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PHOTOCHEMICAL STABILITY AND ADSORPTIVE BEHAVIOR OF BIOMASS-DERIVED GRAPHENE OXIDE SYNTHESIZED FROM 4M NAOH–ACTIVATED COCONUT SHELL CARBON

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ABSTRACT

Coconut shell waste was transformed into graphene oxide through sequential 4M NaOH activation and modified Marcano oxidation. Our work uniquely addresses photochemical durability, a persistently neglected aspect in biomass-derived adsorbent development. Structural examination via X-ray diffraction demonstrated graphitic interlayer expansion reaching 3.564 Å, accompanied by oxygen functionalities (hydroxyl, aromatic, and epoxy) confirmed through FTIR spectroscopy. Dark-condition experiments achieved 71.18% methylene blue removal (50 ppm), yet UV irradiation collapsed performance to 37.62%. We attribute this instability to photocatalytic deterioration mediated by entrapped sodium species, which generate reactive oxygen radicals that degrade functional groups essential for pollutant capture. Our investigation reveals an inherent conflict: aggressive alkali treatment enhances porosity but simultaneously introduces photo-vulnerable residues. Achieving practical solar-exposed wastewater remediation demands balanced activation protocols paired with rigorous sodium elimination. This work bridges laboratory optimization and real-world implementation by quantifying the photostability penalty of extreme activation conditions.

Keywords : graphene oxide, coconut shell, NaOH activation, methylene blue, photochemical stability

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I. INTRODUCTION

Dye-laden effluents from textile manufacturing pose escalating contamination threats, especially across developing regions lacking advanced treatment infrastructure [1]. Among problematic colorants, methylene blue a thiazine-class cationic compound triggers toxic responses, including skin reactions, neurological impairment, and carcinogenic pathways when exceeding 4.7 μg/L thresholds [2–4]. The dye's inherent molecular robustness resists biological breakdown, causing persistent aquatic ecosystem damage [5].

Adsorption strategies present economically accessible remediation alternatives [6], [7]. Graphene oxide has emerged as a promising adsorbent owing to oxygen-decorated edges and remarkable surface properties. Published capacities span 119 – 3333 mg/g for methylene blue capture, with efficiency rates surpassing 95% [8], [9]. Production economics, however, constrain widespread adoption. Pristine graphite feedstocks demand 80 – 99.95% purity specifications, elevating costs beyond feasible wastewater treatment budgets [10].

As the global leader in coconut production, Indonesia accumulates enormous shell waste volumes that remain underexploited [11]. These agricultural residues offer compelling precursor characteristics: 85 – 95% fixed carbon, advantageous lignocellulosic architecture, and merely 0.62% ash attributes supporting efficient thermal conversion and oxidative processing [12]. Sodium hydroxide activation generates porosity while installing surface groups necessary for graphene oxide transformation [13]. Prior investigations successfully converted coconut shells into GO via modified Hummer's protocols, demonstrating substantial dye removal capabilities [14]. This biomass valorization simultaneously resolves waste disposal challenges and sustainable material demands [15].

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Extensive synthesis optimization research has targeted maximum yield and initial adsorption strength. Yet a fundamental oversight persists photochemical durability assessment remains largely absent. Most evaluations occur exclusively within controlled darkness, ignoring UV-induced structural breakdown inevitable in outdoor treatment installations. This limitation becomes critical for biomass-derived materials experiencing extreme alkali processing, where residual inorganics may serve as photoactive degradation centers [16]. Emerging evidence documents severe performance discrepancies between shielded and UV-exposed testing [17]. The nexus connecting activation intensity, residual activator persistence, and resultant photostability lacks systematic investigation despite crucial implications for industrial scaling [18], [19].

We address these deficiencies through systematic examination of coconut shell-derived graphene oxide prepared via 4M NaOH activation, with concentrated focus on UV-irradiation behavior. Our investigation pursues four interconnected aims: (1) multi-technique characterization encompassing XRD structural analysis, FTIR chemical profiling; (2) quantified methylene blue capture assessment spanning 10–50 ppm across both darkness and UV exposure; (3) mechanistic dissection of photo-induced breakdown pathways, particularly emphasizing residual sodium species roles; and (4) practical viability evaluation for solar-exposed remediation deployment. Our novelty emerges from integrated analysis connecting extreme activation parameters, persistent activator contamination, and photochemical vulnerability dimensions not previously examined concurrently in biomass GO investigations. Results should inform photostable adsorbent rational design suited for authentic environmental applications.

