

Adsorption Kinetics and Performance of Methylene Blue onto Alkali-Treated Sugarcane Bagasse Biochar

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ABSTRACT

Sugarcane bagasse (SCB), an abundant agricultural byproduct, was utilized to synthesize an effective biochar adsorbent via NaOH pretreatment and muffle furnace pyrolysis at 500 °C for the removal of methylene blue (MB) dye from aqueous solutions. Surface characterization using Fourier-Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), and Elemental Analysis (EA) confirmed significant structural transformations, including increased carbonization and the development of a well-defined porous network. Batch adsorption experiments demonstrated rapid adsorption kinetics, achieving an equilibrium dye removal efficiency of approximately 95% within 30 min with an equilibrium capacity (q_e) of 14.5584 mg/g. Kinetic modelling revealed that the adsorption process strongly followed the pseudo-second-order model ($R^2=0.9997$, $k_2=0.0676$ g/mg.min) significantly outperforming the Langmuir ($R^2=0.1806$) and Lagergren pseudo-first order ($R^2= 0.3713$). These results confirm that chemisorption involving electron sharing or exchange between MB molecules and biochar surface active sites is the dominant rate-controlling mechanism¹⁰. This study demonstrates the potential of value-added sugarcane bagasse biochar as a sustainable and cost-effective material for industrial dye wastewater remediation.

Keywords: Biochar, methylene blue, sugarcane bagasse, kinetics adsorption, wastewater.

Dyes are widely used in industries such as textiles, paper, plastics, leather, cosmetics, food, and pharmaceuticals, due to their ability to impart vibrant and stable coloration. However, their excessive use leads to a lot of dye wastewater, which poses significant environmental concerns. Moreover, several dyes and their degradation by-products have been reported to exhibit toxic, mutagenic, and carcinogenic properties, thereby threatening aquatic ecosystems and human health [1]. Tetra methylthionine chloride is the chemical name for methylene blue (MB), a basic thiazine (cationic) color. When it is oxidized, it has a distinctive deep blue color, but when it is reduced, it has no color. MB dye is one of the most important basic dyes because of its several uses, which include coloring paper, hair colorant, dying cotton and wool and as a component in black printing inks [2]. It also has many medical purposes. Acute human exposure to MB can result in a variety of illnesses, including elevated heart rate, vomiting, shock, tissue necrosis, and carcinogenic aromatic amines. Therefore, eliminating this dye from wastewater is a top objective worldwide [3].

In recent years, adsorption has gained significant attention as an effective and economical technique for dye removal due to its operational simplicity, high efficiency, and adaptability to various wastewater conditions. Among the numerous adsorbents investigated, biomass-derived materials have emerged as promising candidates because of their abundance, renewability, and cost effectiveness [4]. Agricultural residues such as rice husk, coconut shell, and sugarcane bagasse have been extensively explored as potential precursors to produce biochar-based adsorbents. Among these, sugarcane bagasse (SCB), a lignocellulosic by-product of the sugar industry, is particularly attractive due to its high carbon content

and naturally porous structure, which can be further enhanced through chemical or thermal activation. Owing to its favorable chemical composition, SCB represents a promising renewable feedstock for various value-added applications. It typically contains approximately 44% cellulose, 28% hemicellulose, 21% lignin, 5% ash, and 2% extractives [5]. The conversion of sugarcane bagasse into biochar not only offers an environmentally friendly approach to waste valorization but also produces a functional material with favorable surface characteristics for dye adsorption.

Hence, this study focuses on the preparation, characterization, and kinetic evaluation of sugarcane bagasse biochar for the adsorption of methylene blue from aqueous solutions.

Experimental

Material

Sugarcane bagasse (SCB) was obtained from nearby villages and first sun-dried to eliminate excess moisture. The dried SCB was then cut into smaller pieces to ease the subsequent drying and grinding processes. For the methylene blue preparation, exactly 0.1 grams of methylene blue powder was weighed and dissolved in 1 liter of distilled water to prepare a stock solution. A 30-ppm methylene blue solution was then prepared by diluting 30 mL of the stock solution with 70 mL of distilled water.

Method

Preparation of Biochar from Sugarcane Bagasse Sugarcane bagasse (SCB) was pretreated by soaking in a sodium hydroxide (NaOH) solution for two days to remove cellulose and lignin components. The treated SCB was then washed thoroughly with distilled water, dried, ground, and sieved to obtain a uniform particle size of 250 μm . This alkaline treatment increased the surface area and improved mass transfer, thereby enhancing the adsorption efficiency of methylene blue onto the resulting biochar. The prepared SCB sample was subsequently oven-dried at 70°C for 2 hours, followed by heating in a muffle furnace at 500°C for another 2 hours [6].

