Formaldehyde removal via peroxymonosulfate activated by transition metal-doped bagasse biochar

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Received 6 Sep. 2025; Revised 3 Nov. 2025; Accepted 10 Dec. 2025; Published 25 Dec. 2025.

DOI: https://doi.org/10.54939/1859-1043.j.mst.108.2025.49-56

ABSTRACT

This study introduces a process for formaldehyde (HCHO) treatment using peroxymonosulfate (PMS) activated by copper and cobalt metal-impregnated biochar derived from sugarcane bagasse. The bagasse was subjected to alkali pre-treatment before metal impregnation and subsequent pyrolysis at 700 °C to produce the Co-Cu/Biochar material. Modern analytical methods, including SEM, EDS, XRD, and nitrogen adsorption-desorption isotherms, were employed for structural characterization. The results showed that the Co-Cu/Biochar possesses a high specific surface area (SSA=419 m^2/g), making it suitable for PMS activation to eliminate HCHO. The influence of material dosage, PMS concentration, and solution pH was investigated. The findings demonstrated that HCHO was completely removed after 5 minutes of reaction at an initial concentration of 20 mg/L.

Keywords: Biochar; Formaldehyde; PMS activation; Cobalt; Copper; Bagasse.

1. INTRODUCTION

Volatile Organic Compounds (VOCs) released from industrial activities are a major cause of air pollution. Formaldehyde (HCHO) is one of the VOCs emitted in large quantities. HCHO is considered dangerous to human health due to its high toxicity, pungent odor, and ability to cause damage to the nervous system as well as respiratory diseases [1, 2]. Furthermore, HCHO can react with NO_x in the atmosphere to create photochemical smog [3]. Therefore, the development of technologies for HCHO removal from industrial exhaust gases has attracted significant attention [4]. Many technologies, such as photocatalysis [5] and thermal catalysis [6], have demonstrated high efficiency in treating HCHO-containing gas streams. However, these technologies have drawbacks, including high costs, high treatment temperatures, and the formation of secondary products [7]. In contrast, physical methods for HCHO removal, such as adsorption [8] and wet scrubbing, offer low cost and ease of operation, but these physical methods only capture HCHO in the adsorbent material or absorbent solution and cannot completely mineralize HCHO [9]. Therefore, a proposed solution involves absorbing HCHO vapor from the gas phase into a liquid solution and then achieving complete degradation of HCHO using a sulfate-radical-based Advanced Oxidation Process (AOPs). This study will focus on the degradation of HCHO after it has been absorbed into the solution, utilizing peroxymonosulfate (PMS) activated by metal-impregnated biochar.

Biochar is a carbon-based material that is easily synthesized from biomass at a low cost and possesses a large specific surface area. Utilizing biochar as a support material for transition metals (copper, cobalt, iron) can improve the reactivity between the metal nanoparticles and PMS, while simultaneously mitigating the risk of heavy metal contamination after the reaction.

2. MATERIAL AND METHOD

2.1. Chemical

Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 98.5%), Potassium hydroxide (KOH, 99%), Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, 99%), Formaldehyde (HCHO, 37%), acid sulphuric (H_2SO_4, 98%), acid chromotropic ($C_{10}H_8O_8S_2$, 98%) Sodium bisulfit ($NaHSO_3$, 98%) and Oxone ($2KHSO_5.KHSO_4.K_2SO_4$, 42.8 - 46%) a double salt of potassium, in which the active component is peroxymonosulfate, were used in this study. All chemicals were sourced from Xilong, China, and were used without any additional purification processes. Bagasse is collected, washed and dried before being used to synthesize materials. Distilled water was used throughout all experiments.

2.2. Synthesis of catalyst material

2.2.1.Pretreatment of bagasse

Biomass consists of three main components: hemicellulose, cellulose, and lignin. Therefore, bagasse needs to be pretreated to remove lignin and hemicellulose to obtain high-purity cellulose.

Among the pretreatment methods, alkaline treatment has been shown to be highly effective and easy to perform in the laboratory.

Fifty grams of shredded bagasse were soaked in a beaker containing 1.5 L of distilled water. The beaker was then heated to 70 °C in a heating bath, and 50 g of KOH was added to carry out the bagasse pretreatment process. The process was carried out for 2 hours, and the mixture was stirred with a mechanical stirrer at a speed of 250 rpm. At the end of the process, the pretreated bagasse was washed several times, dried at 60 $H\% = \frac{C_0 - C_t}{C_0} \times 100\%$ °C overnight, and carefully stored before being used for material synthesis.

