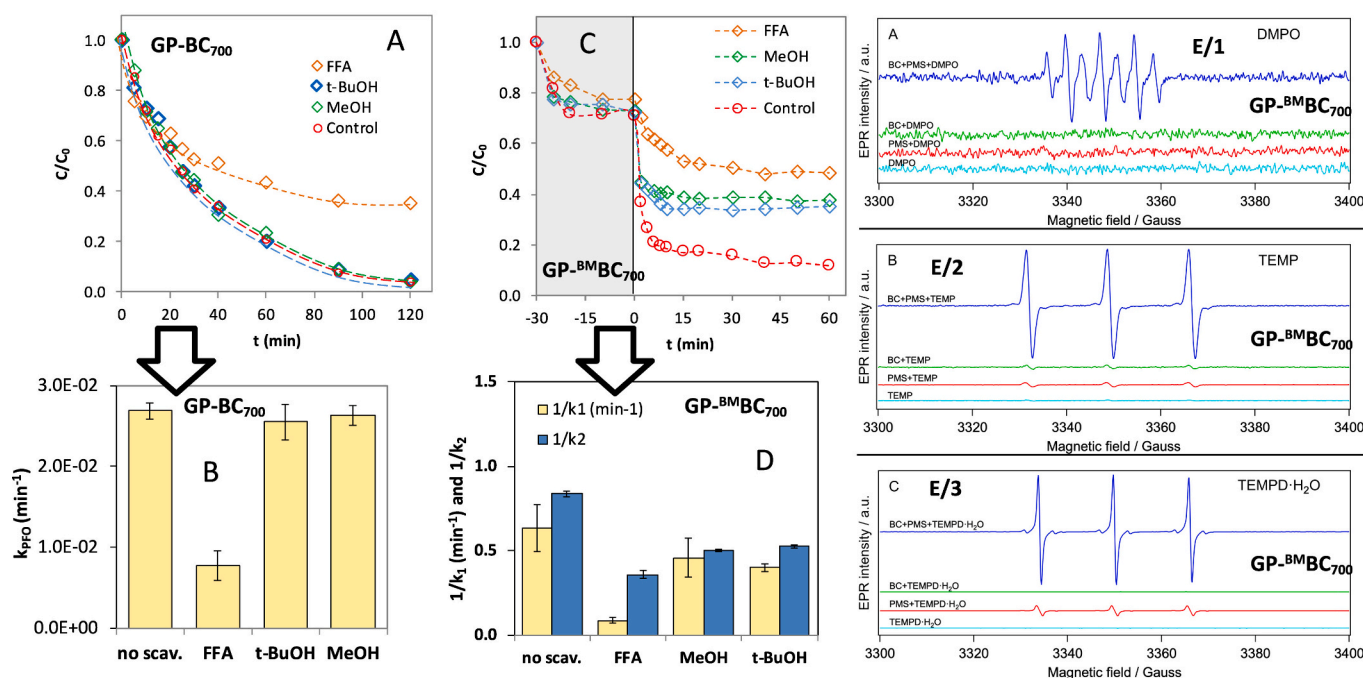


Fig. 6. Effect of radical scavengers on TRIM transformation (A and B: GP-BC_{700} , $c^\text{TMP} = 0.05 \text{ mM}$, $c^\text{PMS} = 2.0 \text{ mM}$ and $c^\text{BC} = 3 \text{ g L}^{-1}$, $c^\text{MeOH} = c^\text{t-BuOH} = 10 \text{ mM}$; $c^\text{FFA} = 1.5 \text{ mM}$; C and D: $\text{GP}^\text{BM}\text{BC}_{700}$, $c^\text{TMP} = 0.1 \text{ mM}$, $c^\text{PMS} = 0.2 \text{ mM}$ and $c^\text{BC} = 0.5 \text{ g L}^{-1}$, $c^\text{MeOH} = c^\text{t-BuOH} = 10 \text{ mM}$; $c^\text{FFA} = 1.5 \text{ mM}$) and EPR signal intensity in the presence of $\text{GP}^\text{BM}\text{BC}_{700}$ and DMPO (E/1), TEMP (E/2) and TEMPD (E/3) (DMPO used for trapping $\text{SO}_4^\bullet$ and $^\bullet\text{OH}$; TEMP and TEMPD were used for trapping $^1\text{O}_2$).

