Cobalt-doped biochar derived from coir fiber activation for peroxymonosulfate degradation of methylene blue

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ABSTRACT

In this work, metal-impregnated biochar (Co-Biochar) was used to activate peroxymonosulfate (PMS) and degrade methylene blue (MB) in aqueous solutions. This procedure illustrates a possible method for transforming garbage into useful commodities. Coconut fiber was pyrolyzed in an inert environment to produce biochar, which was then modified with metal salts using the co-precipitation technique. The structural features of the resultant material were studied using sophisticated analytical methods such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and nitrogen adsorption-desorption isotherms. Following PMS activation, the catalyst degraded MB with remarkable efficiency. More than 90% of the MB was removed within 15 minutes using optimum conditions (0.05 g of catalyst, 100 mL of 50 mg/L MB solution, and 400 mg/L PMS). Additionally, the effects of various reaction parameters, such as catalyst dosage, PMS concentration, solution pH, and reaction temperature, were investigated. The findings suggest that Co-Biochar holds significant potential as a PMS activator for the treatment of MB in textile wastewater.

Keywords: Biochar; Dye; PMS activation; Cobalt; Biomass.

1. INTRODUCTION

Industrial wastewater is heavily polluted by dyes, especially from the textile, printing, and paper industries. These dyes pose significant risks to both human health and the environment, causing skin irritation, respiratory issues, and even cancer. The widespread use of azo dyes in the textile industry accounts for 60-70% of their dyeing activities, posing a significant environmental threat. About 15-20% of these dyes are discharged into the environment during the dyeing process, causing severe ecological damage [1]. Despite regulations and awareness of the dangers, many industries continue to discharge untreated dye wastewater into water bodies. It is crucial to address this issue through effective wastewater treatment processes [2]. Various technologies have been developed to remove dyes from wastewater, including precipitation, membrane processes, adsorption, biodegradation, advanced oxidation processes [3], ion exchange [4], electrochemical methods [5], catalytic ozonation [6], and photocatalysis [7]. Although each method has its advantages and disadvantages, advanced oxidation processes are becoming increasingly popular due to their efficiency and environmental friendliness [8]. However, challenges such as high operational costs and secondary sludge generation still remain. To effectively address dye wastewater issues, a combination of multiple methods may be required, taking into account factors such as cost, efficiency, and environmental impact.

Peroxymonosulfate (PMS) and Persulfate (PS) are strong oxidants that can be activated to

generate sulfate radicals and hydroxyl radicals [9]. Sulfate radical-based advanced oxidation processes (AOPs) are gaining attention due to their high oxidation potential and effectiveness in degrading recalcitrant organic compounds. Sulfate radicals have a longer half-life (30–40 μs compared to 20 ns) [10] compared to hydroxyl radicals and are effective in degrading pollutants. [11] The activation of PMS requires the presence of activators, such as transition metals, ultraviolet (UV) light, heat, ultrasound (US), electron conduction, or carbon catalysts [12]. According to the study by Anipsitakis and Dionysiou, transition metals can be used to activate PMS for the degradation of certain emerging organic compounds [13]. The results indicate that the order of PMS activation by transition metals for the degradation of 2,4-DCP is as follows: $Ni^{2+} < Fe^{3+} < Mn^{2+} < V^{3+} < Ce^{3+} < Fe^{2+} < Ru^{3+} < Co^{2+}$ [13]. Metal-catalyzed activation of PMS can lead to secondary pollution due to the leaching of metals into the environment. [14] Carbon-based catalyst materials have a large specific surface area and thermal stability, and they do not cause secondary pollution. However, the inert structure of carbon affects its ability to activate PMS for pollutant degradation [15]. To limit metal leaching and enhance the PMS activation capability of carbon substrates, some studies suggest that metal impregnation on the surface of carbon can improve PMS activation and pollutant degradation. For example, Co-biochar has been used to treat acetaminophen [16], Co@RBC800 has been effective in treating 100% of Levofloxacin [17], and Co-coffee grounds have been used to treat 0.2 mM tetracycline [18]. Biochar is a promising carbon substrate for PMS activation due to its availability and environmental friendliness [19]. Vietnam, being an agricultural country, generates a large amount of agricultural waste daily. Most of it is either burned or landfilled, with only a small portion being composted for fertilizer. This has a significant negative impact on the surrounding environment. The annual coconut yield in Vietnam in 2022, according to the Department of Science and Technology of Ben Tre, was 111.8 quintals per hectare, with 30% of the coconut fruit being coir fiber [20]. Based on the above overview, utilizing coir fiber as biochar impregnated with Co to activate PMS for dye wastewater treatment is a research area worth exploring. Therefore, the proposed research direction could be focused on "magnetic biochar activated peroxymonosulfate for the degradation of Methylene Blue".