Characterization

To gain a comprehensive understanding of methylene blue (MB) adsorption onto SCB biochar, a set of analytical techniques was employed. Elemental analysis (EA) provided insights into the elemental composition of the biochar, revealing the abundance of elements that may contribute to MB binding. Fourier Transform Infrared (FTIR) spectroscopy identified specific functional groups present on the biochar surface, such as hydroxyl and carbonyl groups, which are potential sites for MB interaction. The spectrum was obtained at a resolution of 4 cm^{-1} over the range of 600 – 4000 cm^{-1} . Scanning Electron Microscopy (SEM) enabled the characterization of the biochar's surface morphology and structural features, including porosity and surface area, which are crucial factors influencing adsorption capacity. Finally, UV-Vis spectroscopy was utilized to monitor the adsorption process by quantifying the decrease in MB concentration in solution, providing valuable data on adsorption efficiency and enabling the assessment of the biochar's potential as an effective adsorbent.

Adsorption of Methylene Blue using SCB Biochar

A 50 mL portion of the 30-ppm methylene blue solution was transferred into a conical flask, followed by the addition of 0.1 grams of the prepared SCB biochar. The mixtures were shaken at 200 rpm for 30 minutes at 25°C to ensure sufficient interaction between the MB and SCB biochar [6]. At predetermined time intervals (10, 20, 30, 60, and 120 minutes), samples were collected, filtered using filter paper and a funnel, and analyzed with a UV-Vis spectrophotometer. The dye concentration was determined using a standard calibration curve, and the removal efficiency (R) of the biochar for MB was calculated based on the absorbance data [7]

$$R (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_t}{m} \times V \quad (2)$$

Where C_0 (mg/L) is initial concentration, C_t (mg/L) is final concentration and R is removal efficiency, meanwhile q_e is adsorption capacity in mg/g, m is mass of SCB biochar (g), and V is volume of solution in mL.

Kinetics Model

The adsorption kinetics were investigated by doing adsorption in contact times which are 10, 20, 30, 60 and 120 minutes. In this study, the rate constant determination for the adsorption of MB was determined by using first-order, pseudo-first-order kinetic model of Lagergren (1898) and pseudo-second-order kinetic model of McKay and Ho [8]. Equation of the first-order kinetic model can be expressed as:

$$\frac{\ln(\frac{C_0}{C_t})}{C_0 - C_t} + k_0 = \frac{k_1 t}{C_0 - C_t} \quad (3)$$

where k_1 is the adsorption rate constant, k_0 is the equilibrium constant, C_0 is the initial concentration of the solution and C_t is the concentration remaining in the solution after adsorption for time t . The adsorption rate constant can be determined from the slope value of the linear curve $\ln(C_0 - C_t) / C_0 - C_t$ versus $t / C_0 - C_t$.

Equation of the Lagergren's pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Equation of the pseudo-second-order kinetic model based on the adsorption capacity of the solid phase:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (5)$$

Where k_2 is the rate constant of the pseudo second order reaction (g/mg min). The integration of the equation with the limit $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ will produce Equation 6.

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{1}{q_e} t \quad (6)$$

value q_e is obtained from the plot slope of the t/q_t versus t and k_2 is obtained from the intercept, q_e can be obtained from the line slope, k_2 can be calculated from the k_2 value (Ho et al., 1999). Where q_e is concentration at equilibrium (mg/g), q_t is concentration of the adsorbed substance at time t (mg/g), t is contact time (minutes), k_1 is a pseudo first order constant and k_2 is a pseudo second order constant.

RESULTS AND DISCUSSION

Elemental Analysis

Table 1 presents the chemical compositions of two materials of raw sugarcane bagasse (SCB) and SCB biochar expressed as percentages of various elemental components including Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur. The raw SCB has a relatively high carbon content (23.69%) due to its primarily composed of cellulose and lignin, which are both rich in carbon [9]. In SCB biochar, carbon content increases from 23.69% to 36.01%. This happens because, during the pyrolysis process many volatile compounds are removed and it is leaving more carbon behind. The higher carbon content makes the biochar better for adsorption purposes as carbon plays a big role in this process [10].