2.2.2. Preparation of metal-impregnated biochar

In this study, copper and cobalt were co-impregnated onto pre-treated bagasse, with the mass loading of each metal being approximately 2.5%. First, 0.1233g of $Co(NO_3)_2{\cdot}6H_2O$ and 0.1025g $Cu(NO_3)_2{\cdot}3H_2O$ were added to a beaker containing 100 mL of ethanol and stirred for 5 minutes to completely dissolve the metal salts. Next, 1 g of pretreated sugarcane bagasse was added to the solution and stirred for 30 minutes. Then, a 1 M KOH solution was slowly added to the beaker until the pH value reached approximately 10, and the mixture was stirred continuously for another 30 minutes. After stirring, the beaker was left to stand for 2 hours to allow the solid to settle naturally. Finally, the solid was filtered and dried at 60 °C overnight before carbonization at 700 °C for 2 hours to form the Co-Cu/Biochar material.

After carbonization, the Co-Cu/Biochar was washed again with ethanol/DI water (v/v = 1/1) to remove impurities remaining after carbonization, then dried at 60 °C and carefully preserved for further studies.

2.3. Characterization material

The surface morphology and energy-dispersive X-ray spectroscopy (EDS) of Co-Cu/Biochar were observed using a Tescan Mira scanning electron microscope (SEM). X-ray powder diffraction patterns were obtained on a Bruker D2 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Nitrogen adsorption-desorption isotherms were analyzed using a BET PMI-201A instrument.

2.4. Formaldehyde degradation experiment

This study was conducted to evaluate the influence of various reaction conditions on the efficiency of Formaldehyde (HCHO) degradation in an aqueous solution using the Co-Cu/Biochar material to activate Peroxymonosulfate (PMS). The initial HCHO stock solution was prepared by bubbling an HCHO gas stream (concentration of 33 mg/m^3 and flow rate of 500 mL/min through 50 mL of DI water for 1 hour. This resulted in 50 mL of an HCHO solution with an initial concentration of 20 mg/L. The HCHO degradation process was initiated in a beaker by adding an appropriate amount of Co-Cu/Biochar to the 50 mL HCHO solution. The mixture was magnetically stirred for 1 minute to ensure complete dispersion of the catalyst material. Subsequently, a suitable amount of PMS was added to start the reaction. The influence of various reaction conditions, including the solution pH, catalyst (Co-Cu/Biochar) dosage, and PMS concentration, was investigated through separate experiments. During the reaction, samples were collected every 1 minute. The HCHO concentration in the samples was analyzed using a UV-Vis Spectrophotometer DR1800 at a wavelength of 580 nm, following the NIOSH 3500 Method. The HCHO removal efficiency was calculated using equation (1):

$$H\% = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

With: H%: Removal efficiency;

C_0: Initial concentration;

C_t: Concentration at time t.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the sample

The SEM images (figure 1) of the material show a fibrous shape with metal oxide flakes on the surface. Additionally, the material with both Co and Cu doped on the surface of biochar, we can clearly see the metal particles with a round spherical shape or clusters of them (metal or metal oxide nanoparticle). The fibers are rough and irregular in surface and size. The surface is typical of biomass, such as irregular, porous, irregular. According to the study of Liu et al., they highlight the root channel pores with the dispersing of a cluster of metal particles from bimetallic CuCo-MOF [10].

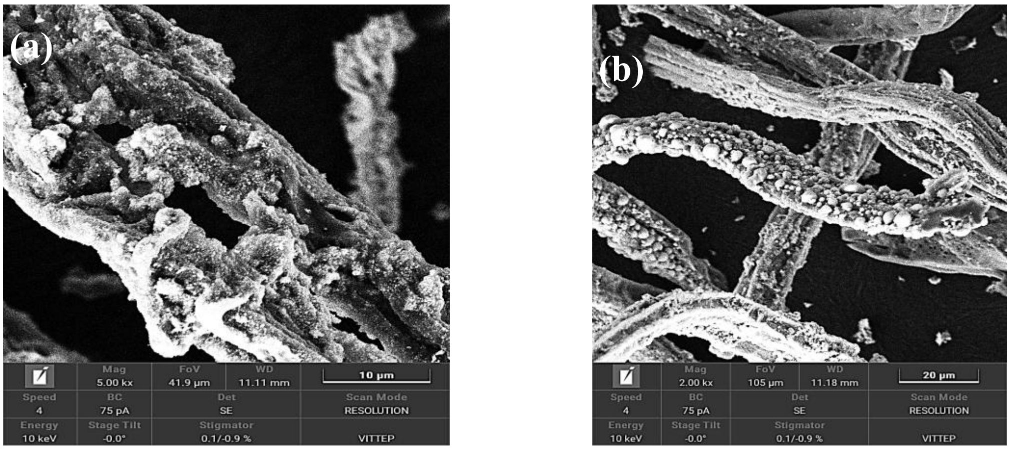

Figure 1. *The SEM image of Co-Cu/Biochar (a) scales up x 5.000 times, (b) scales up x 2000 times.*