2. MATERIAL AND METHOD

2.1. Chemical

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Sodium hydroxide (NaOH), Methylene blue (MB), Hydrogen peroxide (H_2O_2), and Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), a double salt of potassium, in which the active component is peroxymonosulfate ($KHSO_5$), were used in this study. All chemicals were sourced from Xilong, China, and were used without any additional purification processes. The coir fiber fibers were washed and dried before being used as the starting material. All experiments in this study were conducted using deionized water (DI).

2.2. Synthesis of catalysts material

2.2.1. Pretreatment of coir biber

The biomass consists of three main components: hemicellulose, cellulose, and lignin. Therefore, coir fiber, before being used to synthesize catalyst materials, needs to undergo alkali pretreatment to remove lignin and hemicellulose, thus obtaining high-purity cellulose.

The coir fiber, after being cut into small pieces, is alkali-treated with a 3% NaOH solution at a 1:20 weight ratio at 80 °C for 2 hours. After the alkali treatment, the coir fiber is washed several times with water until the pH reaches 7 and then dried at 80 °C until constant weight.

Next, the coir fiber is bleached using 10% H_2O_2 and 1% NaOH (1:1) with a 1:20 weight ratio compared to the coir fiber. This process is carried out at 80 °C for 1 hour. At the end of the process, the coir fiber is washed with water until the pH reaches 7 and dried at 80 °C overnight.

2.2.2. Synthesis of catalysts material

15g of cellulose was added to a 600 mL beaker containing 200 mL of DI water. 7.398 g of $Co(NO_3)_2 \cdot 6H_2O$ was weighed and added to the beaker, then stirred for 30 minutes. Slowly, 0.5 M NaOH solution was added to the beaker until the pH of the solution reached between 9 and 10, and stirring continued for 1 hour. After that, the solid was left to settle naturally for 6 hours. The solid was then vacuum filtered, dried, and heated at 350 °C for 90 minutes. The solid was washed until the pH was around 7 and dried to obtain the catalyst material (Co-Biochar).

2.3. Material preparation

To observe the surface morphology of the material, Scanning Electron Microscopy (SEM) was used. To further investigate the morphology of these samples, SEM was applied. Additionally, the specific surface area and pore size distribution of CoDA were thoroughly examined using nitrogen physical adsorption through the BET PMI-201A method from the United States. Prior to measurement, the samples underwent a vacuum process at 200 °C for 2 hours to ensure optimal conditions for the analysis.

2.4. Catalytic activity

To evaluate the catalytic activity of the synthesized material, Methylene Blue (MB) was used as the pollutant for degradation in the solutions. The degradation experiments were carried out as follows: A certain amount of catalyst material was dispersed into 100 mL of MB solution (50 mg/L), and the mixture was stirred at 200 rpm for 1 minute to ensure the dispersion of the material in the solution. Then, an appropriate amount of PMS was added to the solution to initiate the degradation reaction. At specific time intervals, 1 mL of the mixture was taken and diluted to 25 mL. The solution was then transferred to a UV-Vis spectrophotometer at a wavelength of $\lambda = 664$ nm to determine the MB concentration. The effects of solution pH and initial pollutant concentration were also investigated within the ranges of pH 5-11 and pollutant concentrations of 25-100 mg/L. The MB removal efficiency was calculated using the following equation.

