

Article

Behaviors and Mechanism of Visible-Light-Assisted PMS Activation by Porous Iron Tailing-Based Geopolymer for Methylene Blue Degradation

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Abstract

Novel porous geopolymer (IGP&SS), possessing mesoporous structure and a compressive strength of 9.40 MPa, was synthesized through alkali activation of double solid wastes such as iron tailings and steel slag. To overcome the high activation energy barrier of oxidants for refractory pollutant treatment, the IGP&SS was designed to efficiently activate peroxymonosulfate (PMS) under visible-light irradiation, generating reactive radicals for the rapid degradation of methylene blue (MB). The system achieved nearly complete removal within 30 min. To enhance MB removal, the effects of key factors including IGP&SS dosage, PMS dosage, initial MB concentration, temperature, and pH on the degradation process were systematically investigated. Quenching experiments revealed that several reactive oxygen species contributed to MB degradation, with the order of contribution being $\bullet\text{OH} > {}^1\text{O}_2 > \text{SO}_4\bullet^- > \bullet\text{O}_2^-$. Mechanistic studies indicated that the efficient MB degradation was primarily attributed to the flexible Fe(II)/Fe(III) redox cycling in IGP&SS, which accelerated PMS activation and radical generation. X-ray photoelectron spectroscopy (XPS) analysis of the post-reaction catalyst confirmed its structural robustness, revealing a characteristic binding energy shift in the O 1s peak to 530.8 eV and a quantitative redistribution of iron species (Fe(III) content increasing from 40.4% to 57.0%). Given its outstanding performance, demonstrated stability, and eco-friendly preparation, IGP&SS holds great promise for PMS-based advanced oxidation processes in dye wastewater treatment, offering a sustainable approach for high-value utilization of iron tailings and steel slag while alleviating resource scarcity.

Keywords: geopolymer; methylene blue; photo-assisted PMS activation; peroxymonosulfate



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1. Introduction

Methylene blue (MB), a typical cationic dye, exhibits a highly conjugated structure, strong photosensitivity, and slow natural degradation [1]. Its persistent presence in aquatic environments not only diminishes light penetration, thereby inhibiting photosynthesis in algae and aquatic plants, but also exerts toxic effects on the metabolic functions of aquatic organisms [2]. Moreover, MB can enter the human body through the water cycle, potentially affecting the nervous system and physiological processes [3]. Considering both treatment efficiency and practical feasibility, the effective removal of refractory dyes such as MB remains a significant challenge in water pollution control.

Currently, Advanced Oxidation Processes (AOPs) are regarded as one of the most promising technologies for the efficient removal of refractory dyes, owing to their ability to generate reactive oxygen species in situ, enabling rapid degradation and deep mineralization of pollutant molecules [4,5]. Compared with traditional systems such as Fenton and ozone oxidation, peroxymonosulfate (PMS)-based AOPs offer superior oxidation potential, a broader applicable pH range, and greater adaptability to complex water matrices, highlighting their significant potential for dye wastewater treatment [6–8]. However, the PMS molecule possesses high structural stability and a considerable activation energy barrier, which hinders the full exploitation of its oxidative capacity without effective catalysts [9,10]. This inherent characteristic necessitates the use of highly efficient and stable catalytic materials in practical PMS-based applications, thereby representing the core technical bottleneck in PMS activation processes.

Among various PMS-activation materials, iron-based catalysts have emerged as the most extensively studied catalytic system due to their stable Fe(II)/Fe(III) redox cycling characteristics, favorable environmental compatibility, and relatively low cost of raw materials [11–13]. Iron oxides and various iron-based composites have been demonstrated to effectively promote PMS decomposition via electron transfer mechanisms, significantly enhancing the removal efficiency of dye pollutants. For example, the ZVI-E-Fenton-PMS system achieved 98.16% removal of Methylene Blue in wastewater within 60 min, while nZVI-modified ultrafiltration membranes (nZVI@PES) removed 96.8% of Reactive Black 5 under similar conditions [14,15]. Iron oxides and Fe-based composites have also been reported to efficiently activate PMS for azo dye degradation through enhanced Fe(II)/Fe(III) cycling [16]. However, these highly active iron-based materials often require preparation methods such as high-temperature calcination, chemical reduction, or multi-step component tailoring—processes that involve complexity and high energy consumption. Furthermore, in practical operation, there remains a risk of iron ion leaching, which may lead to secondary pollution. These limitations constrain the large-scale application of iron-based PMS catalytic systems, making it challenging to achieve simultaneously high catalytic activity, low cost, and minimal environmental risk. Strategies such as biochar-supported Fe catalysts derived from Fenton sludge have been proposed to enhance catalytic efficiency while reducing cost and environmental impact [14,17].

Against the background of coordinated resource utilization and pollution control, iron ore tailings have attracted increasing attention as low-cost precursors for iron-based catalytic materials [18]. Iron ore tailings are a typical bulk solid waste generated during mineral processing and metallurgical operations, and their long-term stockpiling not only occupies large areas of land but also poses potential threats to surrounding soil and groundwater environments. Owing to their high contents of Fe, Si, and Al, iron ore tailings show natural advantages for the preparation of environmental functional materials, such as porous supports and catalytic materials [19]. If high-value utilization can be realized, problems related to both resource waste and environmental pollution can be effectively alleviated. However, the iron species in iron ore tailings mainly exist in the form of stable crystalline minerals, resulting in limited surface active sites and low intrinsic reactivity [20]. As a result, the direct use of raw tailings in catalytic reactions usually leads to unsatisfactory performance, and various activation strategies, including chemical activation, calcination, and structural reconstruction, are often required. For example, a porous catalyst derived from iron tailings through a reverse leaching–carrier reconstruction strategy exhibited excellent PMS activation performance, achieving over 96% degradation of tetracycline within 30 min and maintaining good stability after repeated cycles [21]. Similarly, magnetically modified iron tailings have also been reported to efficiently activate PMS with low metal leaching [22]. In addition, raw iron ore tailings have been successfully

applied as heterogeneous Fenton-like catalysts for the degradation of typical dyes such as methylene blue [23] and Acid Orange 7 [24], showing reasonable activity and acceptable reusability. These results demonstrate that iron ore tailings possess considerable potential for application in advanced oxidation processes after appropriate activation or modification.

The development of geopolymer technology provides a feasible low-energy pathway for the functional utilization of iron ore tailings [25,26]. Under alkali-activation conditions, the Si–Al components in solid wastes can undergo dissolution, rearrangement, and polycondensation reactions, resulting in the formation of a three-dimensional inorganic polymer network [27]. Such a structure not only endows the material with good chemical stability and certain porosity, but may also regulate the spatial distribution and coordination environment of iron during structural reconstruction, thereby providing potential conditions for its involvement in PMS activation reactions. Recent advancements have significantly expanded the application of geopolymers beyond construction materials into functional photocatalytic composites. For instance, alkali-activated materials functionalized with Bi-based heterostructures have demonstrated enhanced photocatalytic performance for environmental remediation [28]. Similarly, solar-driven self-cleaning geopolymers fabricated from industrial wastes (slags and fly ash) doped with TiO_2 have shown promising results in degrading organic pollutants, promoting a circular economy approach [29]. These studies highlight the potential of geopolymer matrices to support and stabilize active catalytic phases.

However, achieving high degradation efficiency often requires complex functionalization. Comparative studies of similar systems reveal varying efficiencies for Methylene Blue (MB) degradation. For example, porous geopolymer/ ZnTiO_3 / TiO_2 composites achieved 93% MB removal [30], while Ti-bearing blast furnace slag geopolymers reached 96.4% degradation within 90 min under optimized conditions [31]. Phosphoric acid-based geopolymers have also been reported to degrade up to 91.7% of MB under UV irradiation [32]. While these efficiencies are high, many rely on UV light or precious metal doping. Developing a visible-light-driven, iron-tailing-based system that activates PMS to achieve near-complete removal remains a critical research gap. Recently, advanced photocatalytic systems such as metal–organic frameworks (MOFs) and Z-scheme heterojunctions have set high benchmarks for PMS activation. For instance, recent studies have demonstrated that heterostructure designs can significantly enhance charge separation and apparent reaction rates [33,34]. Similarly, specific composite photocatalysts have achieved notable mineralization efficiencies under visible light [35]. However, while these synthetic materials exhibit exceptional kinetics, they often involve complex preparation procedures or high reagent costs. Therefore, benchmarking waste-derived catalysts like IGP&SS against these high-performance systems—specifically regarding reaction rates, mineralization (TOC), and pH adaptability—is essential to evaluate their practical competitiveness.

Based on the above background and challenges, iron tailings were used to prepare a porous geopolymer through alkali activation and foaming. The resulting geopolymer was applied in a PMS system to catalytically degrade methylene blue. The material's mineral composition, microstructure, pore characteristics, and surface chemistry were examined, and its catalytic performance was tested under different reaction conditions. Quenching experiments and X-ray photoelectron spectroscopy were used to investigate how the main reactive species are formed and how the iron valence changes during the reaction. The results show that this work provides a new solid-waste-based catalytic material for efficient, low-carbon dye wastewater treatment and a practical approach for high-value utilization of iron tailings.