According to the EDS results, the carbon content in the material is approximately 68.82%, which aligns with the study by Guarnieri et al. (Biochar based coir fiber 71.68%) [11] Hedge et al. developed a diagram for classifying carbon after combustion based on the ratio of oxygen to carbon [12] The O:C ratio of the material in this study is 0.22, indicating that the material is in a biochar state, where a smaller ratio signifies higher carbon stability. This demonstrates that the Co-Cu/Biochar material has high stability and the potential for reuse [13]. The EDS results also show 6.48% Co and 7.22% Cu, confirming that the material was successfully synthesized. Furthermore, the EDS results, which indicate a mass percentage ratio of the two metals close to unity (1:1), demonstrate the stability and control of the metal co-precipitation process onto the bagasse substrate.

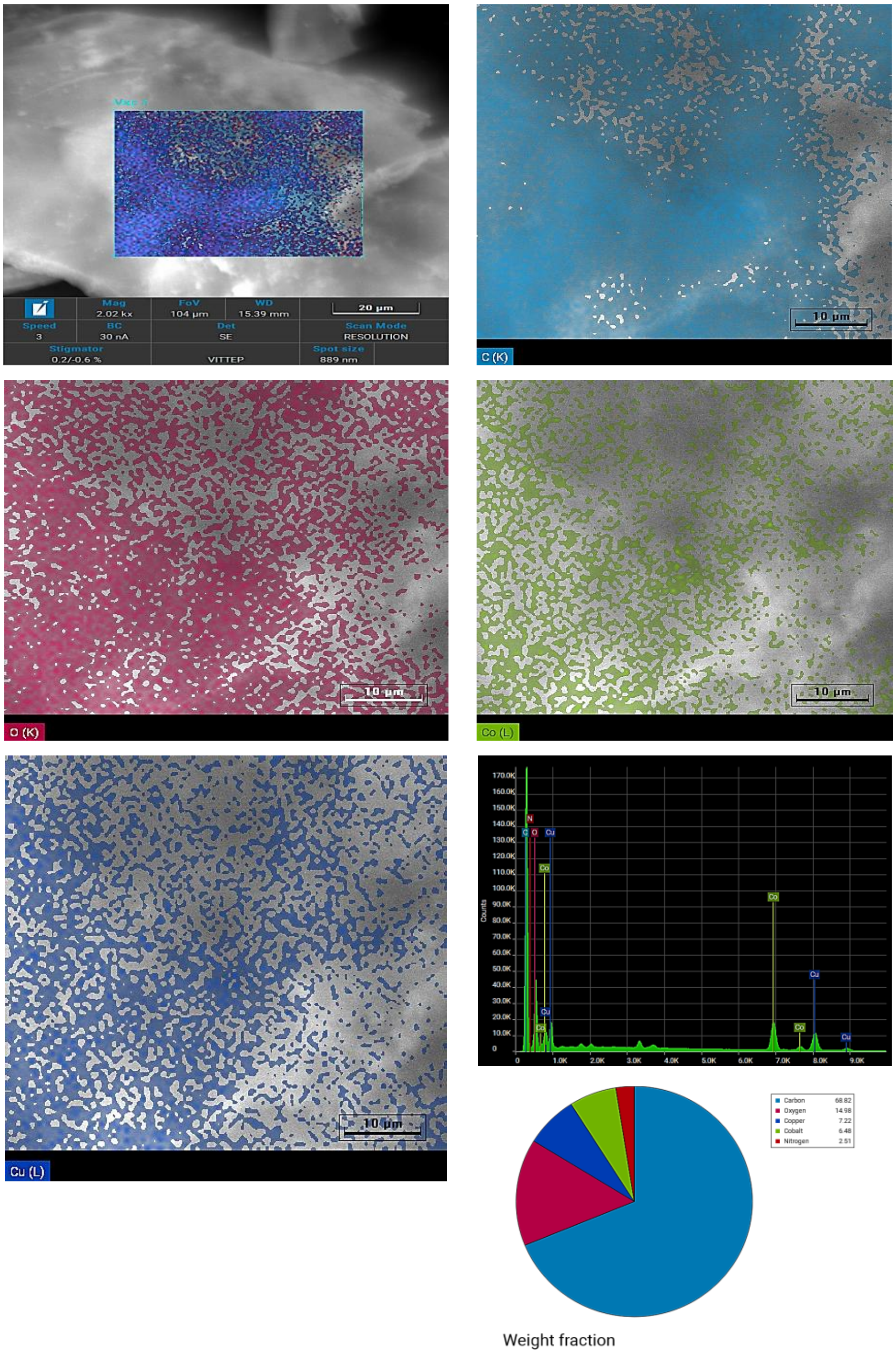

Figure 2. *Elemental distribution on the surface of Co-Cu/Biochar via EDS.*

