Hydrothermally Prepared Sheep-Wool Biochar for Adsorptive Removal of Methylene Blue from Aqueous Solution

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Abstract

Dye-contaminated effluents pose persistent environmental concerns, and low-cost biosource-derived adsorbents are attractive options for wastewater treatment. In this study, sheep wool was evaluated as a precursor for producing effective adsorbents for methylene blue (MB) removal from aqueous solution. Three materials were investigated: raw sheep wool, hydrothermally prepared wool biochar (180 °C, 5 h; 10 g wool in 100 mL distilled water), and solvothermally prepared wool biochar (180 °C, 5 h; 7 g wool in 100 mL ethanol). Batch adsorption experiments were conducted while varying contact time (5–40 min), initial MB concentration (10–50 ppm), adsorbent dose (0.04–0.20 g), temperature (25–55 °C), and solution pH (3–11), and residual dye concentration was quantified using UV–Vis spectrophotometry and percent removal calculations. Under representative conditions (20 ppm MB, 0.08 g adsorbent, pH 7), hydrothermal biochar achieved 81.17% removal, compared with 72.56% for raw wool and 36.54% for solvothermal biochar. Contact-time experiments at 20 ppm showed rapid uptake by hydrothermal biochar (79.93–84.49% from 5–40 min), whereas raw wool and solvothermal biochar exhibited lower performance over the same period. Overall, hydrothermal processing produced the most effective wool-based biochar for MB adsorption under the studied conditions.

Keywords: sheep wool; biochar; adsorption; methylene blue; dye removal; wastewater treatment

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1- Introduction

Water pollution has intensified with industrial development and urban expansion, largely because many activities generate wastewater that is discharged directly or after insufficient treatment into natural water bodies [1]. Industrial effluents are particularly concerning because they often contain complex mixtures of contaminants that can persist and spread through aquatic systems [2]. Among these contaminants, synthetic dyes represent a major class of pollutants due to their strong coloration and chemical stability, which makes them difficult to remove using many conventional treatment approaches [3]. The presence of dyes in receiving waters reduces light penetration and can disrupt photosynthetic processes, thereby affecting aquatic ecosystems [4]. In addition, numerous dyes and their degradation products have been associated with adverse biological effects, increasing the urgency for efficient remediation strategies [5].

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Adsorption is widely recognized as an effective method for dye removal, often providing high efficiency with relatively simple operational requirements [6]. Consequently, research has increasingly focused on low-cost sorbents that can be produced locally and applied without intensive infrastructure [7]. Biochar has emerged as a promising option because it is carbon-rich, can be porous, and typically contains surface functional groups that promote interactions with organic pollutants [8]. Another advantage is that biochar can be synthesized from abundant biomass resources and waste materials, supporting sustainability goals while reducing overall treatment costs [9]. The adsorption performance of biochar depends strongly on the precursor and preparation route, which can tailor porosity and surface chemistry to enhance dye uptake [10].

Beyond dye-specific concerns, water is fundamental to public health, agriculture, and economic activity, and the deterioration of water quality directly threatens these sectors [11]. Population growth and intensified human activities have increased pressure on freshwater resources and have amplified pollutant release into aquatic environments [12]. Water contamination may originate from municipal sewage and industrial drains containing oxygen-demanding organic matter and suspended solids, leading to deterioration of key water quality indicators [13]. Additional contamination can arise from trace pollutants such as toxic metals and other persistent compounds that may accumulate in ecosystems [14]. Biological contamination by pathogenic microorganisms remains a major concern, particularly when sanitation infrastructure is insufficient, requiring reliable treatment approaches for safe water supplies [15].

Industrial wastewater is often difficult to treat because it may contain diverse chemicals such as detergents, pesticides, fertilizers, and dyes, which interact and complicate removal processes [16]. Synthetic dyes are used broadly in textile, paper, cosmetics, tanning, food, and pharmaceutical applications, making dye-containing effluents common across multiple industrial sectors [17]. Historically, the transition from natural dyes to synthetic dyes expanded rapidly after early dye discoveries enabled stable and scalable coloration [18]. Global dye production and consumption have since grown substantially, with the textile industry accounting for a dominant share of dye usage and wastewater generation [19]. Because many textile operations are concentrated in developing regions where wastewater treatment capacity can be limited, dye discharge can persist as a significant source of aquatic pollution [20].