Moreover, the hydrogen content increased from 0.06% in SCB to 5.08% in the SCB biochar. This rise may be attributed to the presence of residual hydrogen-containing compounds that remained in the biochar after the pyrolysis process [7]. The nitrogen content increased slightly from 1.09% to 1.87%, suggesting a concentration of nitrogen containing compounds during thermal treatment. The presence of nitrogen functionalities in biochar can enhance adsorption performance by introducing basic surface sites that interact favorably with certain pollutants. Conversely, the oxygen content decreased significantly from 75.16% in SCB to 57.04% in SCB biochar due to the release of volatile oxygenated species such as CO₂, CO, and H₂O during pyrolysis [4]. The reduction in oxygen-to-carbon ratio confirms progressive carbonization, resulting in a stable, aromatic carbon surface favorable for non-covalent and electrostatic dye interaction. Minor increases in hydrogen and nitrogen contents may further contribute to the structural stability and adsorption efficiency of the biochar [11].

Table 1. Elemental Analysis of SCB and SCB Biochar

Type (wt%)	C	H	N	*O
Raw SCB	23.69	0.06	1.09	75.16
SCB Biochar	36.01	5.08	1.87	57.04

*Oxygen by differences

FTIR

Fourier-transform infrared (FTIR) spectroscopy was employed to identify surface functional groups. Fig.1 represents raw SCB and SCB biochar. A broad absorption band near 3400 cm⁻¹ corresponds to -OH stretching vibrations from hydroxyl groups. This is because raw bagasse contains cellulose and hemicellulose which are rich in hydroxyl groups and make the material hydrophilic. In the biochar, this peak is much smaller meaning that most of the hydroxyl groups are lost during heating due to the high heat [12]. The peaks at approximately 2920 cm⁻¹ are attributed to C-H stretching in aliphatic structures, while the absorption near 1620 cm⁻¹ indicates C=O stretching of carbonyl groups. The band observed around 1100 cm⁻¹ is related to C-O stretching vibrations, confirmed the retention of oxygenated surface functional groups that serve as active adsorption centers for cationic methylene blue.

In contrast, the SCB biochar sample spectrum displays a simpler pattern with broader and less defined peaks. This simplification is a direct consequence of the pyrolysis process, which involves thermal degradation. During this process, volatile components containing functional groups such as those associated with hydroxyl (OH) and aliphatic hydrocarbons are removed, leading to the loss of the corresponding peaks in the FTIR spectrum [13]. These structures make biochar more carbon-rich and thermally stable.

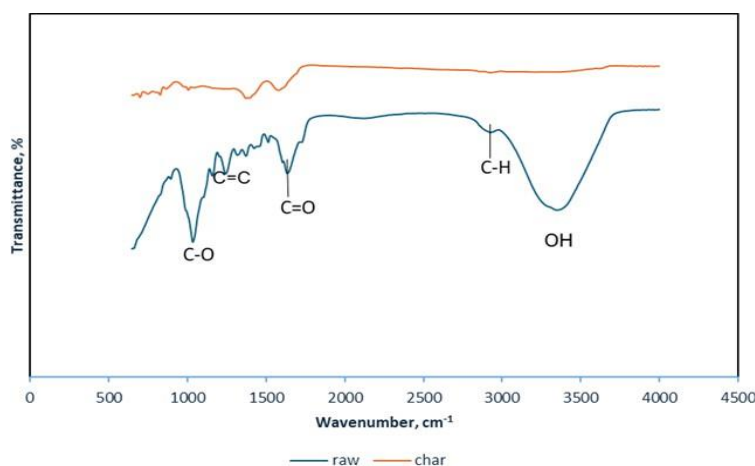


Figure 1. FTIR spectrum for SCB and SCB biochar

SEM

Fig 2A and 2B shows the morphology of raw SCB at magnification 1000x and 2000x. Meanwhile Fig.2C and Fig.2D represent morphology of SCB biochar. In the raw SCB, the structure appears dense and fibrous with minimal visible porosity. This compact arrangement is due to the presence of cellulose, hemicellulose, and lignin which make up the cell walls of the material. The lack of pores suggests a low surface area limiting the raw material's adsorption capabilities. This means its ability to adsorb methylene blue is limited [14].

In contrast, the SCB biochar obtained after pyrolysis (Fig.2C and Fig.2D) exhibited pronounced morphological transformations compared to the raw SCB. The SEM micrographs revealed a more porous structure characterized by well-defined and enlarged pores. During the carbonization process, moisture and other volatile elements are eliminated, leaving primarily carbon left and it will be caused by this transformation. The surface also looks smoother in some areas, indicating a more compact and carbonized structure. The development of a highly porous network and expanded surface area substantially improves the adsorption capacity of the biochar, as these characteristics facilitate greater interaction between the adsorbent surface and methylene blue molecules [15].