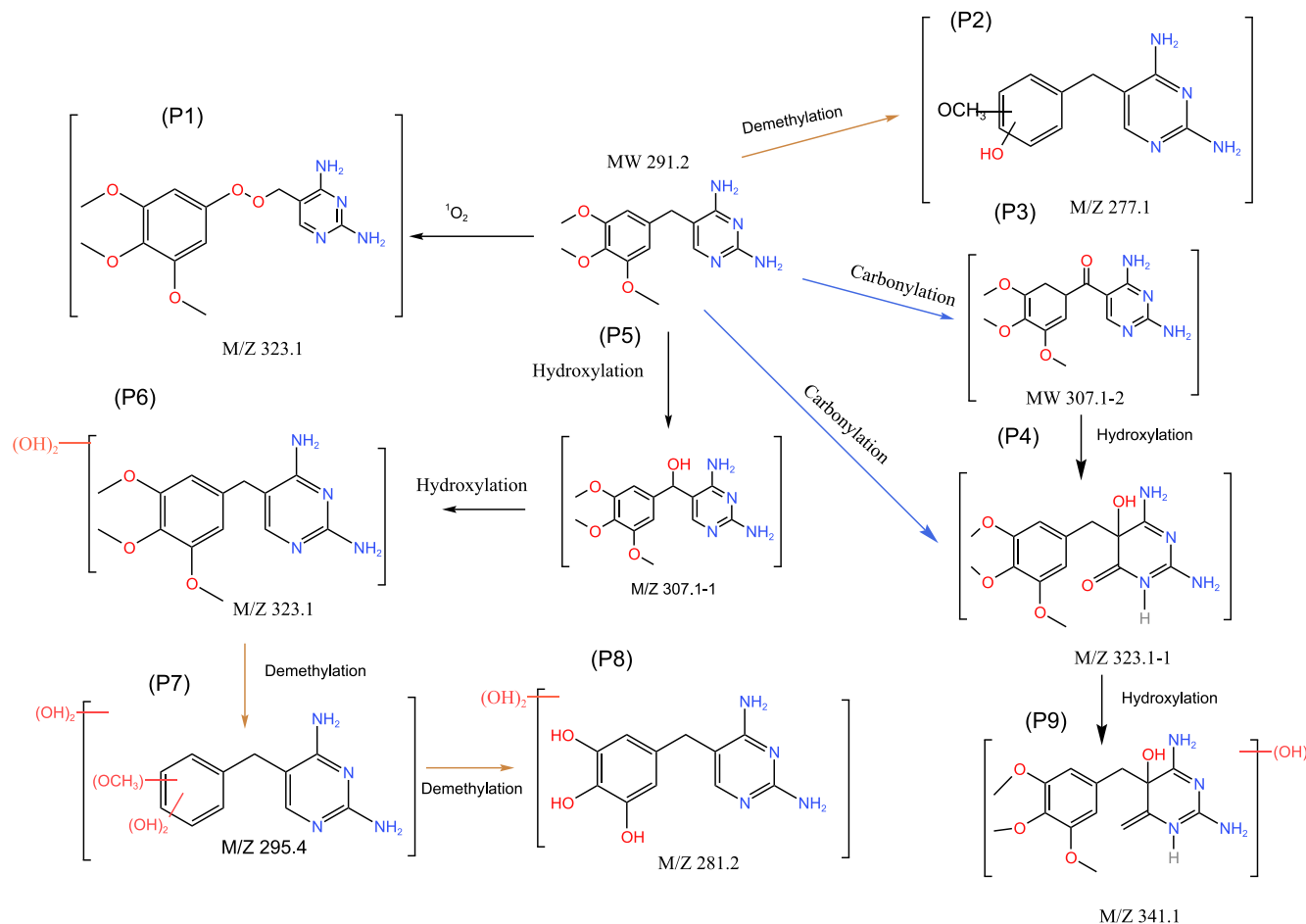


Fig. 7. The detected products and proposed pathways for TRIM degradation.

effect.