In this work, sheep wool was evaluated as an accessible biosource for methylene blue removal from water. Three adsorbents were prepared and compared, including raw wool and wool-derived biochars produced via hydrothermal and solvothermal processing. Batch adsorption experiments were conducted to examine the influence of contact time, initial dye concentration, adsorbent dose, temperature, and solution pH on removal performance, with dye concentration quantified by UV-Vis measurements. The comparative results were used to identify the most effective wool-based material under the investigated conditions and to establish the operating trends relevant to the practical application of these adsorbents for dye-contaminated water treatment.

2- Materials and Methods

2.1 Materials, glassware, and reagents

Sheep wool was used as the precursor material for preparing the adsorbents. The main chemical used in this study was methylene blue (MB) dye (Fluka grade), and distilled water was used for solution preparation and dilution. Standard laboratory glassware and accessories were employed, including filter paper, funnels, beakers, test tubes, thermometers, Erlenmeyer (conical) flasks, spatulas, and pipettes.

2.2 Instruments and equipment

The experimental work utilized a hot air-drying oven, an electric grinder, a sensitive balance, a shaking device, a hot plate/stirrer, a centrifuge, a UV–Visible spectrophotometer, and a Teflon-lined stainless-steel autoclave for hydrothermal/solvothermal synthesis. The UV–Vis spectrophotometer (JWR, China), ultrasonic cleaner (DK SONIC, China), reciprocating shaker (HY-4, China), sieve shaker (UK/Germany), laboratory centrifuge (KISKER, Germany), and laboratory ovens (Thermo Scientific HERATHERM, USA; and a constant-temperature drying oven) were among the devices used in this work.

2.3 Preparation of methylene blue solutions

A stock MB solution (1000 mg/L) was prepared by dissolving 1.0 g of methylene blue (Fluka grade) in 1.0 L of distilled water and mixing until complete dissolution. Working solutions were prepared by appropriate dilution of the stock solution to the desired concentration, followed by thorough mixing. Prepared solutions were stored in dark-colored glass bottles to minimize light exposure.

2.4 Preparation of wool powder and wool-derived biochars

Raw sheep wool was washed twice with RO water, with the water replaced every 5 h. The washed wool was air dried for 12 h and then oven-dried at 75–85 °C for 12 h until completely dry. The dried wool was cut into small fibers, ground, and sieved to obtain a fine powder with a particle size of 250 µm.

Three adsorbent materials were prepared: (i) raw (untreated) wool powder; (ii) hydrothermally treated wool biochar, prepared by loading 10 g of ground wool with 100 mL distilled water in a Teflon-lined stainless-steel autoclave and heating at 180 °C for 5 h; and (iii) solvothermally treated wool biochar, prepared by loading 7 g of ground wool with 100 mL ethanol (97.9%) and heating at 180 °C for 5 h under the same conditions.

2.5 Batch adsorption experiments

Batch adsorption was conducted by transferring 25 mL of MB solution into Erlenmeyer flasks and adding a known mass of adsorbent. Experiments were designed using a one-factor-at-a-time approach, where one variable was varied while the remaining conditions were held constant.

Contact time. Contact time was evaluated at 5, 10, 20, 30, and 40 min using 25 mL of MB solution at 20 ppm, with 0.08 g adsorbent at room temperature (25 °C) and pH 7. At the end of each time interval, samples were centrifuged for phase separation.

Temperature. Temperature effects were studied by adding 25 mL of MB solution (30 mg/L) to flasks containing 0.08 g adsorbent and running experiments at 25, 35, 45, and 55 °C in a thermostatic water bath for the selected adsorption period, followed by centrifugation and analysis.

