Scientific and Social Research, 2025, Volume 7, Issue 4
https://ojs.bbwpublisher.com/index.php/SSR
Online ISSN: 2981-9946
Print ISSN: 2661-4332

Degradation of Tetracycline Hydrochloride by Activated Persulfate from Corn Stalk Biochar

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Abstract: Corn straw biochar (YM) was prepared at 300℃, 450℃, and 600℃ under oxygen-limited pyrolysis temperature (T_r). The degradation efficiency and influencing factors of tetracycline hydrochloride (TCH) by YM-activated peroxonitrosulfate (PMS) were investigated based on the characterization results. The results showed that the increase of T_r was beneficial to increase the specific surface area (BET), total pore volume (PV), and surface oxygen-containing functional groups of biochar, and more active sites were obtained. The maximum degradation efficiency of the YM600/PMS/TCH system was 60.20%. The degradation efficiency of YM600/PMS/TCH decreased with the increase of TCH mass concentration (C_T) and increased with the increase of carbon dosage (C_B) and PMS concentration (C_P).

Keywords: Corn stalk; Biochar; Permonosulfate; Tetracycline hydrochloride

Online publication: May 2, 2025

1. Introduction

Due to the fast advancement in industry and agriculture, as well as the overuse of antibiotics, the soil environment is encountering a severe issue of antibiotic contamination. Tetracycline hydrochloride (TCH), known for its affordability and effective treatment outcomes, has found extensive application in medical aquaculture. However, this kind of organic pollutant proves challenging to remove efficiently through conventional biochemical approaches [1–3].

Currently, the techniques employed for tetracycline removal involve adsorption, biological approaches, and advanced oxidation processes [4–5]. Advanced oxidation technologies utilizing sulfate radicals harness their potent oxidative capabilities to break down organic contaminants rapidly, demonstrating significant potential and benefits in both soil and wastewater treatment. Nevertheless, the energy efficiency and effectiveness of solid heterogeneous catalysts have made them a focal point of research in the activation of PMS [6–7]. Biochar-based heterogeneous catalysts have garnered substantial interest within the realm of PMS/PS activation. These catalysts exhibit

fewer pH constraints, reduced side reactions compared to homogeneous catalysts, and are simpler to recover. Additionally, they can prevent the introduction of certain anions that may lead to free radical quenching [8].

In this study, corn straw biochar was prepared at the pyrolysis temperatures of 300℃, 450℃, and 600℃. Combined with the characterization results, the performance and influencing factors of corn straw biochar-activated PMS degradation of TCH were investigated. This method has the advantages of simple equipment, low cost, and green environmental protection, and it provides a scientific basis for the development and application of carbon-based catalysts made from waste biomass to activate persulfate.

2. Material and method

2.1. Materials and reagents

Corn straw (from Xuzhou farmland), tetracycline hydrochloride (TCH), sodium sulfite, potassium bisulfate (PMS), ultra-pure water.

2.2. Preparation of corn straw biochar

The cleaned corn stalks were dried and crushed, put into a quartz tank, and put into a Muffle furnace at T_r of 300℃, 450℃, and 600℃, respectively, and then removed after pyrolysis for 3h. Clean with ultra-pure water (to remove surface impurities), dry in a vacuum drying oven (105℃, 24h), take out, and seal for use. The original corn stalk biochar was labeled YM300, YM450, and YM600, respectively.

2.3. Characterization and detection methods of the materials

The functional groups of biochar surface were analyzed by FT-IR; N_2 adsorption/desorption tests were determined by aperture and specific surface area analyzer. The TCH mass concentration was measured by ultraviolet spectrophotometry with a wavelength of 356 nm.

2.4. Study on degradation performance of TCH and its influencing factors

Measure the brown wide-mouth bottle containing TCH solution with a mass concentration of 20 mg/L, add biochar (0.2 g/L), put the wide-mouth bottle into the ultrasonic shaker for 10s and then add PMS (0.5 mmol/L), place it on the constant temperature magnetic stirrer (500 r/min, 25℃) and stir continuously, then extract the water sample at the set time. After filtration by 0.45 μm filter membrane, 1 mL of excess Na_2SO_3 (100 mmol/L) was added to terminate the catalytic reaction, and then TCH concentration was measured.

C_P (0.2, 0.5, 0.8, 1.2, 2 mmol/L), C_B (0.1, 0.15, 0.2, 0.25, 0.5 g/L), C_T (10, 20, 30, 40 mg/L) were changed respectively to investigate the influence of different reaction conditions on the removal efficiency of TCH, and the other conditions remained unchanged.

3. Results and discussion

3.1. Characterization and analysis of corn stalk biochar materials

Table 1 shows the BET and pore size distribution of the original biochar material of corn stalk. It can be seen from **Table 1** that both BET and PV of YM gradually increase with the increase of T_r, which is consistent with the results of previous studies [9–10]. The increase of pyrolysis temperature in the Muffle furnace promoted the formation of pores and produced a large number of micro-pores, the diameter of which could be reduced.

Table 1. YM BET and PV

Samples	BET specific surface area (m^2/g)	Total pore volume PV (cm^3/g)	Most can be several diameters (nm)
YM-300	6.47	0.0462	4.74
YM-450	3.58	0.0226	3.79
YM-600	24.69	0.0537	2.36

The stretching vibration peak near 3434cm^{-1}, 2930cm^{-1}, and 2857cm^{-1} was gradually decreased with the increase of T_r in the infrared spectrum of corn straw biochar [11–12]. With the increase of T_r, the stretching vibration peaks of C=C double bond in aromatic ring structure and C=O double bond in carbonyl group (near 1564cm^{-1}) gradually weaken [13-14]. The stretching vibration peak at 875cm^{-1} gradually increased with T_r increasing, and the aromaticity and stability of YM increased [15]. More active sites were provided for YM to adsorb TCH and activate PMS.