2. Results and Discussion

2.1. Structure and Morphology

To evaluate the mechanical stability of the catalysts for practical applications, the compressive strength of geopolymers synthesized with varying H_2O_2 dosages was measured using a YAW-300C testing machine (Zhejiang Yiyu Instrument Equipment Co., Ltd., Shaoxing, China) at a loading rate of 0.3 kN/s. The results, representing the average of three replicates for each condition, are presented in Figure 1. As illustrated, the compressive strength exhibits a distinct downward trend with increasing foaming agent dosage. Specifically, the unmodified base geopolymer achieved a strength of 10.87 MPa after a 28-day curing period. However, upon adding 0.1, 0.3, 0.5, and 0.7 mL of H_2O_2 , the strength declined to 9.83, 9.40, 8.57, and 5.40 MPa, respectively. Notably, at the maximum dosage of 0.7 mL, the material retained only 49.7% of its initial strength, indicating that excessive foaming severely compromises the mechanical integrity of the geo-polymer matrix.

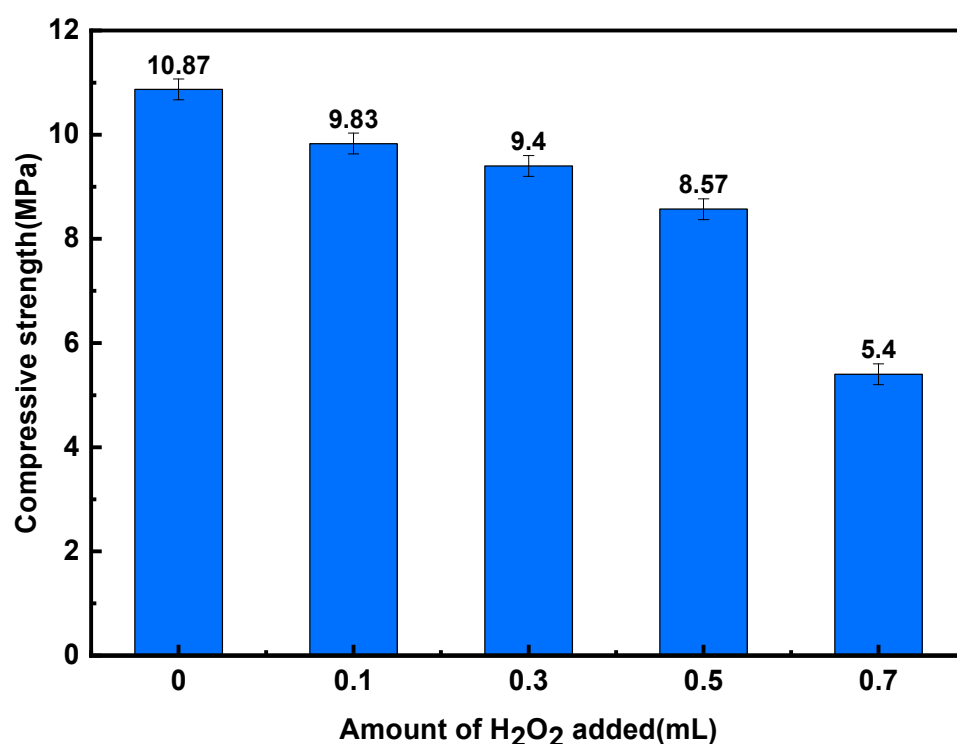


Figure 1. Compressive strength of geopolymer samples synthesized with varying H_2O_2 dosages (0–0.7 mL) after 28 days of curing. The values represent the mean of three replicates, with error bars indicating the standard deviation (Unit: MPa).

Despite the reduction in strength, the introduction of a porous structure is essential for catalytic applications, as it provides accessible active sites and enhances mass transfer efficiency. Therefore, a trade-off between porosity and mechanical stability is critical. Based on the results, the H_2O_2 dosage of 0.3 mL was identified as the optimal condition, yielding a compressive strength of 9.40 MPa. This value is comparable to or higher than that of other iron tailing-based binders reported in the literature (e.g., 6.59 MPa obtained by Levandoski et al. [25]). Although the strength is lower than that of dense geopolymer construction materials (often >30 MPa [26,27]), which is an expected trade-off for the introduction of a mesoporous structure, the optimized IGP&SS maintains sufficient mechanical integrity for handling and recovery in practical water treatment applications while maximizing catalytic efficiency through enhanced porosity.

To further investigate the microstructural characteristics of the optimized catalyst (0.3 mL H_2O_2), a detailed porosity analysis was conducted using a Rapid Air pore structure

analyzer. Figure 2a presents the processed cross-sectional image of the sample. To acquire this image, the specimen surface was polished and filled with zinc oxide (ZnO) paste to enhance the contrast. The software then applied automated color thresholding to segment the image, where the green-colored regions represent the identified pore distribution against the dark geopolymer matrix.

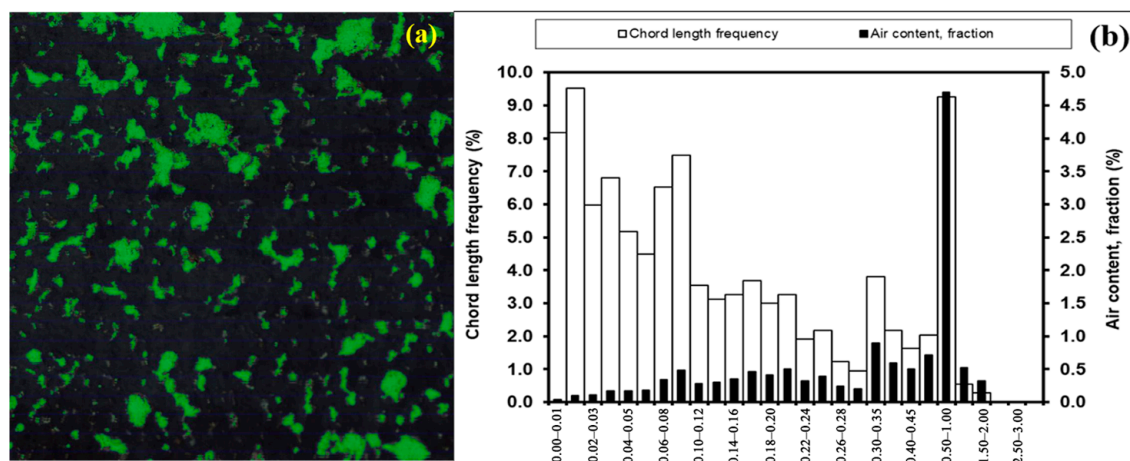


Figure 2. Porosity analysis of the optimized IGP&SS sample (prepared with 0.3 mL H₂O₂) using the Rapid Air system: (a) Processed cross-sectional image where green regions represent identified pores and the black background represents the geopolymer matrix; (b) Quantitative pore size distribution and air content calculated based on chord length measurements.

Based on this segmented image, the quantitative pore parameters were extracted using the linear traverse method. As shown in Figure 2b, the software calculated the chord length (the intercept length of the scan line across a pore) to determine the pore size distribution. The analysis yielded a total porosity of approximately 13.3% and an average chord length of 0.183 mm. This specific pore structure strikes an effective balance, providing ample mass transfer channels for the catalytic reaction while maintaining sufficient structural integrity.

To provide a deeper insight into the micro-textural properties, physisorption measurements were performed on the optimized IGP&SS catalyst (synthesized with 0.3 mL H₂O₂). Figure 3 displays the adsorption–desorption isotherms and the corresponding pore size distribution of this specific formulation. As shown in Figure 3a, the catalyst exhibits a characteristic Type IV isotherm with a distinct hysteresis loop in the relative pressure (P/P_0) range of 0.4–1.0. This profile is indicative of a well-developed mesoporous structure within the material. Specifically, the Brunauer–Emmett–Teller (BET) specific surface area and total pore volume were calculated to be 49.7 m²/g and 0.23 cm³/g, respectively. Furthermore, the pore size distribution curve in Figure 3b reveals that the pore diameter is concentrated around 40 nm. These results confirm that the optimized IGP&SS possesses a dominant mesoporous network, which is favorable for exposing active sites and facilitating mass transport during the catalytic reaction.

Figure 4 presents the SEM images of the used IGP&SS after methylene blue degradation, confirming that the material retains its structural integrity. As visualized in Figure 4b, Fe species remain uniformly distributed across the surface of the catalyst after the reaction. Furthermore, the EDS spectrum in Figure 4c qualitatively confirms the persistent presence of iron signals on the material surface.