Initial concentration. Standard MB solutions were prepared at 10, 20, 30, 40, and 50 ppm. For each run, 25 mL of MB solution was added to flasks containing 0.08 g adsorbent, stirred at room temperature (25 °C) for the selected contact time, centrifuged, and analyzed by UV–Vis.

pH. The pH effect was assessed using MB solutions adjusted to pH 3, 5, 7, 9, and 11 using 0.1 M H_2SO_4 and 0.4 M NaOH. Each flask contained 25 mL MB solution and 0.08 g adsorbent; mixtures were stirred at room temperature for the selected adsorption duration, centrifuged, and analyzed.

Adsorbent dose. The dosage effect was examined using adsorbent masses in the range 0.04–0.20 g. Each flask received 25 mL of MB solution (30 mg/L) and was agitated on a rotary shaker at 100 rpm for the selected adsorption period at 25 °C. After contact time, samples were centrifuged (separation repeated twice at 10-min intervals) and the supernatant was analyzed by UV–Vis.

2.6 Analytical measurements and calculations

After adsorption, the solid phase was separated by centrifugation, and the residual MB concentration in the supernatant was determined using UV–Vis spectrophotometry. The percent removal (R, %) was calculated as:

$R\ (\%) = (C_i - C_e)/\ C_i \times 100$

Where: Ci is the initial concentration of the dye (before adsorption).

Ce is the concentration of the dye at the equilibrium state (after adsorption).

To calculate the adsorption capacity:

$q_e = (C_i - C_e) \times V/ m$

Where:

- q_e is the adsorption capacity (mg/g).

- C_i and C_e are the initial and equilibrium concentrations (mg/L) of the dye, respectively.

- V is the volume (mL) of the effluent. - m is the mass (g) of the adsorbent.

3- Results and Discussions

3-1 Effect of contact time

Textile dye contamination remains a major wastewater concern, and biological and physicochemical treatment routes have been extensively reviewed as viable strategies for mitigation [21,22]. Because adsorption is widely recognized as a simple and effective polishing step for persistent dye molecules, investigating adsorption kinetics is essential for selecting realistic operating conditions [23,24]. In the present work, contact time (5–40 min) was evaluated using raw wool, hydrothermally prepared wool biochar, and solvothermally prepared wool biochar. The hydrothermal biochar displayed rapid uptake and high removal (≈79.93% at 5 min to 84.49% at 40 min), indicating that a large fraction of accessible active sites was occupied early and that equilibrium was approached within short times. Raw wool showed low and fluctuating removal (≈24.24–30.05%), suggesting limited effective binding sites. Solvothermal biochar increased gradually (≈18.09% to 40.76%), consistent with slower site availability and/or weaker interaction with MB. Such “fast-then-slow” behavior is commonly attributed to an initial surface adsorption stage followed by diffusion-controlled transport into internal regions of the sorbent structure. The results are shown in Figure 1.

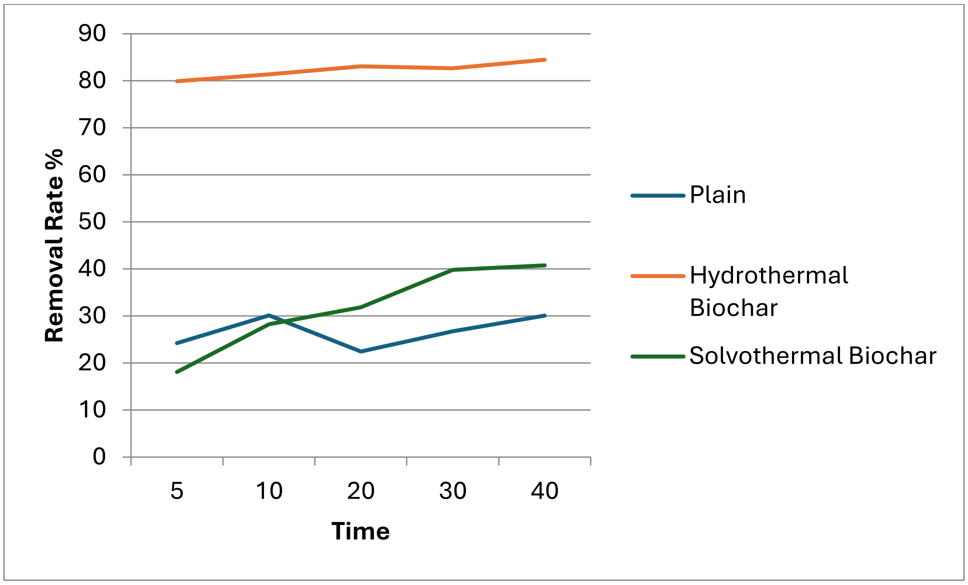

Figure 1 The effect of time on adsorption process.