II. METHOD

Coconut shell (CS) waste was cleaned, dried at 110°C, and carbonized at 350°C for 2 h to obtain coconut shell carbon [20]. The resulting carbon was chemically activated using NaOH solutions of 1 M, 2 M, 3 M, and 4 M for 24 h, followed by washing to neutral pH and drying at 105°C [21].

GO was synthesized using the modified Marcano method employing a H_2SO_4/H_3PO_4 (9:1) mixed acid and $KMnO_4$ oxidant. The product was washed with 5% HCl and deionized water, sonicated for 2 h, and dried at 60°C to obtain brownish-black GO powder [22].

Adsorption performance was evaluated using methylene blue (MB) solutions of 10–50 ppm at pH 7. Experiments were performed under dark and UV-irradiated conditions to assess photochemical stability. After 60 min of adsorption with 10 mg GO, supernatants were analyzed using a UV–Vis spectrophotometer at 665 nm to determine adsorption efficiency [18], [23].

III. RESULTS AND DISCUSSION

X-ray diffraction examination of GO-TK4 (Figure 1) reveals characteristic reflections at $2\theta = 24.99°$ and 44.55°, indexing to (002) and (100) crystallographic planes, respectively, within graphitic frameworks. Compared against reference graphite (COD ID: 9012234, $d_{002} = 3.248$ Å), our oxidized material demonstrates d-spacing expansion to 3.564 Å representing 9.7% interlayer enlargement. This spacing increase validates successful oxygen incorporation between carbon layers. The (002) reflection exhibits notable broadening relative to pristine graphite, signifying diminished long-range crystalline ordering consequent to oxidation-generated defects and heteroatom insertion.

Applying Scherrer analysis yields a crystallite dimension (Lc) approximating 50.94 nm along the stacking direction, suggesting that combined harsh activation and oxidation preserved fundamental layered architecture [24]. Persistence of the (100) reflection at 44.55° confirms maintained in-plane hexagonal symmetry despite aggressive oxidative processing. These structural signatures typify partially oxidized graphene materials exhibiting adsorptive functionality [25].

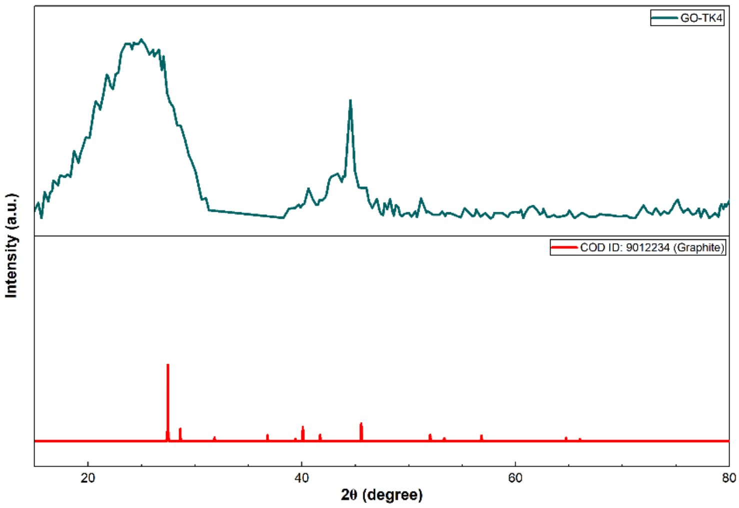

Fig. 1. XRD diffractogram of GO-TK4 compared with graphite standard (COD ID: 9012234).