The biochar/PMS system operated through a highly synergistic mechanism, which yielded efficient TRIM removal. The pyrimidine ring facilitates strong π - π electron-donor-acceptor (π - π EDA) interactions with the electron-rich sp^2 -hybridized aromatic domains. Moreover, the oxygen- and nitrogen-containing functional groups in TRIM ($-NH_2$ and $-OCH_3$) promote hydrogen bonding with surface $-OH$, $C=O$, and $-COOH$ groups on the biochar. Additional contributions arise from n - π interactions and hydrophobic effects. Collectively, these mechanisms drive adsorption, achieving <30 % TRIM removal within 30 min in the absence of PMS. The interaction between the BC surface and TRIM favors direct charge transfer besides reaction with $^1O_2$ and radicals. Most probably, the TRIM transformation occurs through multiple parallel pathways: (i) direct electron transfer from persistent free radicals (PFRs) and defective sp^2 -carbon edges/defects; (ii) non-radical pathway due to the reaction with $^1O_2$ and (iii) the most effective and less selective radical pathway (Fig. S16).

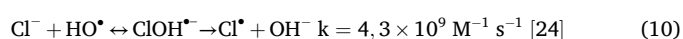
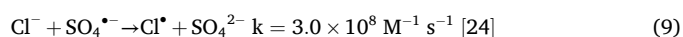
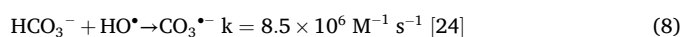
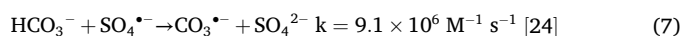
3.3. Effect of inorganic ions, organic matter, and water matrices

To assess the efficiency of the BC-PS process in real aqueous environments, experiments were conducted using biologically treated domestic wastewater (BTWW) as a matrix, collected from the wastewater treatment plant. The wastewater (pH = 7.8) contained organic (TOC = 6.9 mg dm^{-3}) and inorganic substances, mainly HCO_3^- , and Cl^- (Table S3). The organic and inorganic constituents of the wastewater can be adsorbed on the surface of the biochar, hindering its reaction with PMS and behaves as radical scavenger. The surface charge of biochar is negative (Fig. S6), which is not favorable for the adsorption of anions.

This could be the reason, as the negative ions and BTWW just slightly affected the adsorption of TRIM (Figs. 8 and S17). However, the degradation efficiency was significantly reduced (Fig. 8); most probably the radical scavenging effect of matrix components is responsible for this effect.

The increase in biochar and PMS doses could moderate the matrix effect, as was proved in the case of $Gp^{MB}C_{700}$. The increased PMS dose (1.0 mM) and doubled biochar dose (1.0 g L^{-1}) result in higher efficiency. However, the TRIM transformation was significantly slower in BTWW, requiring a 60-minute treatment time instead of 10 min to transform nearly 90 % of TRIM (Fig. 8/A and C).

The reaction of HCO_3^- with $SO_4^{\bullet-}$ and $\bullet OH$ produces $CO_3^{\bullet-}$ ($E^\circ = 1.59 \text{ V}$) (7, 8), having lower oxidation ability and moderated reactivity toward TRIM ($K(\text{TRIM} + CO_3^{\bullet-}) = 1.30 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [56–59]). The Cl^- is an excellent $SO_4^{\bullet-}$ and $\bullet OH$ scavenger (9, 10), the reaction generates Cl -containing secondary radicals, which react with TRIM ($Cl^\bullet$, $ClOH^\bullet$, and $Cl_2^\bullet$) $k(\text{TRIM} + Cl^\bullet) = 1.90 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; [60]). Moreover, the further reactions of Cl -containing radicals can result in $HO^\bullet$, and moderate the scavenging effect. This could be a reason for that, despite the scavenging capacity of Cl^- exceeding that of HCO_3^- , the negative effect of HCO_3^- is better manifested.