3-2 Effect of temperature

Industrial sustainability pressures and the need to reduce chemical/energy demands have motivated studies that assess treatment efficiency under mild conditions [25,26]. Temperature can influence adsorption by changing dye diffusivity and the strength of adsorbate–surface interactions, so it is frequently examined in dye sorption systems. In this study, temperature (25–55 °C) produced distinct trends among the three adsorbents. Raw wool increased from 58.10% at 25 °C to 71.27% at 45 °C, then slightly decreased at 55 °C (70.60%), suggesting improved mass transfer up to an optimum. Hydrothermal biochar performed best at 25 °C (73.06%) and decreased to 64.51% at 55 °C, which is consistent with adsorption dominated by interactions that weaken as temperature rises, a pattern often associated with exothermic uptake. In contrast, solvothermal biochar increased modestly from 32.46% to 39.14% across the same range, implying that thermal activation and diffusion effects partially compensated for its lower inherent affinity. Comparable temperature-dependent behaviors have been reported for various low-cost sorbents and composite adsorbents used for dye removal [27]. Figure 2 shows the results.

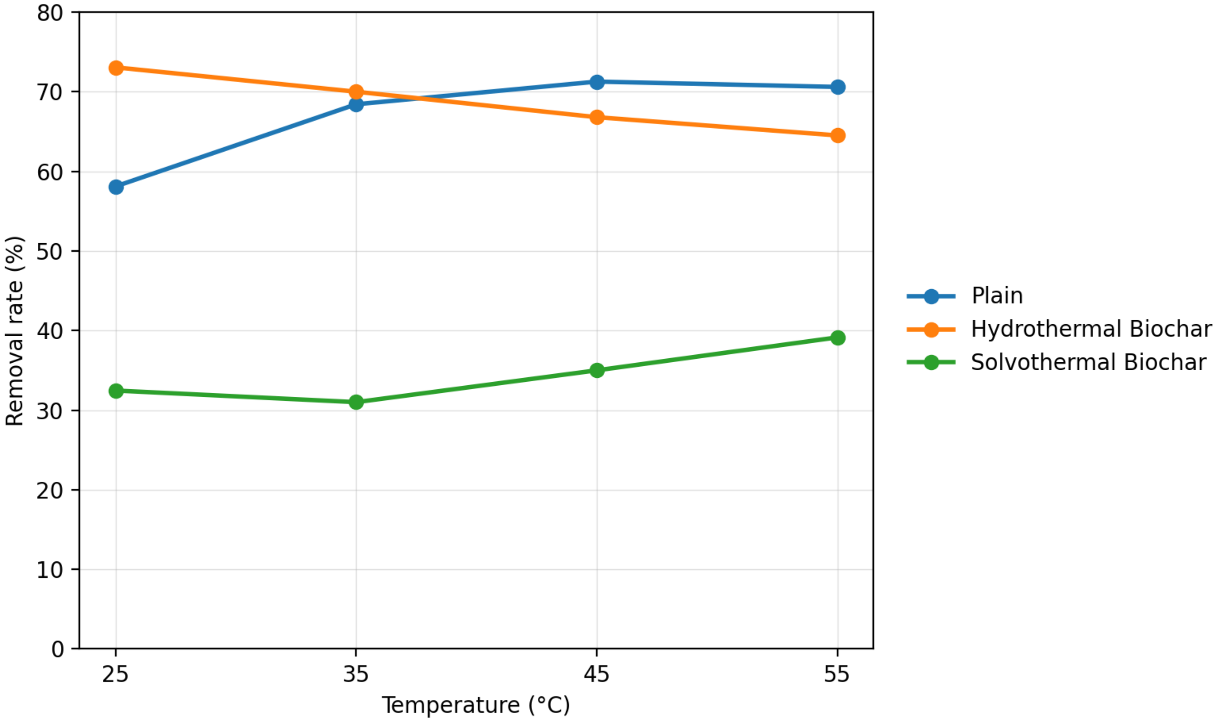

Figure 2: The effect of temperature on the adsorption process.