X-ray Diffraction (XRD) technique was employed to determine the structure of cellulose and Co-Cu/Biochar. In figure 3, the characteristic peaks are clearly visible at 2θ angles of 18° and 26°. These peaks correspond to the [hkl] diffraction planes (101) and (002), respectively. The presence of these characteristic peaks indicates that the pre-treated cellulose derived from sugarcane bagasse belongs to the Cellulose I type [14]. After impregnation and pyrolysis to form the Co-Cu/Biochar, the peaks in the 18°−26° range were altered, and new peaks appeared. The new peaks emerged at approximately 2θ = 42° and 49°, corresponding to the (111) and (020) planes, respectively. These peaks are characteristic of copper and cobalt oxides, and the XRD results therefore indicate that the synthesis process successfully formed metal oxide crystals on the biochar surface.

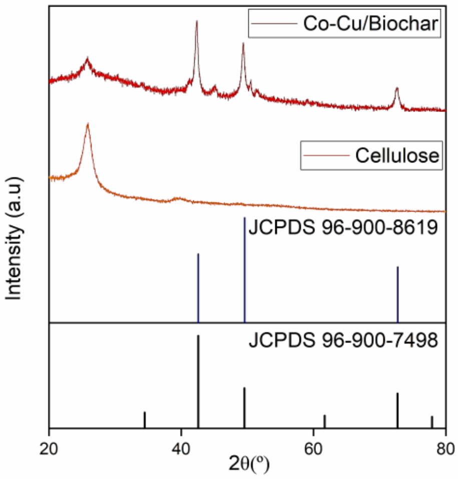

Figure 3. *X-ray Diffraction (XRD) of cellulose and Co-Cu/Biochar.*

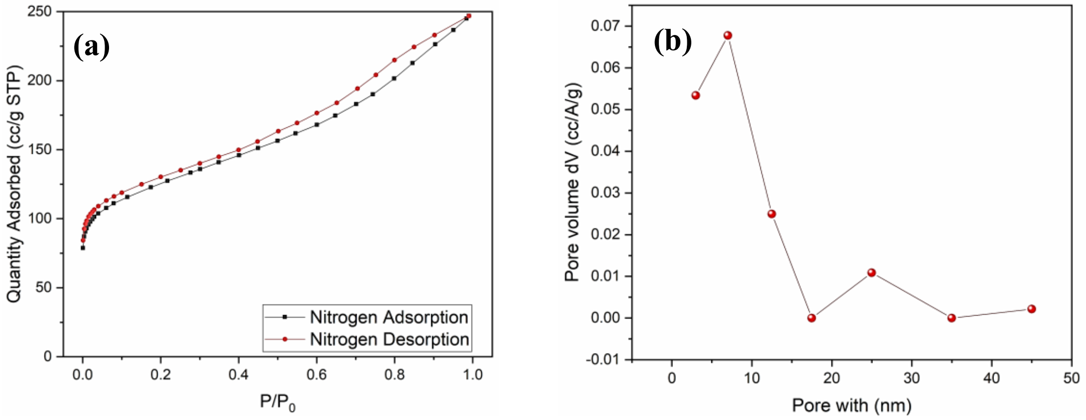

Figure 4. *Adsorption-desorption isotherm of N_2 (a) and pore size distribution of Co-Cu/Biochar (b).*

