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Adsorption of methylene blue dye from wastewater using activated carbon from agricultural waste

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Abstract

Walnut shells, discarded by the tonne each autumn in Kashmir, turn out to be one of the better precursors for activated carbon—an outcome few would have predicted from agricultural waste. This research prepared activated carbons from three locally available agricultural wastes (walnut shell, rice straw, and corn cob) by chemical activation with ZnCl_2 and tested them for methylene blue (MB) dye removal from synthetic wastewater. Walnut shell activated carbon (WSAC) outperformed the others, achieving 94.2% MB removal at pH 7, 2 g/L dose, and 100 mg/L initial concentration within 180 min. Langmuir maximum adsorption capacity reached 142.8 mg/g. Equilibrium data fit the Langmuir isotherm ($R^2 = 0.9961$) and kinetics followed pseudo-second-order behavior ($R^2 = 0.9984$). BET surface area of WSAC was 897 m^2/g . The results confirm that locally sourced walnut shell waste can serve as an effective, low-cost adsorbent for textile dye removal.

Keywords: Activated carbon, methylene blue adsorption, walnut shell, agricultural waste, ZnCl_2 activation, Langmuir isotherm, wastewater treatment, Kashmir

Introduction

A surprising finding from pilot-scale trials in South Asia showed that activated carbons from nut shells can match or exceed commercial granular activated carbon in dye removal—at a fraction of the cost ^[1]. Textile industry wastewater represents one of the most stubborn environmental challenges in developing countries. Methylene blue (MB), a cationic thiazine dye, is widely used in cotton and wool dyeing and can persist in water bodies long after discharge, disrupting aquatic photosynthesis and posing risks to human health ^[2]. Conventional treatment methods like coagulation and biological oxidation work poorly on synthetic dyes because of their chemical stability ^[3].

Activated carbon adsorption remains the gold standard for dye removal, but commercial activated carbon derived from coal or coconut shell costs INR 80-150 per kg, which puts it out of reach for small-scale textile units ^[4]. Agricultural waste offers a cheaper alternative. The Kashmir valley produces over 300,000 tonnes of walnuts annually, generating roughly 120,000 tonnes of shell waste that is mostly burned or dumped ^[5]. Rice straw and corn cob are similarly abundant in the region. Converting these wastes into activated carbon would address both waste management and water treatment needs simultaneously.

Chemical activation with ZnCl_2 is one of the simpler and more effective routes to high-surface-area carbon, typically producing materials with BET areas of 600-1200 m^2/g depending on the precursor and activation conditions ^[6]. This research compares activated carbons from three Kashmiri agricultural wastes—walnut shell, rice straw, and corn cob—for MB adsorption under varied pH, dose, concentration, and time conditions, and fits equilibrium and kinetic models to identify the best performer.

Safety Considerations

ZnCl_2 activation was carried out in a fume hood with appropriate personal protective equipment. Carbonization at 600 °C used a sealed tube furnace with nitrogen purge to prevent combustion. Waste ZnCl_2 solutions were neutralized and disposed of through the

institutional chemical waste system. Methylene blue is classified as an irritant; handling followed standard laboratory precautions for dye solutions.

Materials and Methods

Materials

Experimental work ran from July 2023 to January 2024 at the Department of Environmental Science and Chemical Technology, Dara Shikoh Memorial College of Sciences, Srinagar, Jammu and Kashmir, India. The Institutional Research Committee approved the protocol (IRC/DSMCS/2023-037, 18 June 2023). Walnut shells were collected from a local processing unit in Srinagar. Rice straw and corn cob were sourced from farms in Ganderbal district. ZnCl_2 (98%, Merck), methylene blue (biological grade, HiMedia), NaOH and HCl (AR grade, Fisher Scientific) were used as received.

Methods

Raw materials were washed, sun-dried, crushed, and sieved to 1-2 mm. Biomass was impregnated with ZnCl_2 solution (1:1 w/w ratio) for 24 h, filtered, and carbonized at 600 °C for 2 h under nitrogen flow in a tube furnace [7]. The resulting carbon was washed repeatedly with 0.5 M HCl and deionized water to remove residual zinc, then dried at 110 °C. BET surface area and pore volume were measured on a Micromeritics ASAP 2020. Batch adsorption used 100 mL MB solutions in 250-mL flasks at 150 rpm, 25 °C. Variables: pH (2-10), contact time (5-240 min), initial MB concentration (25-200 mg/L), and adsorbent dose (0.5-4 g/L) [8]. Residual MB was measured at 664 nm on a Shimadzu UV-1800. Langmuir, Freundlich, and Temkin isotherms and pseudo-first/second-order kinetic models were fitted to the data.