3-3 Effect of initial dye concentration

Dye concentration is a key driver of the mass-transfer gradient and controls how rapidly adsorption sites become saturated; therefore, removal efficiency commonly declines when available sites are limited relative to pollutant loading [28]. Here, increasing MB concentration from 10 to 50 mg/L led to strong differentiation among the sorbents. Raw wool achieved very high removal at 10 mg/L (88.91%) but dropped sharply with concentration and reached ~0% at 50 mg/L, indicating rapid exhaustion of accessible binding capacity. Hydrothermal biochar maintained comparatively strong performance: 75.39% at 10 mg/L, peaking at 81.17% at 20 mg/L, and retaining measurable removal even at 50 mg/L (41.67%). This suggests a higher density of effective functional sites and/or better pore accessibility, enabling uptake under higher loading. Solvothermal biochar declined from 57.91% at 10 mg/L to very low removal at 50 mg/L (1.61%), confirming limited capacity in the studied concentration window. The overall concentration response aligns with common observations in MB adsorption studies using biosorbents, where higher concentrations increase competition for finite sites and reduce percent removal unless sorbent capacity is high [29,30]. This behavior is illustrated in Figure 3.

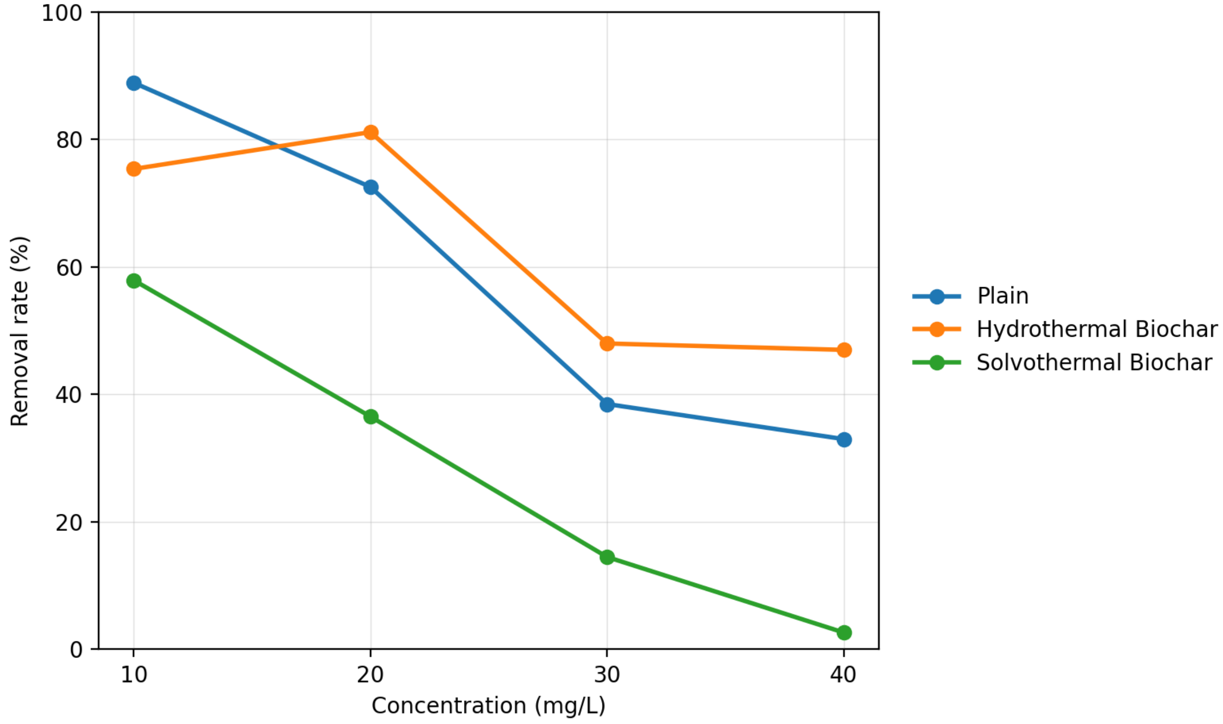

Figure 3. The effect of Concentration on adsorption process.