3. RESULT AND DISCUSSIONS

3.1. Characterization of sample

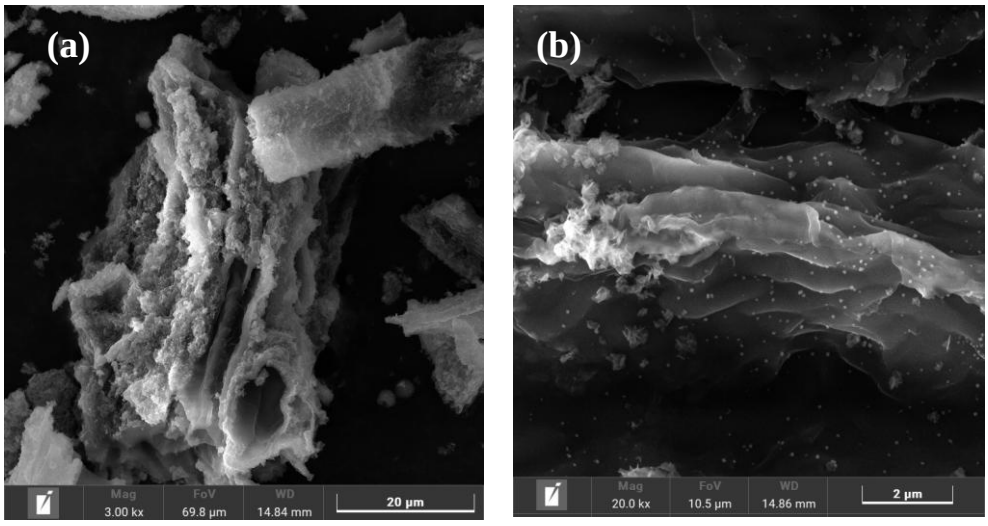

Figure 1. *The SEM image of Co-Biochar scales up x 3.000 times and scales up x 20.000.*

The SEM images (figure 1) of the material show a fibrous shape with metal oxide flakes on the surface. The material has pores approximately 10 µm in size, and its surface is rough. The internal structure of the coir fiber after pretreatment and high-temperature heating has almost lost its original shape. In comparison to the study by Simone et al., the internal structure of the coir fiber

fibers was still preserved, with numerous small pores measuring 9.51 ± 3.44 µm, due to the structural integrity of the cell wall [21]. Additionally, according to the study by Lee et al., the thermal degradation of cellulose and hemicellulose clarified the structure of the cell wall, which primarily consists of lignin [21-22].