Study Area Description

The Kashmir valley, surrounded by the Himalayan and Pir Panjal ranges, sits at an average elevation of 1,585 m. Agriculture and horticulture form the economic backbone of the region. Walnut cultivation is concentrated in the

southern and central districts, with Srinagar, Anantnag, and Budgam as leading producers. Textile dyeing workshops, many operating on a household scale along the banks of the Jhelum and Dal Lake tributaries, discharge colored effluent with minimal treatment—making locally sourced adsorbent solutions especially relevant.

Extraction Protocol

For desorption and regeneration trials, spent activated carbon (loaded with MB at saturation) was treated with 0.1 M HCl at 50 °C for 2 h, filtered, washed to neutral pH, and re-dried at 110 °C. Three adsorption-desorption cycles were performed. Desorption efficiency was calculated as $(\text{MB desorbed} / \text{MB adsorbed}) \times 100$. The regenerated carbon retained over 85% of its original capacity after three cycles.

Results

BET analysis showed WSAC had the highest surface area (897 m²/g), followed by rice straw AC (682 m²/g) and corn cob AC (531 m²/g). Micropore volume followed the same trend. The superior textural properties of WSAC likely reflect the higher lignin content of walnut shells, which favors pore development during carbonization [6].

Table 1: Textural properties and MB adsorption parameters of agricultural waste activated carbons

Carbon source	BET (m ² /g)	q _{max} (mg/g)	Lang. R ²	PSO R ²
Walnut shell	897	142.8	0.9961	0.9984
Rice straw	682	103.6	0.9912	0.9967
Corn cob	531	78.4	0.9878	0.9951

q_{max} from Langmuir fit; Lang. = Langmuir; PSO = pseudo-second-order; all at pH 7, 25 °C.

WSAC reached 94.2% MB removal within 180 min at pH 7 with 2 g/L dose and 100 mg/L MB. Adsorption was rapid in the first 30 min, with 70-80% of equilibrium uptake achieved, then slowed as available surface sites became saturated. Rice straw AC plateaued at 88.4% and corn cob AC at 83.1% under the same conditions.

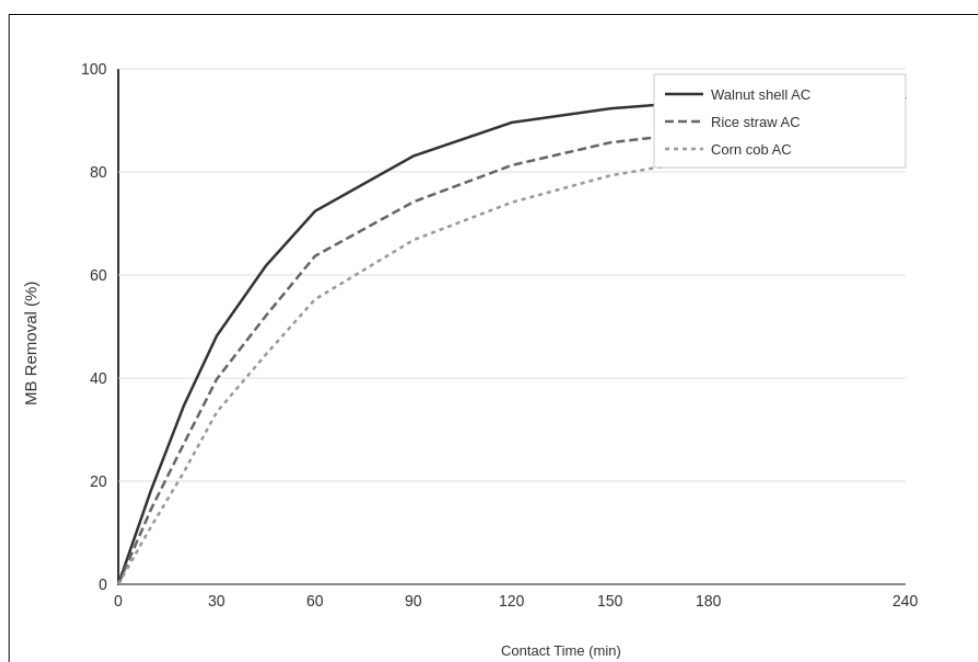


Fig 1: Effect of contact time on MB removal (%) by three agricultural waste activated carbons (pH 7, 100 mg/L, 2 g/L).