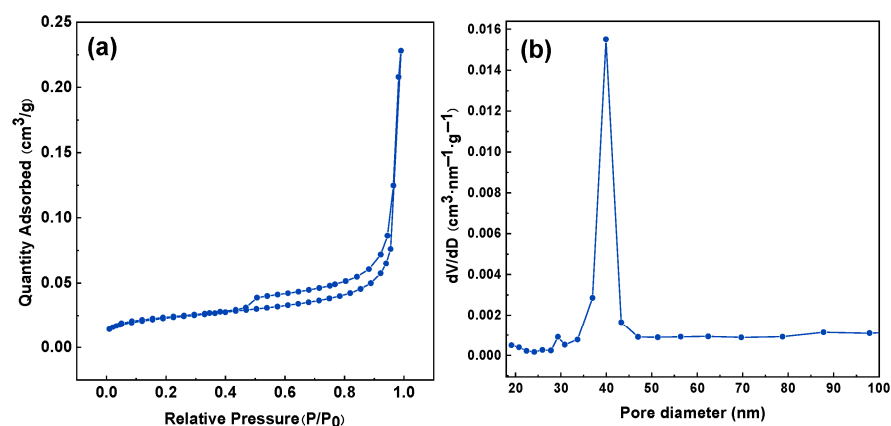


Figure 3. Surface textural properties of the optimized IGP&SS catalyst: (a) N₂ adsorption–desorption isotherms measured at 77 K; (b) Pore size distribution curve derived from the desorption branch using the Barrett–Joyner–Halenda (BJH) method.

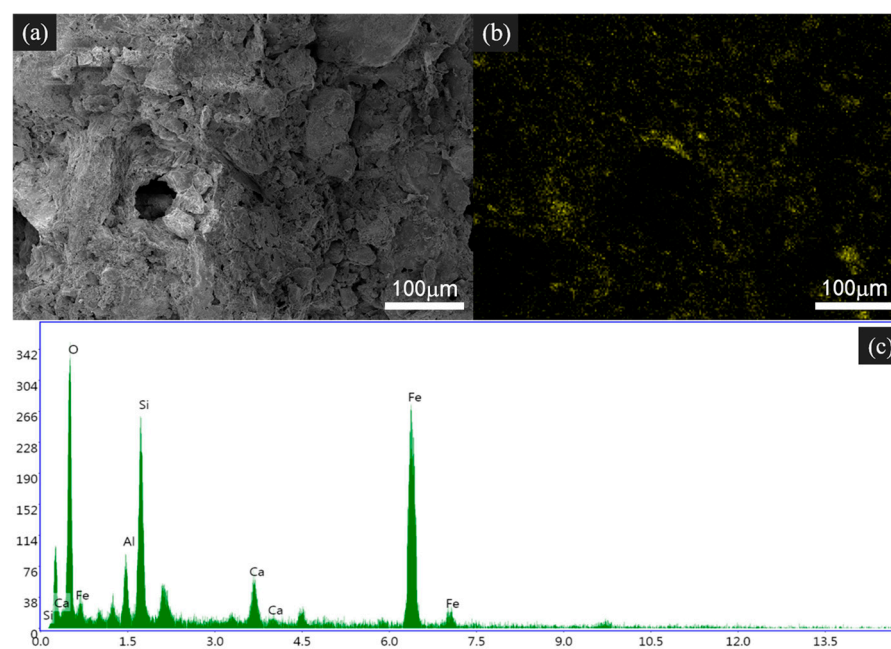


Figure 4. IGP&SS: (a) SEM before reaction; (b) SEM after reaction; (c) EDS after reaction.

To further quantitatively verify the stability of the active sites and assess potential metal leaching, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was conducted. The results showed that the concentration of dissolved iron ions in the solution was initially 0.05 mg/L. After the degradation reaction, the iron concentration increased only marginally to 0.115 mg/L. This negligible leaching demonstrates that the iron species are firmly anchored within the geopolymer framework rather than being simply adsorbed on the surface. Combined with the SEM-EDS characterization, these results confirm that the iron species are actively involved in the reaction while maintaining high stability, preventing secondary pollution and ensuring the catalyst's reusability.

2.2. Adsorption and Photo-Assisted Degradation Performance

To distinguish physical adsorption from chemical degradation, dark adsorption experiments were conducted prior to light irradiation. As shown in Figure 5, the adsorption of MB by IGP&SS reached equilibrium within 30 min in the dark. The removal rate via adsorption was approximately 5.0% ($C/C_0 = 0.95$), indicating that the mesoporous structure provides channels for diffusion but the material itself exhibits limited adsorption capacity

for cationic dyes. This confirms that the subsequent rapid decrease in MB concentration under visible light is primarily attributed to the visible-light-driven PMS activation process rather than physical accumulation on the catalyst surface.

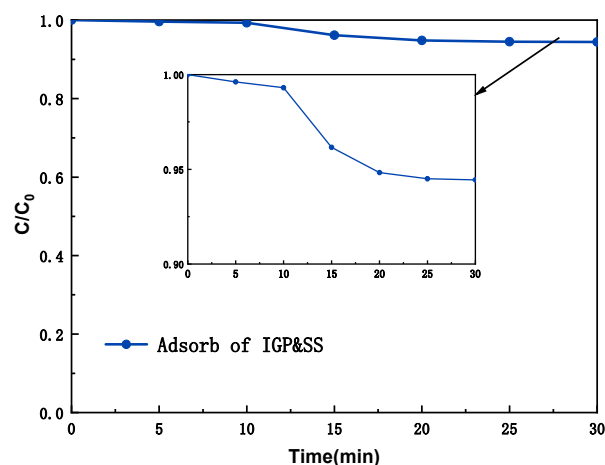


Figure 5. Dark adsorption kinetics of MB on the IGP&SS catalyst to establish adsorption–desorption equilibrium. (Experimental conditions: $[MB]_0 = 10$ mg/L, catalyst dosage = 1.5 g/L, pH = 7, $T = 25$ °C.)

2.3. Factors on MB Degradation by IGP&SS

The influence of varying IGP&SS dosages on the MB degradation rate is depicted in Figure 6a. Under conditions where the initial MB solution concentration was 10 mg/L, PMS dosage was 15 mg, the initial pH of the solution was 7, and the temperature was maintained at 25 °C, the impact of different catalyst dosages on MB degradation within a 30 min period was examined. The results indicate that the IGP&SS-PMS system exhibits rapid and efficient degradation of MB. Without the addition of IGP&SS, PMS activated solely by light achieved approximately 52% removal of MB after 30 min. However, upon incorporation of IGP&SS, the 30 min removal rate escalated to over 95%. At an IGP&SS dosage of 50 mg, approximately 65.0% of MB degraded within 30 min, whereas increasing the IGP&SS dosage to 100 mg and 150 mg led to MB degradation rates of 65.6% and 90.1%, respectively.

To quantitatively evaluate the reaction efficiency, the degradation kinetics were analyzed using the pseudo-first-order kinetic model:

$$\ln(C/C_0) = -k_{obs} \cdot t \quad (1)$$

where C and C_0 are the MB concentrations at the time t and initial time, and k_{obs} is the apparent rate constant. The value of k_{obs} was determined from the negative slope of the linear plot of $\ln(C/C_0)$ versus reaction time. As the IGP&SS dosage increased from 50 mg to 150 mg, the calculated k_{obs} values increased from 0.0338 min^{-1} to 0.0927 min^{-1} . This enhancement is attributed to the increased availability of active sites on the IGP&SS surface for PMS activation and the generation of more excited electrons for redox reactions. However, further increasing the dosage beyond 150 mg yielded only a marginal improvement (~5%). This limitation is likely due to the “shielding effect,” where excessive catalyst particles cause light scattering and reduce the penetration depth of the irradiation, thereby decreasing the effective photo-activation efficiency. Consequently, 150 mg was selected as the optimal dosage.

The effect of varying PMS dosage on the MB degradation rate is illustrated in Figure 6c. As evident from the figure, the degradation rate of MB increases with escalating PMS dosages within a 30 min period. When the PMS dosage is incremented from 10 mg to 25

mg, the MB removal rate rises from 88.4% to 98.9%. Concurrently, the first-order kinetic degradation rate constant (k_{obs}) for catalytic degradation increases from 0.0622 min^{-1} to 0.1132 min^{-1} . An augmented PMS dosage generates a higher concentration of reactive radicals ($\bullet\text{OH}$ and $\text{SO}_4\bullet^-$), enhancing the oxidation potential and the probability of collision with dye molecules. However, doubling the dosage from 10 mg to 20 mg only improved degradation by $\sim 10\%$, suggesting diminishing marginal returns. This may be caused by the self-quenching of radicals at high concentrations or the saturation of catalyst active sites. Considering both economic cost and degradation performance, 15 mg was chosen for subsequent experiments. This dosage corresponds to an active peroxymonosulfate (HSO_5^-) concentration of approximately 0.49 mM (calculated based on the molecular weight of the pure triple salt, $M_w \approx 614.7 \text{ g/mol}$).