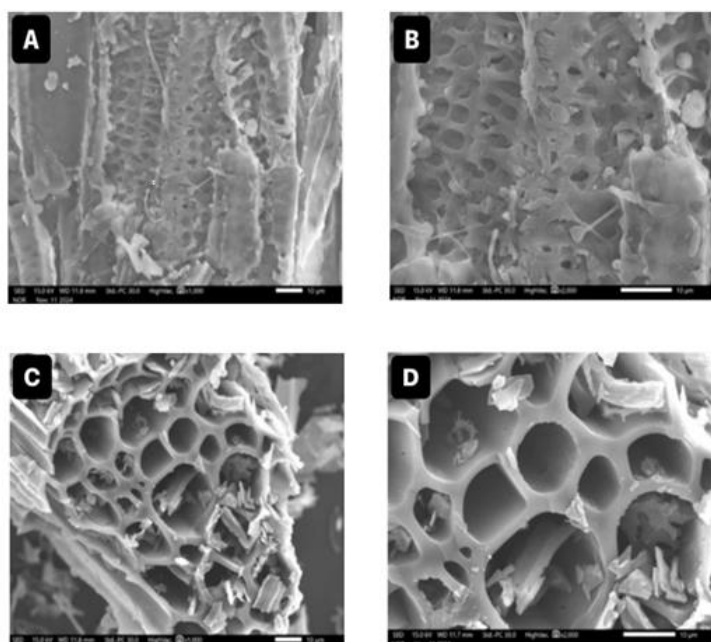


Figure 2. (a) raw SCB 1000 x magnification; (b) raw SCB x 2000 magnification; (c) SCB biochar x 1000 magnification; (d) SCB biochar x 2000 magnification

Adsorption Study and Kinetics Analysis

Figure 3 illustrates the variation of adsorption capacity and percentage removal of methylene blue (MB) by SCB biochar as a function of contact time. With a very rapid rise in both removal efficiency and adsorption capacity within the first 10 minutes, this indicates that there are ample active sites available on the surface of biochar at the beginning of adsorption. Later on, the rate of adsorption slowed down and reached equilibrium at about 30 minutes, reflecting the saturation of the adsorption sites. The equilibrium adsorption capacity (q_e) was approximately 14.5584 mg/g and a removal efficiency of about 95%. The fact that equilibrium was so quickly attained reflects the fact that MB adsorption onto SCB biochar is dominated by surface adsorption rather than intra-particle diffusion. The rapid initial adsorption may be attributed to electrostatic interaction and π - π interaction between MB molecules and aromatic carbon structure of biochar [16].

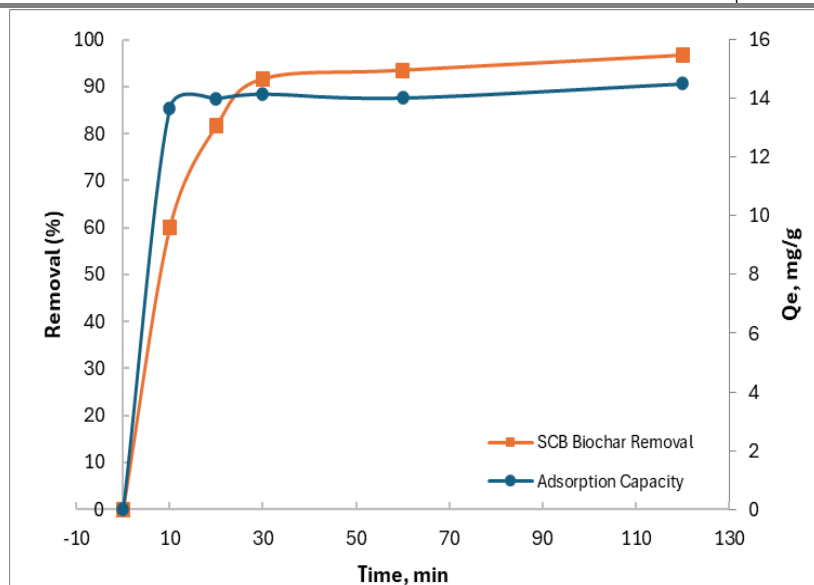


Figure 3. Adsorption capacity and % removal of MB

To further interpret the adsorption processes of MB on SCB biochar, a few kinetic models were analyzed using first order Langmuir-Hinshelwood kinetic model, pseudo-first order of Lagergren, and pseudo-second-order kinetic model of McKay and Ho models. Table 2, Fig.4, Fig 5 and Fig.6 point out the fitting outcomes.