In figure 4a, the Nitrogen (N_2) adsorption-desorption isotherm of the Co-Cu-Biochar material exhibits a Type IV shape with a hysteresis loop in the P/P0 range of 0.0-0.2 and 0.6-0.9. This is attributed to capillary condensation, which is characteristic of porous materials. The diagram showing the average pore size distribution of the material (figure 4b) indicates that the majority of pores have diameters primarily in the 2-50 nm range. According to the Barrett-Joyner-Halenda (BJH) method, the Co-Cu/Biochar has an average pore diameter of 3.62 nm. This result confirms that the material possesses a mesoporous structure. Furthermore, the BJH method determined the specific surface area (SSA) of the material to be 419 m^2/g, while the micropore specific surface area was found to be 171 m^2/g. The results from the N_2 adsorption-desorption isotherm analysis suggest that the material has the potential to enhance the storage and delivery of Reactive Oxygen Species (ROS).

3.2. Effect of operating parameters on formaldehyde removal efficiency

Figure 5a illustrates the significant impact of the Co-Cu/Biochar dosage on Formaldehyde (HCHO) removal efficiency in the presence of Peroxymonosulfate (PMS).

The Co-Cu/Biochar material provides active sites essential for activating PMS, which subsequently generates the free radicals necessary to eliminate HCHO. Consistent with this mechanism, the overall HCHO removal process is notably enhanced as the material dosage increases. Critically, when the material concentration exceeded 0.5 g/L, HCHO was almost completely removed in just 3 minutes. Reducing the concentration to 0.15 g/L still yielded a comparable high removal efficiency, though taking slightly longer at 4 minutes. This suggests that optimizing the material concentration is vital for balancing high performance with minimizing treatment costs.

Furthermore, the data in figure 5a clearly show that when either Co-Cu/Biochar or PMS was present alone, HCHO was virtually not removed from the solution. These results emphatically demonstrate that the primary mechanism for the HCHO elimination in this study is the synergistic activation of PMS by Co-Cu/Biochar.

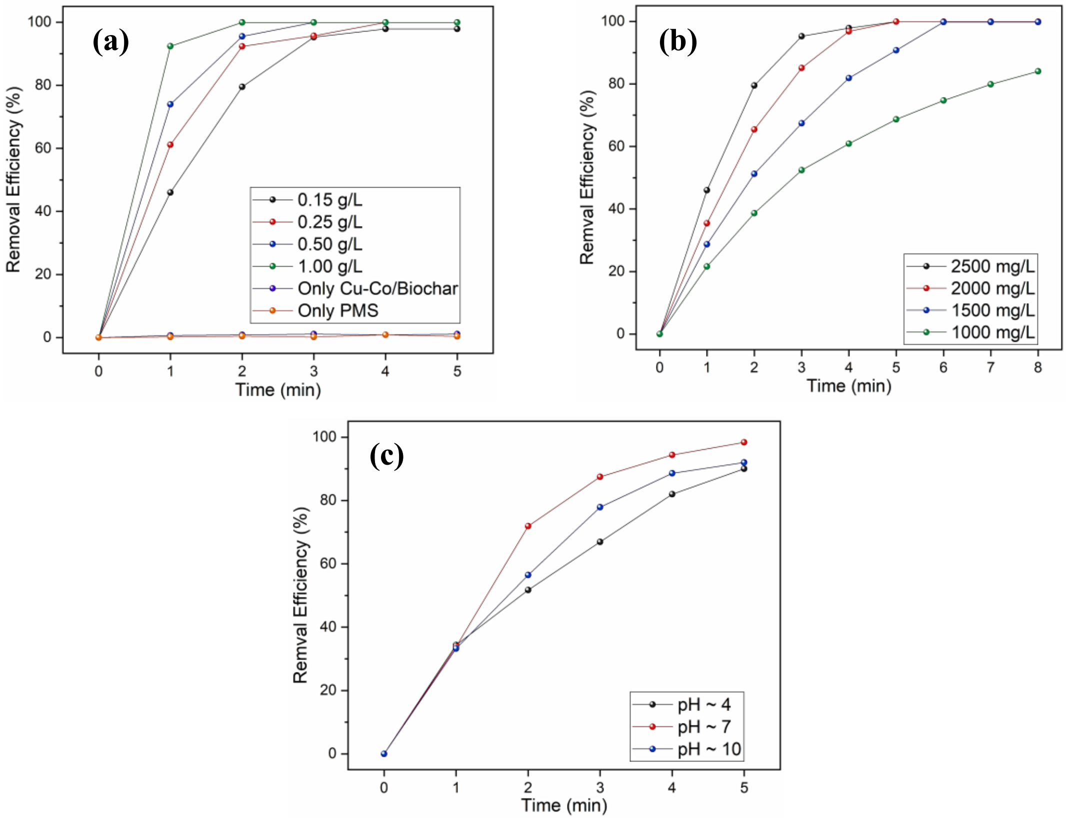

Figure 5. *Effect of Co-Cu/Biochar dose (a), PMS dose (b) and initial pH (c) on HCHO degradation. (C_0 = 20 mg/L).*