The influence of initial MB concentration is shown in Figure 6e. The degradation rate decreased significantly as the initial concentration increased. Specifically, the removal rate dropped from 95.8% at 5 mg/L to 60% at 20 mg/L. This phenomenon is attributed to several factors: (1) Competitive light absorption: High concentrations of dye molecules absorb a significant portion of incident light, reducing the photons available for activating the catalyst and PMS; (2) Site saturation: Adsorption sites on the catalyst surface become saturated by MB molecules and degradation intermediates, hindering the catalytic cycle; and (3) Radical scavenging: Excess dye molecules and intermediates may act as scavengers, consuming active radicals non-selectively and reducing the overall mineralization efficiency.

Figure 6g illustrates the impact of temperature. The removal rate increased from 62.4% to 91.0% as the temperature rose from 20°C to 50°C . At 20°C , the reaction was initially slow due to the lower thermal energy required to overcome the activation energy barrier. As the reaction proceeded and the temperature increased (due to the thermal effect of irradiation), the rate accelerated. At 50°C , 80% degradation was achieved within the first 15 min. This thermal enhancement promotes radical generation and molecular diffusion. However, considering energy consumption and the fixed reagent dosages, further temperature increases were not pursued.

The effect of initial pH is demonstrated in Figure 6i. The degradation efficiency increased with pH, rising from 56.5% at pH 3 to 81.3% at pH 9. When the initial pH was further increased to 12, the system achieved a remarkable degradation efficiency, with an MB removal rate of 94.4% after 30 min. At lower pH, the high concentration of H^+ may scavenge sulfate radicals or protonate the catalyst surface, inhibiting the catalytic activity. Conversely, in alkaline environments, the IGP&SS which releases OH^- due to its alkali-activated nature performs optimally. Furthermore, under alkaline conditions, $\text{SO}_4\bullet^-$ can be converted into $\bullet\text{OH}$, thereby enhancing the degradation rate. This pH-dependent behavior aligns with the radical quenching results discussed later, which identify $\bullet\text{OH}$ as the dominant active species.

To evaluate the competitiveness of IGP&SS, its catalytic performance was compared with recent visible-light-driven PMS activators reported in the literature, focusing on apparent rate constants (k_{obs}), TOC removal, and operational pH ranges. High-performance synthetic catalysts, such as Z-scheme heterojunctions and functionalized MOFs, typically exhibit k_{obs} values ranging from 0.05 to 0.2 min^{-1} and TOC removal rates of 50–70% depending on the pollutant [33,34]. The IGP&SS system achieved a competitive k_{obs} of 0.1132 min^{-1} (at optimized PMS dosage) and a superior TOC removal of 75%. While some noble-metal-doped or highly engineered composites may offer slightly faster initial kinetics [35], IGP&SS offers a distinct advantage in pH adaptability. Unlike traditional iron-based catalysts that are strictly limited to acidic conditions (pH 3–4) to prevent precipitation, IGP&SS maintains high activity in alkaline environments (pH 9–12) due to the in situ generation of $\bullet\text{OH}$ facilitated by the geopolymer's alkaline nature. Furthermore, the use

of iron tailings and steel slag significantly reduces raw material costs compared to the organic linkers and metal precursors required for MOFs, presenting a more sustainable “waste-to-catalyst” solution for large-scale applications.

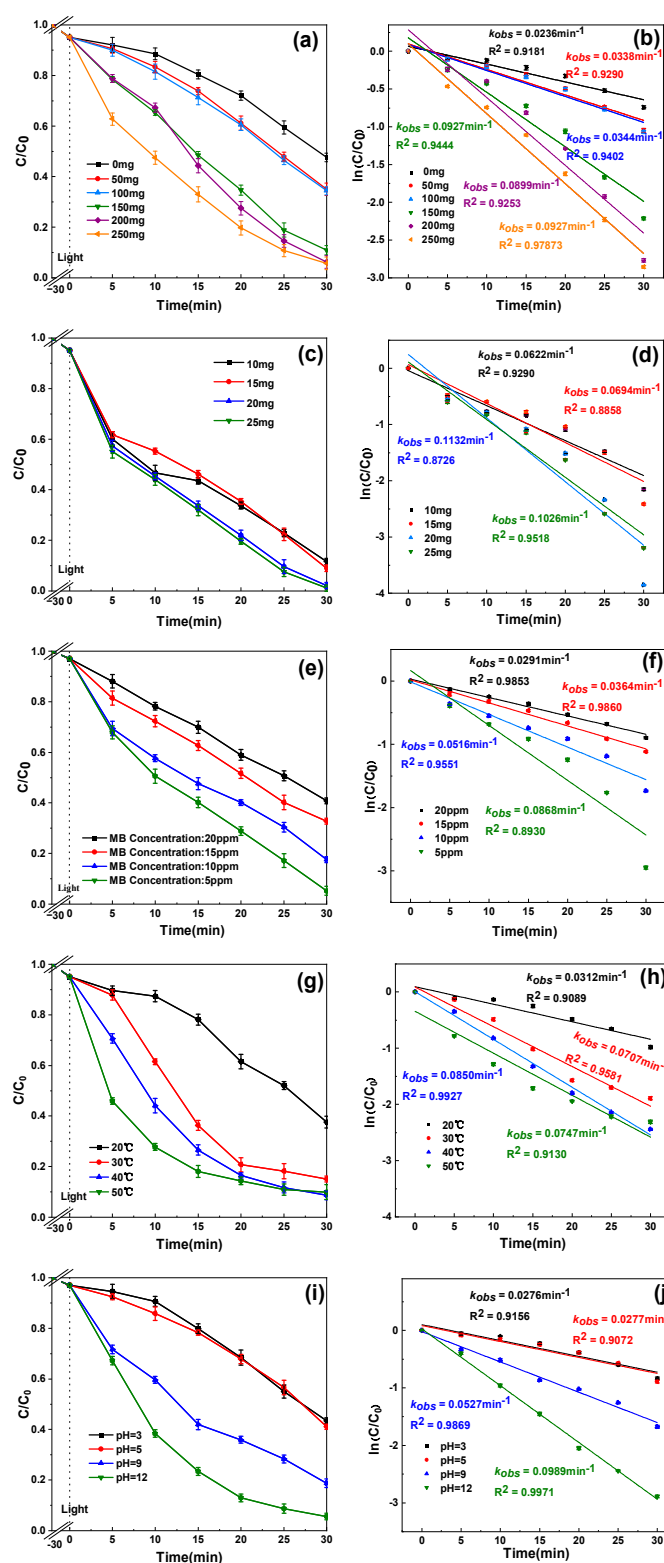


Figure 6. Effects of different parameters on MB degradation efficiency and the corresponding pseudo-first-order kinetic fitting curves: (a,b) IGP&SS dosage (50–150 mg); (c,d) PMS dosage (10–25 mg); (e,f) initial MB concentration (5–20 mg/L); (g,h) reaction temperature (20–50 °C); and (i,j) initial pH (3–12). (Standard conditions unless otherwise varied: $[MB]_0 = 10$ mg/L, catalyst = 1.5 g/L, PMS = 15 mg, pH = 7, T = 25 °C.)

2.4. Stability and Reusability of the IGP&SS

A crucial aspect of evaluating the practical efficacy of IGP&SS in the degradation of MB is to assess its reusability. Figure 7a depicts the results of a study that examined the degradation performance of MB in response to repeated cycles. The findings revealed a marginal reduction in MB degradation efficacy over multiple cycles, with the degradation rate of MB still reaching approximately 80% even after five cycles of experiments. These results indicate the potential for reusing IGP&SS for the degradation of printing and dyeing organic wastewater. The structural stability of the IGP&SS before and after the reaction was further evaluated by XRD. As shown in Figure 7b, the identified crystalline phases in the catalyst consist of Quartz, Hematite, and Nickel Titanate. It is important to note that Nickel Titanate is a refractory mineral component inherent to the raw iron tailings and steel slag, rather than a newly formed phase generated during the low-temperature geopolymerization (60 °C). The prominent diffraction peak observed in the 26–30° range (specifically at 26.6°) is associated with the (101) plane of Quartz. Additionally, the peak at approximately 50.1° corresponds to the (112) plane of Quartz. It is noteworthy that the intensity of these Quartz peaks exhibits an increase after five consecutive cycles. This enhancement is attributed to the “relative enrichment” effect: during the aqueous catalytic process, the dissolution of minor unstable amorphous components or soluble surface species within the geopolymer matrix leads to a reduction in the amorphous background signal, thereby effectively increasing the relative diffraction intensity of the stable crystalline quartz skeleton. These results confirm that the IGP&SS catalyst possesses excellent structural robustness and maintains its core mineral phases during the reaction.