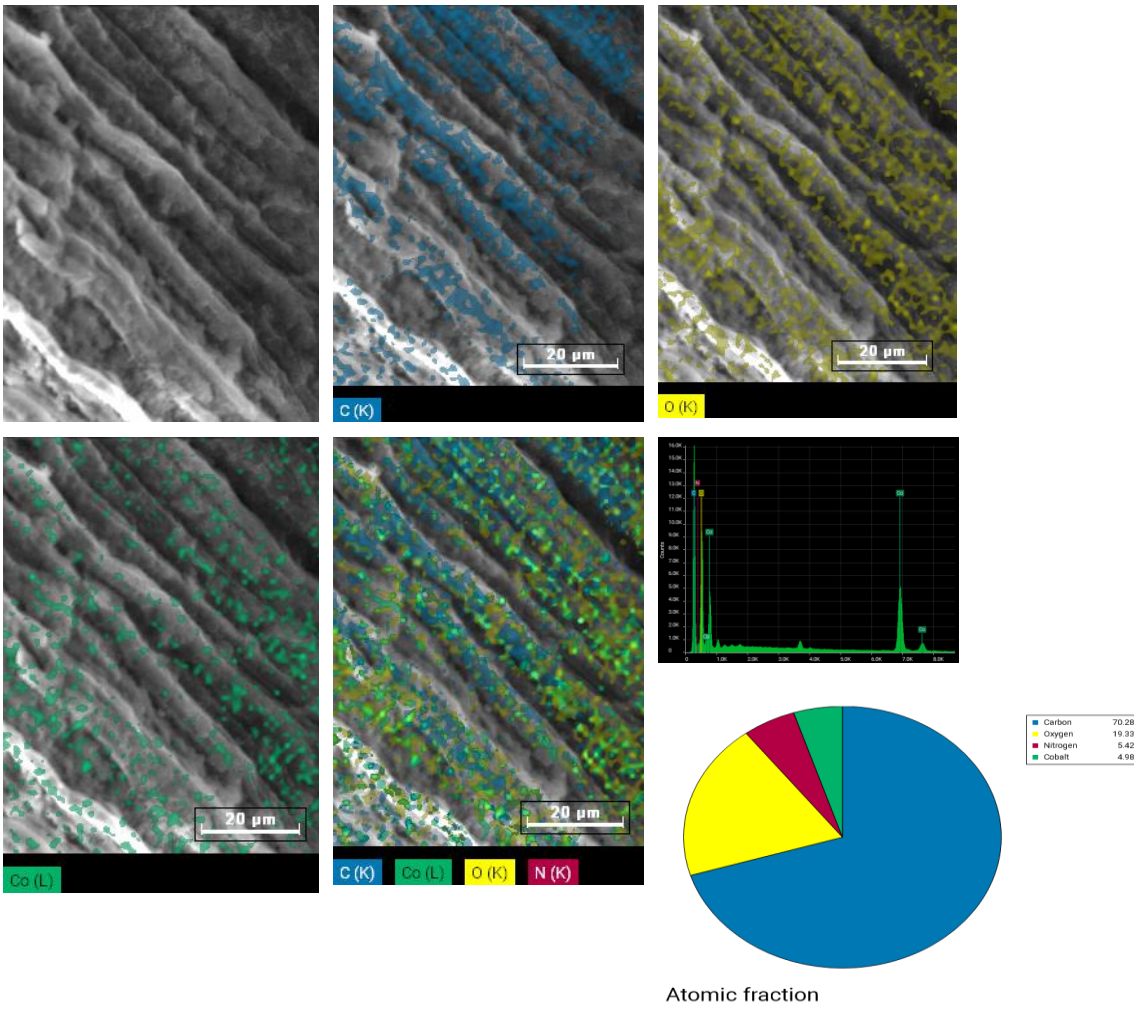

Figure 2. *Elemental distribution on the surface of Co-Biochar via EDS.*

According to the EDS results, the carbon content in the material is approximately 70.29%, which aligns with the study by Guarnieri et al. (Biochar based coir fiber 71.68%) [21]. Hedge et al. developed a diagram for classifying carbon after combustion based on the ratio of oxygen to carbon [23]. The O:C ratio of the material in this study is 0.28, indicating that the material is in a biochar state, where a smaller ratio signifies higher carbon stability. This demonstrates that the Co-Biochar material has high stability and the potential for reuse [24]. The EDS results also show 4.98% Co, confirming that the material was successfully synthesized.

The N_2 adsorption-desorption isotherm and the average pore size distribution curve are shown in figure 3. The N_2 adsorption-desorption isotherm follows a Type IV hysteresis curve with a P/P_0 range of 0.6-0.9, indicating capillary condensation, which is characteristic of mesoporous material structure. The diagram of the average pore diameter distribution shows that the majority of the material's pore diameters are greater than 500 Å (50 nm), indicating that the material's structure is mainly in the form of macropores.

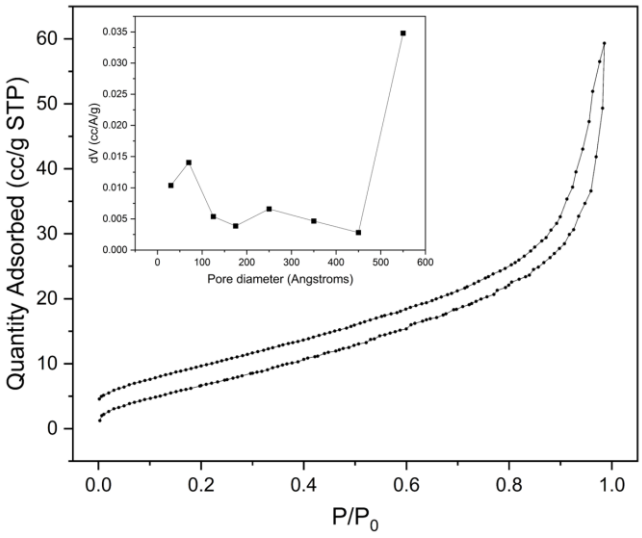

Figure 3. *Adsorption-desorption isotherm of N_2 and pore size distribution of Co-Biochar.*