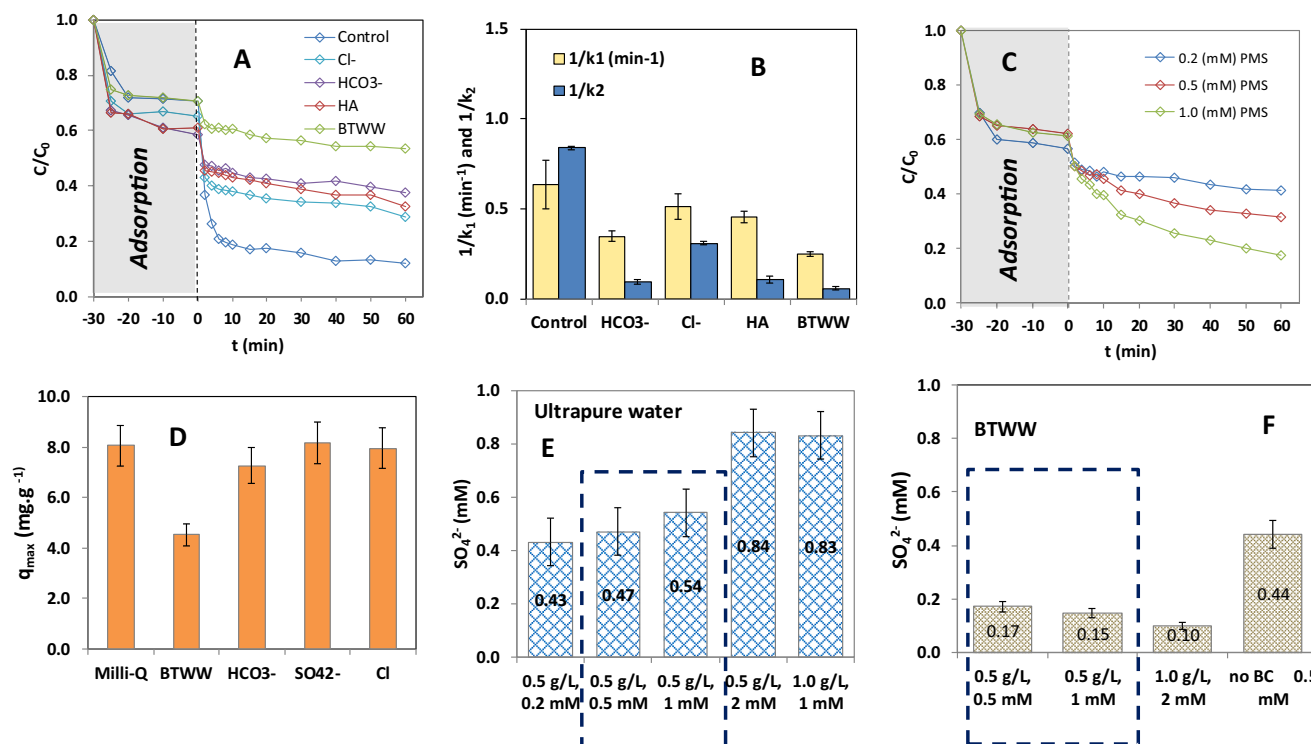
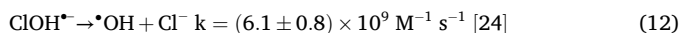
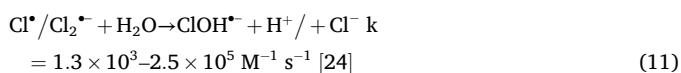


Fig. 8. Effect of BTWW as matrix and matrix components in the case of GP-^{BM}BC₇₀₀ (A: kinetic curves; B: adsorption and degradation efficiency of TRIM (BTWW: biological treated wastewater; $c^{\text{PMS}} = 0.2 \text{ mM}$, $c^{\text{TRIM}} = 0.1 \text{ mM}$, $c^{\text{BC}} = 0.5 \text{ g L}^{-1}$); C: effect of PMS dose in BTWW; D: The effect of BTWW and matrix components on the adsorption capacity (q_{max} determined from Langmuir isotherm); E and F: SO_4^{2-} concentration, determined in Milli-Q (E) and BTWW (F) after 10 min treatment time.