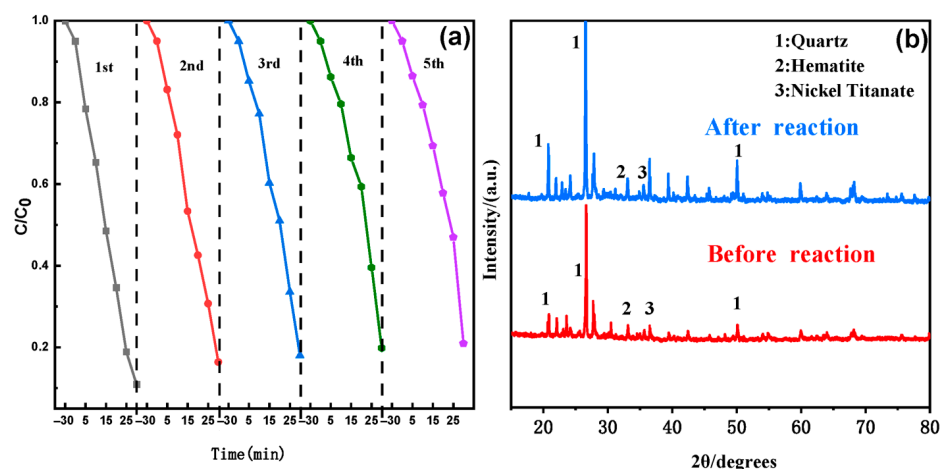


Figure 7. (a) Reusability of IGP&SS for MB degradation over five consecutive cycles (Conditions: $[MB]_0 = 10$ mg/L, catalyst = 1.5 g/L, PMS = 15 mg, pH = 7); (b) XRD patterns of the fresh IGP&SS and the used catalyst after the 5th cycle, identifying crystal phase stability.

To quantitatively assess metal leaching and catalyst stability, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was employed to monitor iron concentration in the solution after reaction and across five consecutive reuse cycles. The dissolved Fe concentration remained very low (<0.15 mg/L even after five cycles), indicating negligible iron leaching and confirming that iron species are firmly anchored within the geopolymer framework rather than loosely adsorbed on the surface. While iron is the primary active component and the focus of this study, we acknowledge that comprehensive leaching tests for other trace metals potentially present in iron tailings and steel slag were not conducted, which represents a limitation of the current work.

The low iron leaching and retained catalytic performance over multiple cycles highlight the excellent stability of IGP&SS and its low risk of secondary pollution from the

active component. But the potential release of other heavy metals (e.g., Cr, Ni, Mn) inherent in the iron tailings and steel slag was not systematically evaluated in the current scope. Standardized environmental risk assessments, such as the Toxicity Characteristic Leaching Procedure (TCLP), are recognized as essential for comprehensive validation. Consequently, these broader leaching protocols will be strictly implemented in follow-up research to further substantiate the environmental safety of the material.

2.5. Mechanism of Photo-Assisted PMS Activation in IGP&SS-PMS System

To elucidate the catalytic mechanism and identify the primary reactive oxygen species (ROS), radical quenching experiments were conducted. Typically, scavengers are introduced in excess to competitively inhibit specific radicals. In this study, tert-butanol (TBA, 100 mM), methanol (MeOH, 100 mM), ethanol (EtOH, 100 mM), p-benzoquinone (BQ, 2 mM), and L-histidine (10 mM) were employed to quench hydroxyl radicals ($\bullet\text{OH}$), sulfate/hydroxyl radicals ($\text{SO}_4\bullet^- / \bullet\text{OH}$), sulfate radicals ($\text{SO}_4\bullet^-$), superoxide radicals ($\bullet\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$), respectively.

As illustrated in Figure 8, the degradation efficiency of MB (90.1% in the control group) was inhibited to varying degrees by the scavengers. The addition of p-BQ resulted in a negligible decrease in degradation efficiency to 89.1%, suggesting that $\bullet\text{O}_2^-$ plays a minor role in the system. The introduction of L-histidine and EtOH reduced the degradation rates to 74.34% and 84.09%, respectively, indicating the partial contribution of $^1\text{O}_2$ and $\text{SO}_4\bullet^-$. Notably, the presence of TBA (a specific scavenger for $\bullet\text{OH}$) caused a significant drop in efficiency to 57.68%. Furthermore, MeOH (which quenches both $\text{SO}_4\bullet^-$ and $\bullet\text{OH}$) exhibited the strongest inhibitory effect, suppressing the degradation to 43.05%. The substantial inhibition by TBA confirms that $\bullet\text{OH}$ is the dominant active species. This aligns with the pH influence discussed in Section 2.3; the alkaline microenvironment provided by the geopolymer matrix facilitates the transformation of $\text{SO}_4\bullet^-$ to $\bullet\text{OH}$ (Equation (2)).

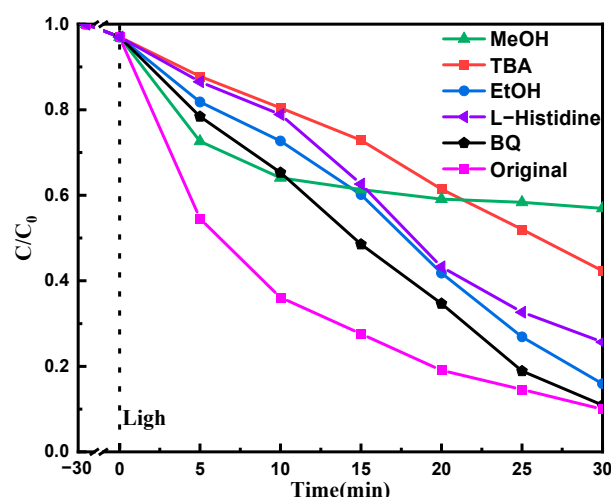


Figure 8. Effect of different radical scavengers on the degradation of MB in the IGP&SS-PMS system. (Experimental conditions: $[\text{MB}]_0 = 10 \text{ mg/L}$, catalyst = 1.5 g/L , PMS = 15 mg , initial pH = 7, $T = 25^\circ\text{C}$. Scavenger concentrations: p-BQ = 2 mM , L-histidine = 10 mM , EtOH = 100 mM , TBA = 100 mM , and MeOH = 100 mM .)

Based on the magnitude of inhibition, the contribution of reactive species follows the order: $\bullet\text{OH} > ^1\text{O}_2 > \text{SO}_4\bullet^- > \bullet\text{O}_2^-$. It is worth noting that this result differs from many conventional iron-based PMS activation systems, where $\text{SO}_4\bullet^-$ is typically the dominant active species [36,37]. This distinction is attributed to the inherent alkalinity of the steel slag-

based geopolymer matrix. In the alkaline micro-environment on the catalyst surface, the generated $\text{SO}_4^{\bullet-}$ can react with OH^- to form $\bullet\text{OH}$. This finding highlights a key novelty of the IGP&SS catalyst: unlike neutral supports, the alkaline solid waste matrix naturally modulates the radical generation pathway towards $\bullet\text{OH}$ dominance without the need for external pH adjustment. Since $\bullet\text{OH}$ is a non-selective oxidant with a higher redox potential (1.9–2.7 V) than $\text{SO}_4^{\bullet-}$ in basic conditions, this feature is particularly advantageous for the broad-spectrum degradation of complex organic pollutants.

Iron serves as the primary active site in the catalytic mechanism, exerting a pivotal influence on methylene blue degradation efficiency. XPS analyses were performed on pristine and post-reaction IGP&SS specimens to elucidate iron's valence alterations (Figure 9). The survey spectrum for the fresh IGP&SS revealed prominent signals for Fe 2p, O 1s, Si 2p, Ca 2p, Na KL1, C 1s, and Cl s; post-reaction, the profile remained largely intact, except for the complete disappearance of the Na KL1 signal and reduced intensities of Ca 2p and Cl s—likely due to aqueous leaching—highlighting the structural stability of IGP&SS. High-resolution Fe 2p scans (Figure 9b,c) showed that, before the reaction, the spectrum was dominated by Fe(II) species, with deconvoluted peaks suggesting contributions from Fe(II) in the 2p_{3/2} and 2p_{1/2} regions along with minor Fe(III) presence. After the reaction, a clear shift to higher binding energies occurred, with prominent peaks at 709.9 eV and 723.5 eV corresponding to Fe(II), accompanied by broadened envelopes and enhanced high-energy shoulders indicative of significantly increased Fe(III) content.

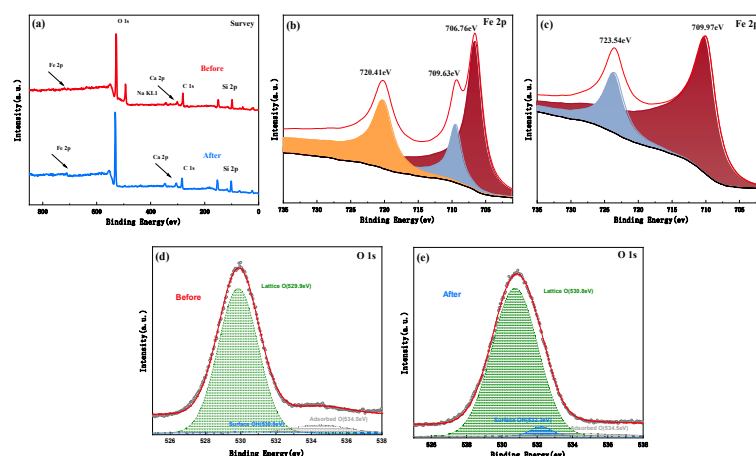


Figure 9. XPS spectra of IGP&SS before and after the reaction: (a) Wide-scan survey spectra; High-resolution core-level spectra of (b) Fe 2p (before), (c) Fe 2p (after), (d) O 1s (before) and (e) O 1s (after) illustrating the valence changes of iron species and surface oxygen evolution.