The investigation of Peroxymonosulfate (PMS) concentration on Formaldehyde (HCHO) degradation in the Co-Cu/Biochar/PMS catalytic system was conducted in the range of 1000 to 2500 mg/L. As shown in figure 5b, the HCHO removal efficiency generally increased as the PMS dosage was raised from 1000 to 1500 mg/L. The HCHO treatment efficiency was significantly improved (reaching over 98%) when the PMS concentration was 1500 mg/L, and there was almost no further difference when the concentration was continuously increased. In the advanced oxidation process, PMS acts as a free radical donor to participate in the decomposition of HCHO. Using excess PMS is both costly and increases the Chemical Oxygen Demand (COD) in the post-reaction solution. Therefore, 1500 mg/L was determined to be the optimal PMS concentration and was utilized in the subsequent study.

In addition, the degradation of HCHO was investigated across a pH range of 4 to 10 using the optimal concentrations of material and PMS determined in prior experiments. The pH values were adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH solutions. The results shown in figure 5c indicate that the HCHO removal efficiency remained relatively stable (achieving over 85% removal after 5 minutes) throughout the pH range investigated. This stability is one of the key advantages of the PMS oxidation method compared to the conventional Fenton process. Table 1 presents the HCHO removal efficiency in this study compared to the photocatalytic process for HCHO treatment. The results from table 1 demonstrate that HCHO treated via PMS activated by Cu-Co/Biochar exhibited superior efficiency and a faster treatment time.

Table 1. *Compared with the results of other studies.*

Degradation method	HCHO concentration	Removal efficiency	References
Photocatalysis	2,4 mg/m^3	90% in 10 mins	[5]
Photocatalysis	18 mg/m^3	90% in 20 mins	[6]
PMS activation	33 mg/m^3	95% in 6 mins	This study

4. CONCLUSIONS

Copper-Cobalt Metal-Impregnated Biochar Derived from Sugarcane Bagasse demonstrated effective HCHO removal when combined with Peroxymonosulfate (PMS). This research successfully provides an additional solution for utilizing agricultural byproducts as precursors for material synthesis and for eliminating HCHO using a PMS-based Advanced Oxidation Process (AOP). Modern analytical techniques such as SEM, EDS, XRD, and BET were employed to analyze the structural characteristics of the material. The influence of operating parameters was thoroughly investigated, and the results showed that HCHO was rapidly removed after 5 minutes using optimal concentrations of 0.15 g/L of material and 1500 mg/L of PMS. Furthermore, the wide effective reaction pH range of 4–10 highlights the significant potential of the Co-Cu/Biochar and PMS system for practical HCHO treatment.

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TÓM TẮT

Xử lý Formaldehyde bằng peroxymonosulfate được hoạt hoá bằng than sinh học từ bã mía tẩm kim loại chuyển tiếp

Nghiên cứu này giới thiệu về quá trình xử lý formaldehyde bằng peroxymonosulfate (PMS) được kích hoạt bằng than sinh học từ bã mía đồng tẩm kim loại đồng, cobalt. Bã mía được tiền xử lý bằng kiềm hoá trước khi tẩm kim loại và than hoá tại 700 để tạo thành Co-Cu/Biochar. Các phương pháp phân tích hiện đại như SEM, EDS, XRD và đường đẳng nhiệt hấp phụ - giải hấp phụ nito đã được sử dụng. Kết quả cho thấy, Co-Cu/Biochar có diện tích bề mặt riêng cao (SSA = 419 m2/g) phù hợp để hoạt hoá PMS loại bỏ HCHO. Ảnh hưởng của nồng độ vật liệu, hàm lượng PMS và pH dung dịch đã được nghiên cứu. Kết quả cho thấy, tại nồng độ 20 mg/L, HCHO bị loại bỏ hoàn toàn sau 5 phút phản ứng.

Từ khoá: Than sinh học; Formaldehyde; Chất hoạt hóa PMS; Cobalt; Đồng; Bã mía.