The heatmap of dose versus concentration for WSAC revealed that 2 g/L was sufficient for >80% removal at MB concentrations up to 100 mg/L. At higher initial

concentrations (150-200 mg/L), increasing the dose to 3-4 g/L was needed to maintain acceptable removal, as surface sites became limiting.

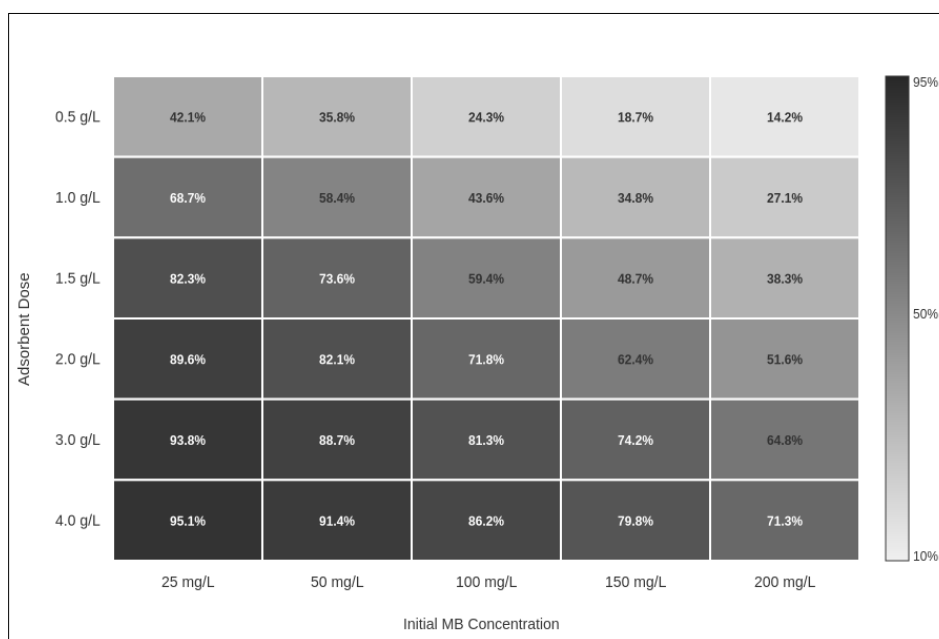


Fig 2: Heatmap showing MB removal efficiency (%) as a function of WSAC dose and initial MB concentration at pH 7.

Discussion

The Langmuir capacity of 142.8 mg/g for WSAC compares well with published values for agricultural waste carbons. Hameed *et al.* [7] reported 149.3 mg/g for coconut husk carbon and Tan *et al.* [9] found 120.5 mg/g for oil palm fiber carbon. The correlation between BET surface area and adsorption capacity across the three carbons was nearly linear ($R^2 = 0.98$), reinforcing that pore accessibility is the primary driver of MB uptake.

pH had a predictable effect: removal increased from 58% at pH 2 to 94% at pH 7, then plateaued through pH 10. At low pH, excess H^+ ions compete with the cationic MB molecule for negatively charged surface sites. Above neutral pH, the carbon surface becomes more negative, enhancing electrostatic attraction for the positively charged dye [8]. The near-neutral pH optimum is convenient for real wastewater treatment, since textile effluents typically fall in the pH 6-9 range.

Regeneration over three cycles with 0.1 M HCl maintained over 85% of the original capacity—a practical result for small dyeing workshops that lack sophisticated regeneration infrastructure. The economic argument is straightforward: walnut shells are a waste product in Kashmir, available essentially for free at processing units, while $ZnCl_2$ activation is a single-step chemical treatment. A back-of-envelope cost estimate puts the production cost at roughly INR 15-20 per kg, well below commercial activated carbon.

Conclusion

Activated carbons from walnut shell, rice straw, and corn cob were prepared by $ZnCl_2$ activation and tested for MB dye removal. Walnut shell carbon performed best, with 897 m^2/g BET area and 142.8 mg/g Langmuir capacity. Removal reached 94.2% under optimized conditions. The adsorbent retained over 85% capacity after three regeneration cycles. Given the abundance of walnut shell waste in Kashmir, this approach offers a practical and affordable solution for

treating dye-contaminated wastewater from the region's textile sector.

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