3.2. Effect of parameters on MB degradation

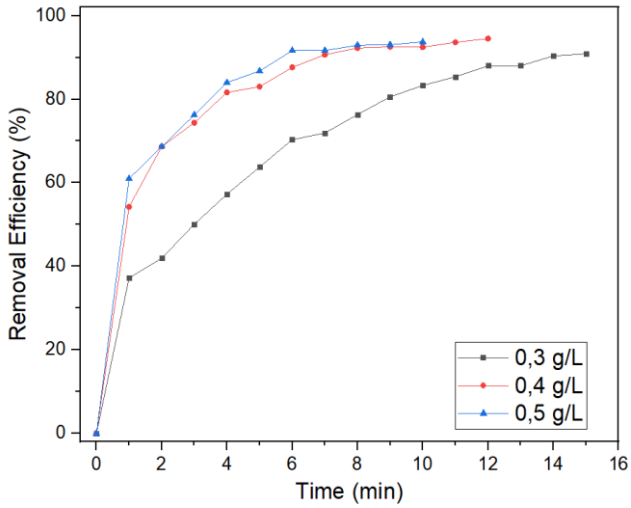

Figure 4. *Effect of catalysts dose on MB degradation.*

The effect of catalyst amount on MB removal efficiency was studied within the concentration range of 0.3 - 0.5 g/L, and the results are presented in figure 4. When a constant PMS amount of 400 mg/L was added to the solution, increasing the catalyst concentration resulted in a higher pollutant removal efficiency. At a concentration of 0.3 g/L, the removal efficiency was only 76.34% after 8 minutes. When the catalyst concentration was increased to 0.4 g/L and 0.5 g/L, the removal efficiency reached 92.26% and 92.94%, respectively, after 8 minutes of reaction. The catalyst plays a crucial role in activating PMS to generate oxidizing agents, which then degrade MB in the solution. At a catalyst concentration of 0.3 g/L, the lower efficiency compared to 0.4 and 0.5 g/L is due to insufficient catalyst to activate PMS. When the catalyst concentration was further increased, there was no significant difference in the removal efficiency between 0.4 g/L and 0.5 g/L, with the efficiency at 0.5 g/L being slightly lower than at 0.4 g/L. This is because an excess of catalyst can generate multiple oxidizing agents simultaneously, and these agents may not have enough time to degrade MB before they are lost due to their short-lived existence. Additionally, determining the appropriate catalyst amount ensures economic feasibility.

Therefore, the optimal concentration used in this study was 0.4 g/L, which was applied to many other experiments.

The effect of PMS concentration on the MB degradation process in the Co-Biochar/PMS system was studied within the range of 300 – 600 mg/L. As shown in figure 5, the removal efficiency of MB generally improved as the PMS concentration increased from 300 – 600 mg/L. At a PMS concentration of 300 mg/L, the treatment efficiency reached approximately 80%.

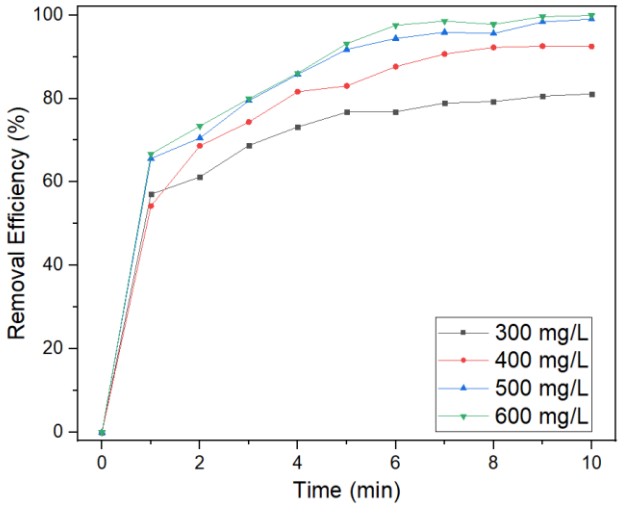

Figure 5. *Effect of PMS dose on MB degradation.*

The MB removal efficiency improved as the PMS concentration increased from 300 to 400 mg/L, but it did not change significantly when the concentration was further increased from 400 to 600 mg/L. Similar to the Fenton process, PMS acts as a source of oxidizing agents to degrade MB. When the PMS concentration was lower than 400 mg/L, the treatment efficiency reached only 80%. When the PMS concentration increased from 500 to 600 mg/L, the treatment efficiency did not change significantly after 10 minutes compared to the 400 mg/L concentration, likely due to the excess PMS. Therefore, a PMS concentration of 400 mg/L was considered optimal.