Humic acid (HA), a characteristic natural organic matter, was used to demonstrate the effect of organic content of BTWW on elimination efficiency. The HA decreased the transformation efficiency by 18–30 %. HA has dual effect; as it can serve as an electron source to activate PMS [61,62], at the same time, it also competes with TRIM primarily for radicals. However, HA adsorption on biochar through hydrophobic and π - π interactions is able to hinder the interaction between PMS and biochar surface. Its effect on adsorption and transformation efficiency clearly indicates that the lower transformation rate of TRIM is primarily due to the radical scavenging effect of HA.

Fig. 8/E and F shows the concentration of SO_4^{2-} originating from the

PMS transformation. Using of a 0.5 g dm^{-3} biochar dose, the increase of PMS dose from 0.2 mM to 2.0 mM enhanced the SO_4^{2-} concentration. Using 1.0 mM PMS, the doubled biochar dose ($0.5 \rightarrow 1.0 \text{ g dm}^{-3}$) almost doubled the amount of transformed PMS, reflecting the importance and efficiency-limiting effect of this parameter. In BTWW, the low SO_4^{2-} concentration indicated the inhibition of PMS transformation. This is partly due to the effect of organic and inorganic components of BTWW on the surface properties of biochar, which may alter the interaction between biochar and PMS and change the rate of radical formation. Surprisingly, BTWW itself can initiate PMS transformation; likely because of the electron transfer processes between some organic substances of the matrix, e.g. hydroquinones, and PMS. However, their adsorption on the biochar surface mitigates this effect.

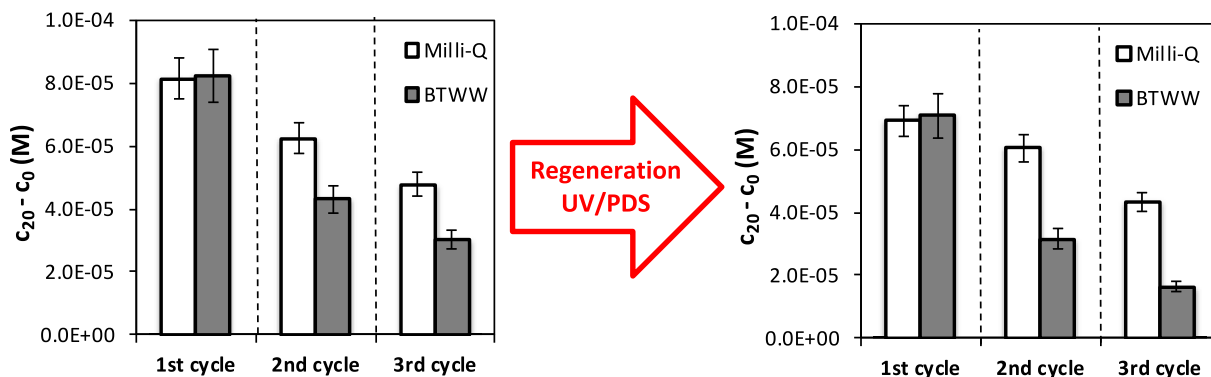


Fig. 9. Reusability and regeneration of GP-^{BM}BC₇₀₀ biochar (Milli-Q: $c^{\text{BC}} = 0.5 \text{ g L}^{-1}$; $c^{\text{PMS}} = 0.5 \text{ mM}$; $c^{\text{TRIM}} = 1.0 \text{ mM}$; BTWW: $c^{\text{BC}} = 1.0 \text{ g L}^{-1}$; $c^{\text{PMS}} = 1.0 \text{ mM}$; $c^{\text{TRIM}} = 1.0 \text{ mM}$) ($c_{20} - c_0$: the concentration of the transformed TRIM during 20 min treatment time) Figures show the transformed concentration of TRIM during 20 min treatment (duration of a cycle).