3.2. Analyzed the degradation efficiency and influencing factors of TCH on YM

The degradation efficiency of TCH by the YM/PMS system is shown in **Figure 1(a)**. **Figure 1(a)** shows that YM300, YM450, and YM600 can remove TCH by 16.19%, 21.28%, and 25.61%, respectively, during the reaction time when only biochar is present, and YM600 has the highest removal effect on TCH. When PMS was added to the reaction system, the removal rates of TCH on YM300, YM450, and YM600-activated PMS during the reaction time were 55.48%, 58.88%, and 60.20%, respectively. According to the research, the surface adsorption of organic matter by carbon material catalyst is considered to be the key step for catalyst-activated PMS to degrade pollutants [16]. The increase of T_r greatly improves the BET and PV of biochar, improves the functional groups of aromatic ring on the surface of carbon material, improves more active sites for TCH adsorption and activation of PMS, and removes TCH from the improvement of biochar /PMS system adsorption and degradation.

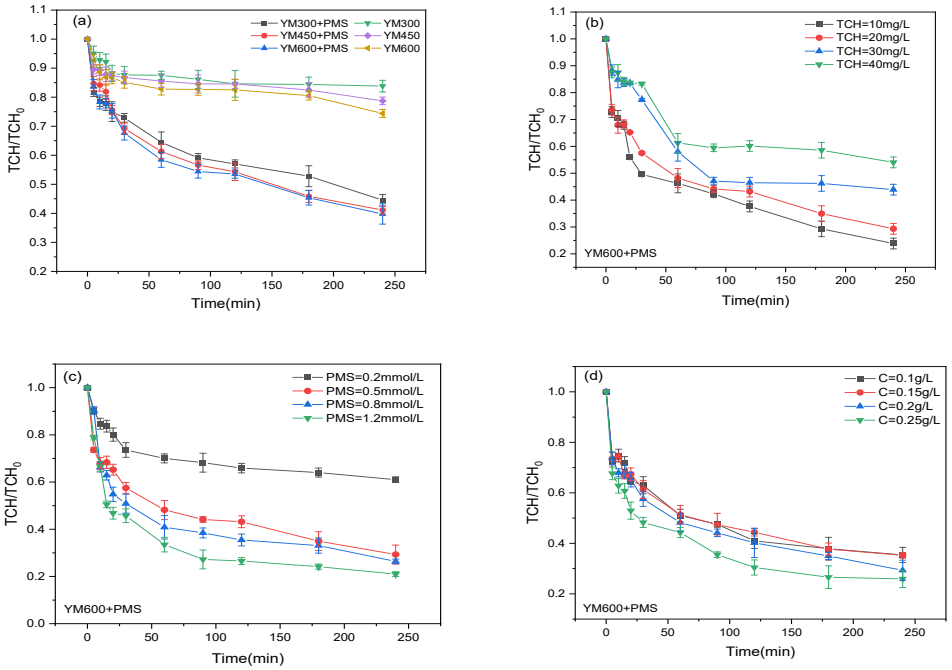

Figure 1. Degradation efficiency and influencing factors of TCH in the YM/PMS system

According to **Figure 1(b)**, it can be seen that the removal efficiency of the YM600/PMS/TCH system gradually decreases with the increase of C_T. When C_T is 10mg/L, the YM600/PMS/TCH system has the best degradation efficiency for TCH. The active sites in the reaction system are fixed when C_B is unchanged, so the lower C_T reaction rate is faster and has a better degradation effect.

According to **Figure 2(c)**, the removal efficiency of the YM600/PMS/TCH system on TCH gradually increases with the increase of C_P. When C_P=1.2 mmol/L, the removal rate of YM600/PMS/TCH reached about 80%, and the removal rate of TCH gradually leveled off with the increase of PMS concentration.

As can be seen from **Figure 2(d)**, in the same reaction time, with the increase of C_B, the removal rate of TCH by the YM600/PMS/TCH reaction system continues to increase. This is mainly because more biochar can provide more active sites for the adsorption of TCH and activation of PMS.

4. Conclusions

The characterization results showed that increasing T_r was beneficial to increase BET, PV, and surface functional groups of biochar. Among them, YM600 has the largest BET and PV and more abundant surface oxygen-containing functional groups, providing more active sites for TCH adsorption and PMS activation.

In the raw corn stalk biochar, the YM600/PMS/TCH reaction system had the highest removal efficiency of TCH, reaching 60.20%.

The removal efficiency of the YM600/PMS/TCH reaction system decreased with the increase of C_T, increased first with the increase of C_P and then tended to be stable, and increased with the increase of C_B.

Funding

Jiangsu Province College Students “Innovation and Entrepreneurship Training Program Project (xcx2023025), Jiangsu Province College Students” Innovation and Entrepreneurship Training Program Project (xcx2024170), Science and Technology Guidance Project of Jiangsu Provincial Department of Housing and Urban-Rural Development (2019JH009003), Xuzhou Science and Technology Planning Project (KC22344), Major Project of Basic Science (Natural Science) Research in Jiangsu Higher Education Institutions (24KJA610005), Fund Project of Xuzhou Ecological Civilization Construction Research Institute (2021ZD-02)

Disclosure statement

The authors declare no conflict of interest.

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