Infrared spectroscopic analysis (Figure 2) discloses multiple oxygen-bearing moieties introduced during oxidative treatment. A broad absorption envelope centered around 3336 cm⁻¹ stems from hydroxyl (-OH) stretching modes, evidencing abundant surface hydroxyl populations and potentially intercalated water molecules. The 1637 cm⁻¹ feature corresponds to aromatic C=C stretching, confirming partial retention of graphitic sp² domains through oxidation. Strong absorption at 547 cm⁻¹ is attributed to C-O-C epoxide functionalities, which, collectively with hydroxyl groups, establish active centers for cationic pollutant binding via electrostatic forces and hydrogen bridges [26]. The increase in the d-spacing value to 3.564 Å indicates a larger interlayer gap, thereby providing sufficient space for methylene blue molecules (dimension ~1.43 nm) to diffuse into the GO-TK4 structure [27]. This condition directly contributes to the measured adsorption capacity of 177.95 mg/g under dark conditions. On the other hand, the broadening of the (002) peak, reflecting a decrease in crystallinity, indicates an increase in the number of structural defects and active edge sites in the material. These defects play a dual role: they are beneficial as additional binding sites for pollutants under dark conditions, yet they are susceptible to oxidative attack under UV exposure, as evidenced by the significant decline in adsorption performance under irradiation conditions [28].

These oxygen functionalities prove crucial for methylene blue capture. Negatively polarized oxygen sites create electrostatic pull toward cationic MB molecules, while hydroxyl moieties enable hydrogen bonding with MB's nitrogen and sulfur atoms. The coexistence of aromatic sp² regions alongside oxidized domains furnishes both π-π stacking opportunities and polar attachment sites, collectively enhancing overall capture capacity [26].

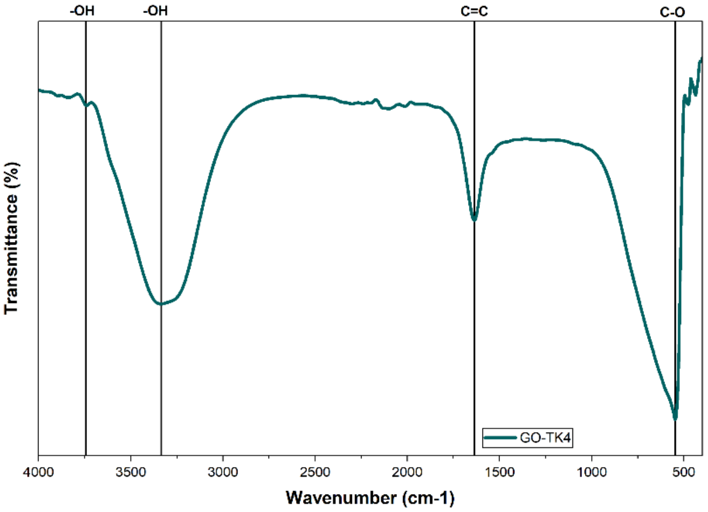

Fig. 2. Infrared spectroscopic fingerprint of GO-TK4 displaying oxygen functional signatures.

Table 1 compiles adsorption outcomes across darkness and UV-exposed conditions. Within dark environments, GO-TK4 exhibited concentration-dependent behavior: 91.11% efficiency at 10 ppm, progressively declining to 71.18% at 50 ppm. This pattern reflects gradual saturation of available binding sites as dye loading increases. Conversely, adsorption capacity escalated from 45.55 mg/g to 177.95 mg/g with rising concentration, indicating enhanced uptake driving force despite percentage efficiency reduction.

The presence of -OH groups (3336 cm^{-1}) and C-O-C epoxide groups (547 cm^{-1}) detected by FTIR directly explains the mechanism of MB adsorption under dark conditions: the -OH groups provide hydrogen-bonding sites with N and S atoms in the MB molecule, while the epoxide groups contribute to electrostatic interactions with the positive charge of MB [26]. The gradual decrease in adsorption efficiency from 91.11% (10 ppm) to 71.18% (50 ppm) under dark conditions is consistent with the active-site saturation model, in which these functional groups are progressively occupied as the pollutant load increases. Conversely, under UV irradiation, reactive species generated by sodium residues attack these functional groups primarily -OH and epoxide thereby reducing active site density and weakening the surface affinity for MB. This explains the collapse of adsorption efficiency to 37.62% at a concentration of 50 ppm under UV exposure.

Although direct surface morphological characterization via SEM was not performed in this study, the structural characteristics inferred from the broadening of XRD peaks and the density of functional groups in FTIR indicate a defect-rich layered structure with high surface irregularity [25]. Such morphology is generally associated with increased exposure of active edge sites, which supports adsorption performance under dark conditions [28]. However, simultaneously, these defect sites can act as initiation points for photochemical degradation under UV irradiation, accelerating functional group damage and contributing to the observed performance decline [29]. Thus, the adsorption–photostability relationship in GO-TK4 can be interpreted as a balance between surface reactivity and structural resilience, where a highly defective structure benefits adsorption under dark conditions but becomes less stable under sustained UV exposure [18]. Further research integrating SEM and BET analyses is needed to quantitatively validate this morphological interpretation.