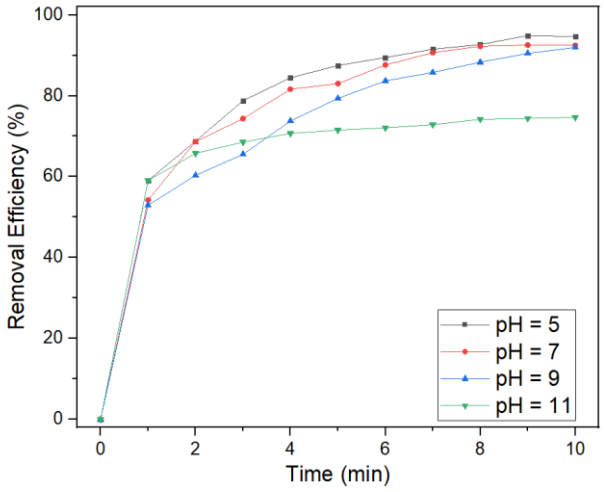

Figure 6. *Effect of initial pH on MB degradation.*

In addition, the degradation of MB at pH values ranging from 5 to 11 was studied using the same amount of catalyst (0.4 g/L) and PMS concentration (400 mg/L) (figure 6). The pH values were adjusted using H_2SO_4 and NaOH solutions. The results showed that the MB removal

efficiency remained relatively stable (over 90% removal after 10 minutes) in the pH range of 5-9, which is one of the advantages of the PMS oxidation method compared to the Fenton process. However, when the pH increased to 11, a competitive reaction between OH^- and HSO_5^- with Co^{2+} could occur, leading to a decrease in MB removal efficiency.

4. CONCLUSIONS

The study successfully synthesized cobalt-doped biochar derived from coir fiber, providing a novel solution for treating methylene blue in wastewater. Coir fiber was utilized as a raw material for synthesizing the catalytic material, addressing environmental issues related to agricultural waste and wastewater treatment. Modern analytical methods such as scanning electron microscopy (SEM) and N_2 adsorption-desorption isotherms were used to analyze the structural characteristics of the synthesized material. The catalytic material, with cobalt active sites, demonstrated the ability to degrade MB in a short period when combined with PMS. The optimal conditions were determined to be 0.04 g of material, 100 mL of 50 mg/L MB solution, and 400 mg/L PMS, achieving more than 90% removal efficiency after 10 minutes. Notably, the catalytic material combined with PMS showed effective performance over a wide pH range (5-9).

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TÓM TẮT

Than sinh học tẩm cobalt có nguồn gốc từ xơ dừa hoạt hóa peroxymonosulfate để phân hủy methylene blue

Trong nghiên cứu này, than sinh học tẩm kim loại (Co-Biochar), đóng vai trò là chất hoạt hóa peroxymonosulfate (PMS) để phân hủy Methylene blue (MB) có trong nước. Quá trình này đóng vai trò then chốt trong việc biến chất thải thành vật liệu có giá trị. Than sinh học được tổng hợp từ xơ dừa bằng quá trình nhiệt phân trong môi trường khí trơ và sau đó biến tính với muối kim loại bằng phương pháp đồng kết tủa. Các đặc tính cấu trúc của vật liệu được phân tích bằng các phương pháp phân tích hiện đại như kính hiển vi điện tử quét (SEM), phổ tán sắc năng lượng nguyên tử (EDS), đường đẳng nhiệt hấp phụ-giải hấp phụ N_2. Vật liệu xúc tác sau khi hoạt hóa PMS cho thấy hiệu quả cao trong việc xử lý MB. Trong điều kiện cụ thể 0,05 g chất xúc tác, 100 mL dung dịch MB 50 mg/L và 400 mg/L PMS, hiệu suất loại bỏ MB khoảng hơn 90% sau 10 phút. Ngoài ra, ảnh hưởng của điều kiện phản ứng như hàm lượng xúc tác, hàm lượng PMS và pH dung dịch đã được nghiên cứu. Kết quả nghiên cứu cho thấy vật liệu có tiềm năng trong việc hoạt hóa PMS xử lý MB có trong nước thải dệt nhuộm.

Từ khoá: Than sinh học; Thuốc nhuộm; Chất hoạt hóa PMS; Cobalt; Sinh khối.