3-4 Effect of solution pH

pH controls surface charge development and functional group ionization, which can strongly affect uptake of cationic dyes such as methylene blue through electrostatic attraction and related interactions [31]. In this work, pH was varied from 3 to 11. Raw wool showed moderate dependence, with the lowest removal at pH 5 (43.51%) and the highest at pH 11 (65.98%). Hydrothermal biochar increased substantially from pH 3 (34.28%) to pH 7 (81.09%), then remained relatively high at pH 9–11 (≈58–59%). This indicates that near-neutral conditions provided a favorable balance of surface chemistry and dye accessibility for the hydrothermal material. Solvothermal biochar was weak under acidic conditions (7.5% at pH 3) but improved markedly in alkaline media (67% at pH 11), consistent with stronger electrostatic contribution when surface sites become more negatively charged. Similar pH-dependent trends have been reported for dye adsorption by inorganic/biopolymer composites and other low-cost sorbents [32]. Figure 4 shows the results.

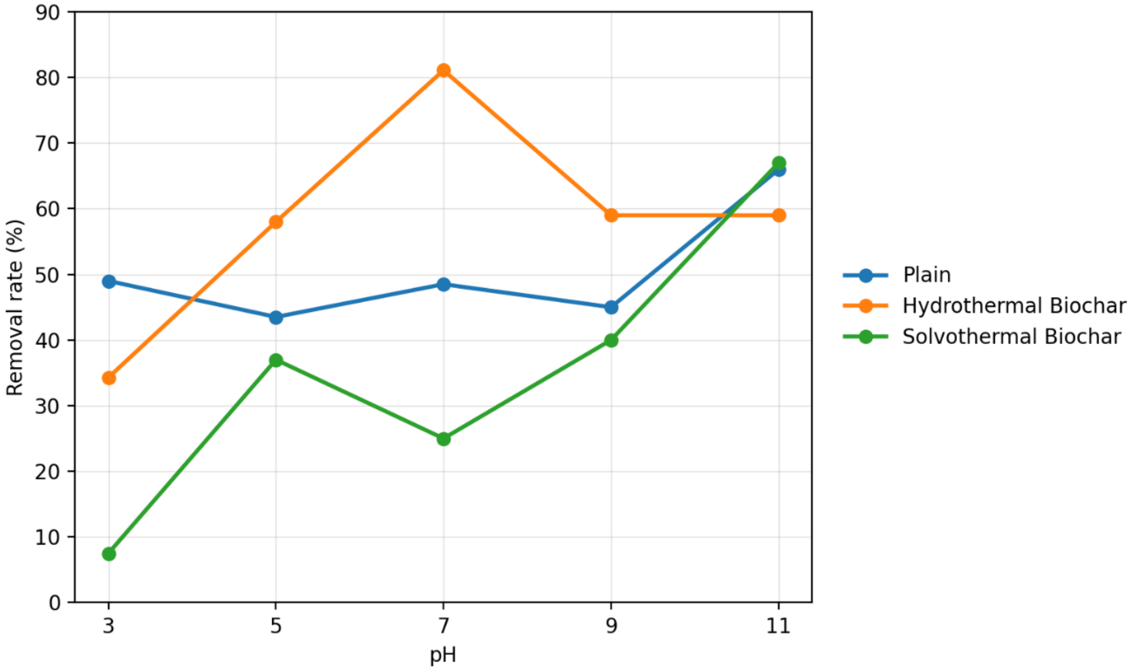

Figure 4. The effect of pH on the adsorption process.