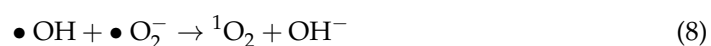
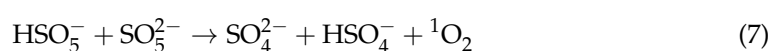
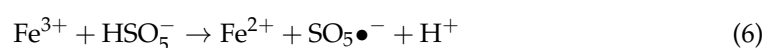
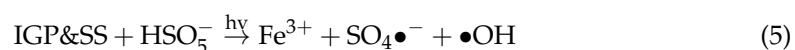
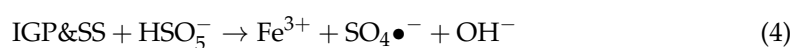
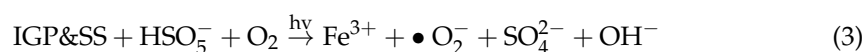
The O 1s spectra (Figure 9d) provide direct evidence of surface reconstruction during the catalytic process. The IGP&SS before reaction exhibited a main characteristic peak at 527.6 eV, which is attributed to low-coordinate lattice oxygen (O^{2-}) or electron-rich oxygen species inherent to the specific mineral phases of the iron tailings [38]. However, after the reaction, a substantial positive binding energy shift of approximately +3.2 eV was observed, with the dominant peak appearing at 530.8 eV.

This large shift is indicative of a fundamental transformation in the surface chemical environment. It confirms that the catalyst surface undergoes rigorous hydration and oxidation upon contact with the aqueous PMS solution, transforming from an initial low-binding-energy oxide state to a phase dominated by surface metal-hydroxyl groups ($\text{M}-\text{OH}$) and adsorbed oxygen species [39]. Such a phenomenon of binding energy shift caused by surface restructuring is consistent with observations in other advanced oxidation catalysts, where the formation of active hydroxyl layers leads to higher binding energy states due to the electronegativity of hydrogen and the change in metal coordination [40].

The surface iron speciation of IGP&SS underwent profound redistribution during the peroxymonosulfate-activated degradation of methylene blue. Quantitative deconvolution of the Fe 2p_{3/2} envelope revealed that the relative Fe(II) content plummeted from 59.6% to 43.0%, while Fe(III) increased sharply from 40.4% to 57.0%. This consumption of Fe(II) and the dominant conversion to trivalent iron are consistent with a classic Fenton-like redox cycling mechanism, wherein surface Fe(II) act as primary electron donors for PMS activation to generate $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals [41–43]. The persistence of a minor Fe(II) fraction post-reaction suggests either limited in situ regeneration via reductive pathways or kinetically protected sites within the geopolymer framework. To strictly verify the surface chemical states, the O 1s spectra were calibrated referencing the C 1s peak at 284.8 eV and deconvoluted using Gaussian-Lorentzian line shapes with constrained FWHM. As shown in Figure 9d,e, the O 1s spectrum of the fresh IGP&SS was resolved into three characteristic peaks: lattice oxygen (O_{lat}) at 529.9 eV, surface hydroxyl groups (O_{sur}) at 530.8 eV, and adsorbed oxygen species (O_{ads}) at 534.5 eV. The dominance of the O_{lat} peak confirms the oxide-rich nature of the pristine geopolymer skeleton.

Following the catalytic reaction, a significant surface reconstruction was observed. The binding energy of the lattice oxygen shifted positively to 530.8 eV, accompanied by a substantial increase in the intensity of the surface hydroxyl peak, which shifted to 532.3 eV. This positive binding energy shift (~ 0.9 – 1.5 eV) indicates a change in the surface electron environment, attributed to the strong protonation and hydration of the catalyst surface in the aqueous solution. The marked increase in the $\text{O}_{\text{sur}}/\text{O}_{\text{lat}}$ ratio confirms the in situ generation of abundant metal-hydroxyl active sites (M–OH) during the degradation process, which are essential for the activation of PMS and the production of reactive radicals.

Based on the previous studies, quenching experiments and XPS analysis, the possible degradation mechanism of MB in the IGP&SS-PMS system was proposed in Equations (3)–(8) and Figure 10 as follows: Under visible-light irradiation, the IGP&SS catalyst mediates the rapid cycling of Fe(III)/Fe(II) and $\bullet\text{O}_2^-$ (Equation (7)) [44,45], leading to the generation of superoxide radicals ($\bullet\text{O}_2^-$) that effectively degrade MB. The PMS was activated on IGP&SS, attributed to the cleavage of the –O–O– bond in PMS and the rapid Fe(II)/Fe(III) cycle. Initially, the Fe(II) was oxidized into Fe(III) used HSO_5^- ; however, the HSO_5^- was reduced to produce $\text{SO}_4^{\bullet-}$, OH^- and $\bullet\text{OH}$ (Equations (4) and (5)). Then, the generated Fe(III) can also act as an electron acceptor, the Fe(III) was reduced to Fe(II) by HSO_5^- to form a virtuous Fe(II)/Fe(III) circle, at the same time, HSO_5^- was oxidized into $\text{SO}_5^{\bullet-}$ and H^+ (Equation (6)). In addition, PMS can decompose to produce $^1\text{O}_2$ (Equation (7)) [46]. The previously formed $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ can react to form $^1\text{O}_2$ and OH^- (Equation (8)) [47]. This produces reactive radicals such as $\bullet\text{O}_2^-$, $\bullet\text{OH}$, $\text{SO}_5^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ which synergize with inactive radicals as $^1\text{O}_2$ to effectively remove MB.



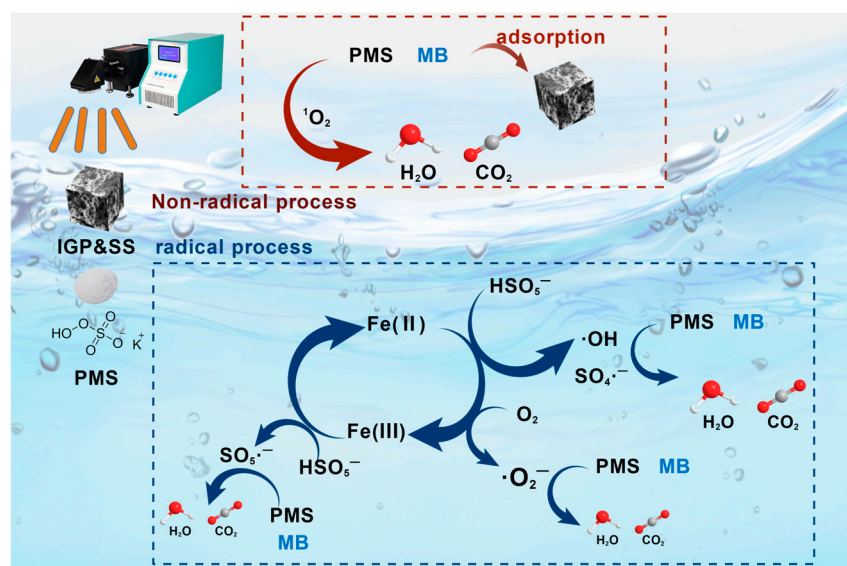


Figure 10. Proposed mechanism for MB degradation in IGP&SS-PMS system.

2.6. Degradation Pathway of Methylene Blue

During the initial stage of the reaction, the MB molecule undergoes a deionization process in which chloride ions are released. Based on the intermediates identified by HPLC-MS analysis, the possible degradation pathway I involves the cleavage of C–N bonds and demethylation induced by active radical species ($\bullet\text{O}_2^-$, $\text{SO}_4\bullet^-$, and $\bullet\text{OH}$). Products MB1, MB2, and MB3 are attributed to the successive demethylation of MB. Additionally, product MB4 is formed through oxidative ring-opening of products MB1, MB2, or MB3, followed by further consecutive demethylation steps. Pathway II likely involves oxidation of the sulfur atom, yielding product MB5. Subsequently, the carbon–nitrogen bond (C–N bond) in product MB5 breaks, accompanied by continuous demethylation, leading to the formation of products MB6 and MB7. Finally, these intermediates are further oxidized as the reaction proceeds.