3.4. Reusability and regeneration

The reusability and regeneration of biochar as a catalyst is one of the important factors to evaluate its practical application. The GP-^{BM}BC₇₀₀ was investigated across three consecutive cycles (Fig. 9). At the beginning of each cycle, a new portion of TRIM (0.1 mM) and PMS (0.5 mM in the case of Milli-Q and 1.0 mM in the case of BTWW) was added to the biochar (0.5 g L⁻¹ in MilliQ and 1.0 g L⁻¹ in BTWW) suspension. The transformation of TRIM concentration was determined after each cycle, having 20 min treatment time.

The transformation efficiency decreased across successive cycles, likely due to the accumulation of TRIM intermediates. The adsorbed intermediates can compete with TRIM for radicals and by adsorbing onto the biochar surface, thereby occupying active sites responsible for PMS activation and radical formation. Compared with previous studies, the reusability of the biochar in this work surpasses that of the baby-diaper-based biochar, which achieved over 95 % degradation in the first run but only 9 % in the second cycle [52]. N₂-doped ball-milled biochar was reported to achieve 97, 68, and 66 % transformation across 3 cycles for TRIM degradation [1].

From a practical application perspective, restoring biochar activity is fundamental. Zhu et al. [63] successfully used PDS and UV light to regenerate NOM-saturated GAC. The 254 nm UV photolysis is effective for SO₄[•] generation and decomposes organic material dissolved in the aqueous solution or adsorbed on the biochar surface. Additionally, UV irradiation can promote PFR formation [64] and partially restore the biochar surface's active sites. The combination of 254 nm UV light and PDS (1.0 mM) was used in this work. PDS was added to the biochar suspension after the third cycle, and irradiated with 254 nm UV light for 40 min. After the regeneration period, the three TRIM removal cycles were repeated. The biochar recovered its catalytic activity; the removal efficiency of the regenerated biochar in the first cycle was 88 % of the original.

4. Conclusion

This work presents the synthesis of biochar catalysts and the investigation of biochar and PMS-based AOP for the elimination of the antibiotic TRIM. The effect of pyrolysis temperature and ball-milling modification confirmed that the appropriate degree of graphitization was a crucial factor for catalytic efficiency, and 700 °C was found to be the optimal pyrolysis temperature. The effects of different radical scavengers and EPR measurements proved that ball milling greatly enhanced the catalytic efficiency of the biochar. In the case of non-ball-milled biochar, TRIM transformation occurs via reaction with ¹O₂, whereas ball-milled biochar showed good activity in generating radicals, so the contribution of radical-based processes to the degradation became decisive. Despite the efficiency of the TRIM transformation, the negative matrix effect and the rapid decrease in biochar's catalytic efficiency represent bottlenecks to its application. However, it is encouraging for future applications that the biochar regenerated by PDS/UV treatment retained its catalytic activity, confirming that no significant structural changes occurred during catalytic cycles and regeneration.

CRedit authorship contribution statement

Dinesh Chandola: Writing – original draft, Investigation, Data curation. **Bence Veres:** Writing – review & editing, Investigation. **Gábor Varga:** Writing – review & editing, Writing – original draft, Investigation. **Ákos Szamosvölgyi:** Writing – review & editing, Writing – original draft, Investigation. **Tibor László Páli:** Writing – review & editing, Writing – original draft, Investigation. **Krisztina Sebők-Nagy:** Writing – original draft, Investigation. **Gábor Kozma:** Investigation. **Zsuzsanna László:** Writing – review & editing, Conceptualization. **Zoltán Kónya:** Resources. **Tünde Alapi:** Writing – review & editing, Writing – original draft, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dinesh Chandola reports financial support was provided by Tempus Public Foundation for awarding a Stipendium Hungaricum scholarship. If there are other authors, they 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2025.109371>.

Data availability

Data will be made available on request.

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