3-5 Effect of adsorbent dose

Adsorbent dosage directly affects the number of available binding sites and the total surface area in contact with the dye solution; therefore, removal efficiency typically increases with dose until site under-utilization or aggregation effects become limiting [33]. In the current experiments (0.04–0.20 g), raw wool increased from 27.35% at 0.04 g to 44.40% at 0.20 g, reflecting the need for higher mass to compensate for its lower affinity. Hydrothermal biochar increased from 64.53% to 90.07% across the same dose range, confirming that it is the most efficient material among the three and that higher dosage strongly improves overall removal at the studied loading. Solvothermal biochar improved from 11.88% to 42.13% with dose, but remained consistently below the hydrothermal material. The dose–response behavior is consistent with adsorption studies in which increasing sorbent mass increases the availability of active sites and improves removal, especially for porous or functionalized materials. Figure 5 presents the results.

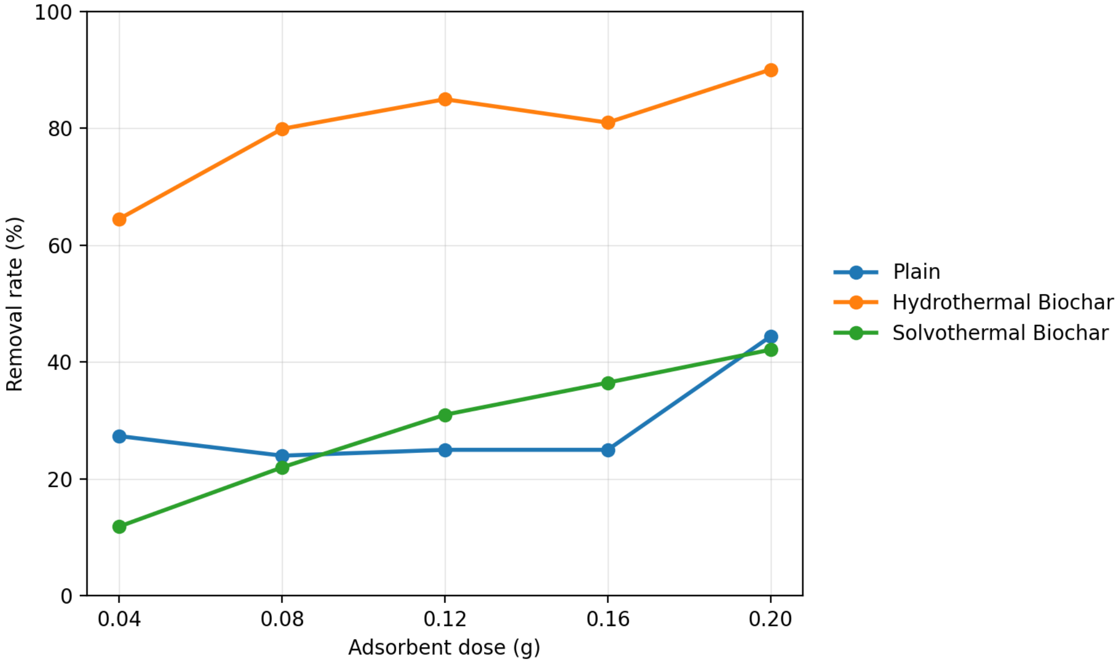

Figure 5. The effect of Dose on the adsorption process

4- Conclusions

This study demonstrated the feasibility of valorizing sheep wool into effective adsorbent materials for the removal of MB from aqueous solution. Among the tested materials, hydrothermally prepared wool biochar showed the best overall performance, achieving high and rapid MB removal under a wide range of operating conditions. Contact-time experiments indicated fast uptake and near-equilibrium behavior within short periods, while concentration studies showed that the hydrothermal biochar retained measurable removal even at higher MB loadings compared with raw wool and solvothermal biochar. The adsorption response was influenced by solution pH and adsorbent dosage, with improved removal generally observed at higher doses and under neutral-to-alkaline conditions. Temperature effects suggested that efficient operation is achievable under ambient conditions without the need for energy-intensive heating. Overall, hydrothermal conversion of wool produced a more active and reliable sorbent than raw wool or solvothermally treated material, supporting its potential as a low-cost, sustainable option for treating dye-contaminated water.

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Conflicts of Interest

The authors declare no conflict of interest.

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