While complete mineralization to CO_2 and H_2O is the ideal goal, it is important to note that in AOPs, the rate of TOC removal typically lags behind decolorization. Similar studies on Fe-based PMS activation systems have reported TOC removal rates ranging from 30% to 60% depending on reaction time and conditions [45,48]. To verify the degree of mineralization and substantiate the effective treatment of the pollutant, Total Organic Carbon (TOC) removal was experimentally determined. Figure 11 illustrates the control experiment using PMS alone resulted in a negligible TOC removal of only 10%, indicating that the oxidant alone could primarily induce partial oxidation or chromophore destruction. In contrast, the IGP&SS-PMS system achieved a substantial TOC removal efficiency of 75% under the same conditions. Although the TOC removal rate lags slightly behind the decolorization efficiency (>98%), this result confirms that the majority of Methylene Blue molecules were successfully mineralized into CO_2 and H_2O rather than merely being transformed into colorless organic intermediates. This high degree of mineralization, combined with the oxidative ring-opening pathway identified by HPLC-MS, suggests a significant reduction in the accumulation of toxic aromatic by-products, thereby ensuring the environmental safety of the treated effluent. Regarding the potential risks of reactive species in the effluent, the generated radicals ($\bullet\text{OH}$ and $\text{SO}_4\bullet^-$) possess extremely short half-lives (in the microsecond range) and are rapidly quenched in the aqueous environment upon the cessation of the reaction. Furthermore, any residual PMS can be effectively neutralized by mild reducing agents or naturally consumed by the water matrix in practical applications, preventing

downstream ecological risks. A schematic diagram of the degradation pathways is shown in Figure 12.

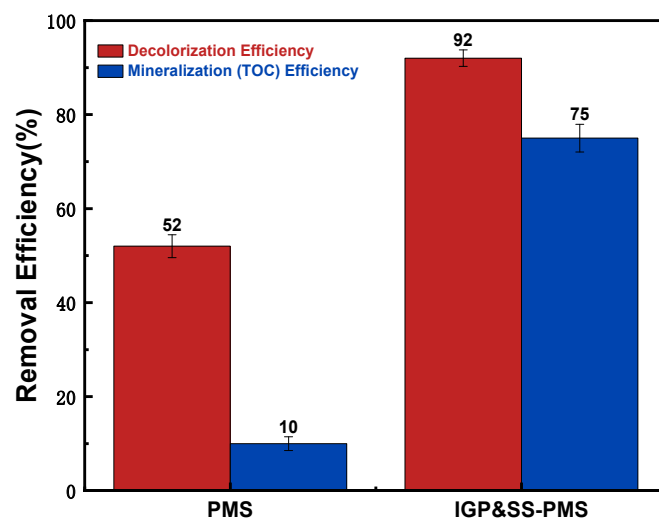


Figure 11. Comparison of decolorization and mineralization (TOC removal) efficiencies between the Light/PMS system (control) and the Light/IGP&SS/PMS system. Experimental conditions: [MB] = 10 mg/L, [PMS] = 15 mg, [Catalyst] = 1.5 g/L (for IGP&SS system), initial pH = 7.0, T = 25 °C. Both systems were irradiated by a 300 W Xenon lamp ($\lambda > 420$ nm). The reaction time was 30 min.

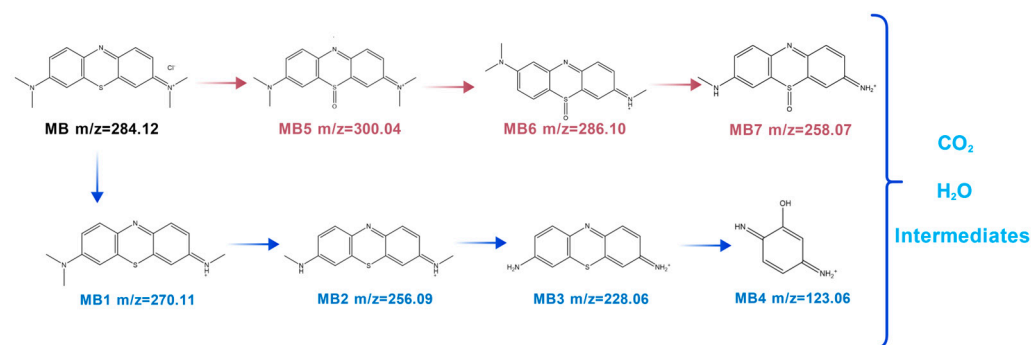


Figure 12. Methylene blue possible degradation pathway.

3. Materials and Methods

3.1. Synthesis of Iron Tailings Geopolymers

The iron tailings were obtained from mine tailings in Kunming, Yunnan, the composition of iron tailings is presented in Table 1, with the primary constituents SiO₂ (45.07 wt%), Fe₂O₃ (24.92 wt%) and Al₂O₃ (13.38 wt%) as well as the others. The steel slag was provided by Shuolong Mineral Products Processing Factory, Lingshou County, Shijiazhuang City, Hebei Province, China. The composition of the dried steel slag is presented in Table 2. The results indicate that the slag is primarily composed of CaO (41.21 wt%), Fe₂O₃ (18.42 wt%), and SiO₂ (15.83 wt%), along with minor constituents including MgO (7.15 wt%), P₂O₅ (3.59 wt%), and Al₂O₃ (2.04 wt%). Liquid sodium silicate (molar ratio: SiO₂/Na₂O = 3.3) provided by Shandong Youso Chemical Technology Co., Ltd. (Zibo, China) Potassium peroxydisulfate (PMS, commercial name Oxone®, Lanxess, Memphis, TN, USA) was used as the oxidant source. The reagent is a standard triple salt with the formula 2KHSO₅·KHSO₄·K₂SO₄ (active oxygen ≥ 4.5%) and was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (96%), hydrogen peroxide (30%), and hydrochloric acid (36%) were reagent grade and from Sinopharm, MB was provided by McLean.

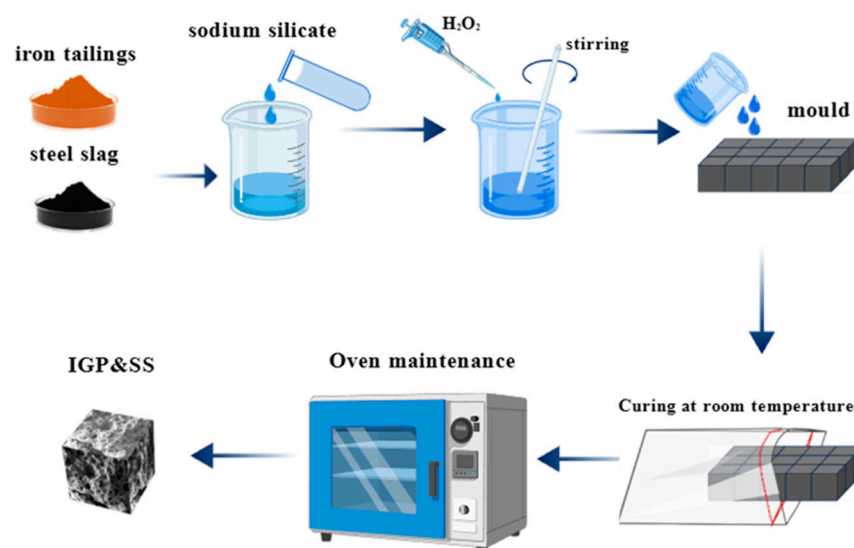
Table 1. Composition of iron tailings.

Component	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂
Content (wt%)	45.07	13.38	6.91	24.92	2.47	2.42	2.03	1.75

Table 2. Composition of steel slag.

Component	CaO	Fe ₂ O ₃	SiO ₂	MgO	P ₂ O ₅	Al ₂ O ₃
Content (wt%)	41.21	18.42	15.83	7.15	3.59	2.04

The preparation procedure of iron-tailings-based geopolymers (Figure 13). First, the raw iron tailings were thermally activated by calcination in a muffle furnace at 600 °C for 2 h. To prepare the solid precursor, the calcined iron tailings and steel slag were mixed in a mass ratio of 7:3. 40 g of water glass (SiO₂/Na₂O molar ratio = 3.3) was added to the 100 g solid mixture (yielding a liquid-to-solid mass ratio of 0.4), and the mixture was stirred at high speed to form a homogeneous geopolymer slurry.

**Figure 13.** Schematic diagram of IGP&SS preparation process.

Subsequently, 0.3 mL of hydrogen peroxide (H₂O₂) was added to the slurry as the foaming agent and mixed uniformly using an electric stirrer. The resulting slurry was cast into 30 mm × 30 mm × 30 mm cubic molds. The molds were vibrated to eliminate large entrapped air bubbles and level the surface. The curing process consisted of three stages: (1) the samples were sealed in plastic bags and cured at room temperature for 12 h to allow initial setting; (2) the samples were then placed in an oven at 65 °C for 8 h to accelerate geopolymerization; (3) finally, the samples were aged at room temperature for 28 days to ensure complete geopolymerization. For the photocatalytic applications, the cured IGP&SS blocks were crushed and sieved, and particles with a size range between 5 and 10 mesh were collected for use.