Table 1. Methylene blue adsorption performance of GO-TK4 across illumination conditions.

MB Concentration (ppm)	Dark Efficiency (%)	UV Efficiency (%)	Dark Capacity (mg/g)	UV Capacity (mg/g)
10	91.11	95.89	45.55	47.95
30	78.02	95.87	117.03	143.80
50	71.18	37.62	177.95	94.04

UV irradiation induced progressively severe performance degradation escalating with dye concentration. At low concentrations >10 ppm, UV exposure does not reduce adsorption efficiency and even slightly increases removal, suggesting a possible contribution from concurrent photodegradation of methylene blue [17]. However, at 50 ppm, efficiency collapsed to 37.62% a dramatic 47% relative decline versus dark conditions. This substantial loss indicates UV-triggered adsorbent structural deterioration rather than mere photocatalytic dye decomposition.

Under UV illumination, residual sodium species induce photochemical degradation through multiple pathways. First, NaOH or Na^+ ions generate reactive oxygen species, such as hydroxyl radicals (OH) and superoxide anions (O_2^-), which attack GO's oxygen functionalities, decomposing structural groups [30]. Second, UV photons drive oxidative breakdown of hydroxyl, epoxy, and carboxyl moieties the very groups responsible for adsorption reducing available binding sites and increasing surface hydrophobicity, thereby lowering MB affinity [29]. Third, photogenerated reactive species disrupt interlayer bonding, causing partial sheet exfoliation or paradoxical reaggregation, which diminishes the effective surface area accessible for dye molecules[18].

The concentration dependent severity of UV effects supports this mechanistic framework. At elevated MB concentrations (50 ppm), adsorbent function demands maximum functional group availability. UV-induced degradation rapidly exhausts this capacity, yielding drastic efficiency loss. Conversely, at low concentrations (10 ppm), initially abundant sites accommodate dye molecules even after partial degradation, maintaining acceptable performance. These findings contrast with investigations employing milder activation or more rigorous purification, which report stable or enhanced UV performance due to photocatalytic dye degradation without significant adsorbent compromise [17], [18]. Our results demonstrate that extreme alkali activation (4M NaOH), while potentially amplifying initial surface area, introduces photochemical fragility outweighing capacity advantages for solar-exposed applications.

Our maximum adsorption capacity of 177.95 mg/g remains below reported ranges spanning 119 – 3333 mg/g for diverse GO materials [8], [9]. This comparatively modest performance likely reflects (1) incomplete sodium residue elimination occupying potential binding sites, (2) possible over-oxidation from aggressive activation creating excessive hydrophilicity promoting aqueous aggregation, and (3) structural defects that, while generating edge sites, simultaneously disrupt optimal sheet stacking for surface area maximization. Relative to other coconut shell derived GO investigations [13], our material demonstrates competitive dark-conditioning performance yet inferior UV stability. This underscores the critical importance of post-synthesis purification and activation parameter optimization. For authentic wastewater treatment systems experiencing sunlight exposure, GO-TK4 presents significant operational limitations. A treatment system achieving 71% removal under laboratory darkness might deliver merely 40% efficiency outdoors under continuous solar UV bombardment. This performance discrepancy would necessitate substantially increased material quantities or multiple treatment cycles, negating economic advantages of waste-derived materials.

IV. CONCLUSION

Coconut shell derived graphene oxide prepared via 4M NaOH activation exhibits oxygen-rich functional groups and porous nanosheets, achieving 71.18% methylene blue removal under dark conditions. However, UV irradiation drastically reduces efficiency to 37.62% at 50 ppm due to residual sodium species likely contribute to photochemical degradation via reactive oxygen species. Extreme activation enhances porosity but introduces photo-vulnerable residues, limiting practical solar-exposed application. Future development should focus on moderate activation combined with thorough purification to balance adsorption capacity and photochemical stability, specifically by exploring reduced NaOH concentrations (1 – 2M) balanced with extended treatment duration and implementing more stringent washing protocols, including acid treatment cycles for effective sodium elimination.

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