3.2. Photo-Assisted Degradation Experiments

The Photo-assisted catalytic degradation of methylene blue (MB) was conducted in a 100 mL cylindrical quartz reactor under visible-light irradiation. A 300 W Xenon lamp (Microsolar 300, Beijing Perfectlight Technology Co., Ltd., Beijing, China) equipped with a 420 nm cut-off filter was employed as the light source, positioned 20 cm above the liquid surface to maintain a light intensity of approximately 100 mW/cm². Prior to the

reaction, a standard MB stock solution (1 g/L) was prepared and diluted to the desired initial concentration. In a typical run, a specific amount of crushed geopolymer catalyst (5–10 mesh) was dispersed into 100 mL of the MB working solution. Prior to irradiation (defined as $t < 0$), the suspension was magnetically stirred in the dark for 30 min to ensure adsorption–desorption equilibrium. At $t = 0$, a predetermined dosage of PMS was added, and the Xenon lamp was switched on to initiate the visible-light-assisted catalytic reaction. Considering the thermal effect of the Xenon lamp, the reaction temperature was maintained at 25 ± 1 °C using a circulating cooling water system surrounding the reactor (unless focusing on the effect of temperature). At 5 min intervals, a 3 mL aliquot of the suspension was withdrawn, and a quenching agent (sodium thiosulfate) was immediately added to terminate the reaction. The sample was then centrifuged and filtered through a 0.22 μm membrane to remove the catalyst. The residual MB concentration was determined by measuring the absorbance at 664 nm using a UV–vis spectrophotometer (GENESYS 50). The degradation efficiency is expressed as C/C_0 , where C_0 represents the initial concentration of the MB solution before catalyst addition. To ensure statistical reliability, all experiments were performed in triplicate ($n = 3$). Data are reported as mean values with error bars representing the standard deviation (SD). Goodness-of-fit for kinetic models is reported as the coefficient of determination (R^2).

3.3. Performance and Characterization

The physicochemical properties of the raw materials and synthesized catalysts were comprehensively characterized. The composition of the iron tailings and steel slag was quantified by X-ray fluorescence (XRF) spectrometry (PANalytical Axios, Malvern Panalytical, Almelo, The Netherlands, calibrated with standard reference materials). Crystalline phases were identified using an X-ray powder diffractometer (XRD, Empyrean/DY1602, Malvern Panalytical) with monochromatic Cu-K α 1 radiation ($\lambda = 1.5406$ Å). The instrument operated at 40 kV and 40 mA. Samples were ground to pass through a 200-mesh sieve (<75 μm), and patterns were recorded from 5° to 70° (2θ) at a scan rate of $0.1^\circ/\text{s}$ and a step size of 0.02° , with phase identification performed using Jade 9.0 software. The mineralization efficiency of MB was evaluated by measuring the Total Organic Carbon (TOC) content. Samples were withdrawn at predetermined time intervals and immediately quenched with excess sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to terminate the oxidation reaction. Subsequently, the samples were filtered through a 0.45 μm PES membrane to remove suspended solids/catalysts. The TOC concentration was determined using a Shimadzu TOC-L analyzer (Shimadzu Corp., Japan) based on the high-temperature catalytic combustion method at 680 °C. The analysis was conducted in the Non-Purgeable Organic Carbon (NPOC) mode to eliminate interference from inorganic carbon. Standard curves were established using potassium hydrogen phthalate (KHP) solutions.

The surface chemical states were investigated using X-ray Photoelectron Spectroscopy (XPS) on a Thermo Fisher Scientific ESCALAB 250 system (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromatic Al K α radiation source (1486.6 eV). The survey scans were acquired with a pass energy of 100 eV and a step size of 1.0 eV, while high-resolution spectra for Fe 2p, O 1s, and C 1s were collected with a pass energy of 30 eV (step size: 0.1 eV). All binding energies were calibrated referencing the adventitious C 1s peak at 284.8 eV. Peak fitting was performed using Avantage (v6.9.0, Thermo Fisher Scientific) software, employing a Shirley-type background subtraction and Gaussian-Lorentzian (30:70) line shapes with constrained full width at half maximum (FWHM).

Microstructural and textural analyses were conducted using multiple techniques. The morphology and elemental distribution were examined by Scanning Electron Microscopy (SEM, Quanta 250, Thermo Fisher Scientific) equipped with an Energy Dispersive Spec-

trometer (EDS) at an accelerating voltage of 20 kV. Samples were dried at 60 °C for 12 h prior to analysis. Images were acquired at an accelerating voltage of 20 kV and a working distance of 10–12 mm. Additionally, to evaluate the leaching of iron species, the leaching concentrations of Fe was systematically determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Agilent 5110, Agilent Technologies, Santa Clara, CA, USA). The analysis was performed with an RF power of 1.2 kW, a plasma gas flow of 12 L/min, and an auxiliary gas flow of 1.0 L/min. All samples were filtered through a 0.22 µm membrane prior to injection. For macroscopic pore structure analysis (e.g., air content and spacing factor), a Rapid Air pore structure analyzer (Concrete Experts International CXI, Vedbæk, Denmark) was employed. The samples were polished and treated with a zinc oxide paste to enhance contrast. The pore content distribution and chord lengths were calculated using the linear traverse method based on the automated color thresholding of the white ZnO-filled pores against the dark matrix. The specific surface area and mesoporous structure were determined by N₂ adsorption–desorption isotherms at 77 K after degassing samples at 150 °C for 8 h under vacuum (<10 Pa) using a Micromeritics ASAP 2460 analyzer (Micromeritics (Shanghai) Instrument Co., Ltd., Shanghai, China). Before measurement, samples were degassed under vacuum at 150 °C for 8 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method ($P/P_0 = 0.4–1.0$), and the Barrett–Joyner–Halenda (BJH) model (desorption branch), respectively.

The mechanical strength was evaluated using a YAW-300C microcomputer-controlled compression testing machine (Jinan Tianchen Co., Ltd., Jinan, China). The tests were performed on 30 mm × 30 mm × 30 mm cubic specimens after 28 days of curing. The loading rate was set at 0.3 kN/s. The reported compressive strength values represent the average of three replicates for each condition. Finally, for the degradation experiments, the reaction products were analyzed using a liquid chromatography-ion trap mass spectrometry (HPLC-MS) system (Agilent Technologies Germany, Waldbronn, Germany). The instrument was equipped with ESI and APCI sources, operating in a mass range of m/z 50–2200 with a scan speed of 26,000 u/s, a resolution of 0.55 u, and a mass accuracy of ±0.2 u.

4. Conclusions

This study demonstrates a sustainable strategy for converting bulk iron tailings and steel slag—two major industrial solid wastes—into a functional porous geopolymer (IGP&SS) via simple alkali activation and foaming. The resulting material combines mesoporous structure, adequate mechanical strength, and abundant surface iron sites, enabling highly efficient visible-light-assisted activation of peroxymonosulfate (PMS) for methylene blue (MB) degradation. Near-complete MB decolorization (>98%) was achieved under optimized PMS dosage (25 mg), while highly efficient degradation (94.4%) was observed at pH 12. Performance enhanced by increased catalyst/PMS dosage, elevated temperature, and alkaline pH. HPLC-MS analysis confirmed the degradation of the MB molecule into smaller intermediate fragments through demethylation and ring-opening pathways. Radical quenching experiments clarified the contribution order of reactive species as $\bullet\text{OH} > {}^1\text{O}_2 > \text{SO}_4\bullet^- > \bullet\text{O}_2^-$. The dominance of $\bullet\text{OH}$ is attributed to the alkaline micro-environment facilitating the conversion of $\text{SO}_4\bullet^-$, driven primarily by rapid Fe(II)/Fe(III) redox cycling within the stable geopolymer framework. Crucially, XPS analysis of the used catalyst revealed a significant positive binding energy shift (approximately +3.2 eV) in the O 1s spectrum. This phenomenon confirms that the catalyst undergoes dynamic surface restructuring during the reaction, transforming from initial oxides into active surface metal-hydroxyl (M–OH) species. This surface evolution provides the structural basis for the sustained generation of reactive radicals. Notably, IGP&SS exhibits excellent reusability over multiple cycles, minimal iron leaching, and structural integrity, addressing

key limitations of conventional iron-based catalysts. This work not only provides an effective, low-cost catalyst for PMS-based advanced oxidation of dye wastewater but also offers a scalable pathway for high-value utilization of iron-rich mining wastes, contributing to circular economy principles and reduced environmental burden from tailings stockpiling. Future efforts should explore broader pollutant scopes and pilot-scale implementation to advance practical deployment.

Author Contributions: Conceptualization, L.Y.; Methodology, S.Z. and L.Y.; Validation, K.Z.; Formal Analysis, S.Z.; Investigation, K.Z.; Resources, F.R.; Data Curation, S.Z.; Writing—Original Draft, K.Z.; Writing—Review and Editing, L.Y. and F.R.; Visualization, K.Z. and S.Z.; Supervision, F.R.; Project Administration, F.R.; Funding Acquisition, F.R. All authors have read and agreed to the published version of the manuscript.

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