As shown in Table 2 and Fig.4, Langmuir model demonstrates a weak correlation with the experimental data, as shown by its low R^2 value of 0.1806. The rate constant ($k_1 = 0.0241 \text{ min}^{-1}$) indicates a slow adsorption process. This poor correlation suggests that the Langmuir model is unsuitable for describing the adsorption kinetics of methylene blue onto SCB biochar, likely due to its assumptions about reaction mechanisms, which do not align with the experimental conditions. Consequently, the poor correlation suggests that the adsorption of methylene blue onto SCB biochar does not proceed via a heterogeneous surface reaction mechanism [7].

The Pseudo-First Order Lagergren model (Fig.5) assumes that the adsorption process is primarily governed by Van Der Waals forces, hydrogen bonding, or electrostatic interactions between the MB and the SCB biochar [17]. The correlation coefficient for this model was $R^2 = 0.3713$, which is slightly higher than Langmuir-Hinshelwood model but still relatively low. The adsorption rate constant ($k_1 = 0.0203 \text{ min}^{-1}$) suggests that the adsorption process occurs at a slow rate. The equilibrium adsorption capacity ($q_e = 33.5065 \text{ mg/g}$) indicates that MB is adsorbed onto SCB biochar to some extent, but the low R^2 value suggests that physisorption is not the dominant mechanism [18]. The weak correlation indicates that the adsorption of MB onto SCB biochar does not strictly follow the pseudo-first order kinetic model, implying that other mechanisms, such as chemical interactions, may be involved.

In contrast, pseudo-second order model provided the best correlation ($R^2 > 0.99$), as presented in Table 2 and Fig.6, suggesting that chemisorption is the dominant rate-controlling step involving electron sharing or exchange between the dye molecules and surface functional groups. This model implies that the adsorption process involves valence forces through electron sharing or exchange between dye molecules and surface functional groups, representing a more accurate description of chemically driven adsorption [18]. The adsorption rate constant (k_2) obtained from this model is higher than those of the other kinetic models, suggesting a faster and more efficient adsorption process. However, the equilibrium adsorption capacity ($q_e = 14.5584 \text{ mg/g}$) is slightly lower than that predicted by the pseudo-first-order model. Nevertheless, the extremely high correlation value confirms that chemisorption is the primary mechanism governing the adsorption of MB onto SCB biochar.

Overall, the high adsorption capacity and strong kinetic fit demonstrate that SCB biochar is a promising low-cost and eco-friendly adsorbent for dye removal applications. Its performance can be attributed to its porous

morphology, high surface area, and rich surface chemistry resulting from the activation and carbonization treatment.

Table 2. Calculation of the kinetics of adsorption of methylene blue dye

Adsorbent	Kinetic Model	Parameter	Value
SCB Biochar	First order Langmuir	R^2	0.1806
		k_1 (min^{-1})	0.0241
	Pseudo first-order Lagergren	R^2	0.3713
		k_1 (min^{-1})	0.0203
		q_e (mg/g)	33.5065
	Pseudo second order McKay & Ho	R^2	0.9997
		k_2 (g/mg. min)	0.0676
		q_e (mg/g)	14.5584

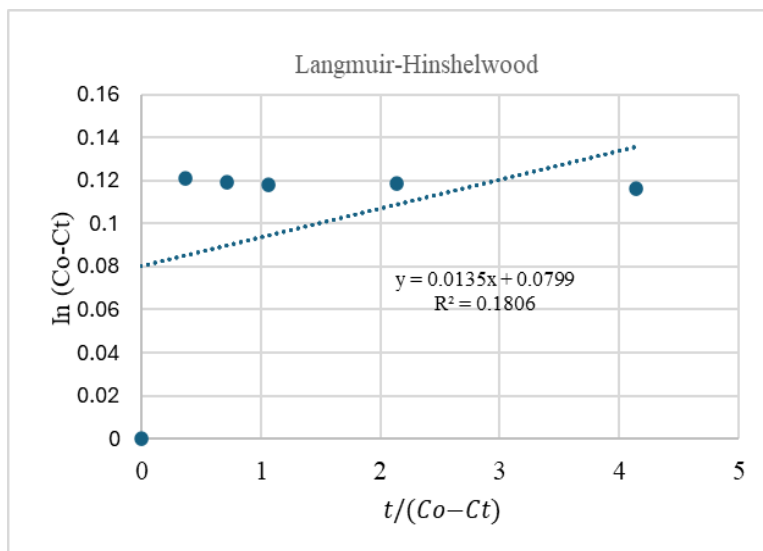


Figure 4. Linear curve of the Langmuir first-order kinetic model

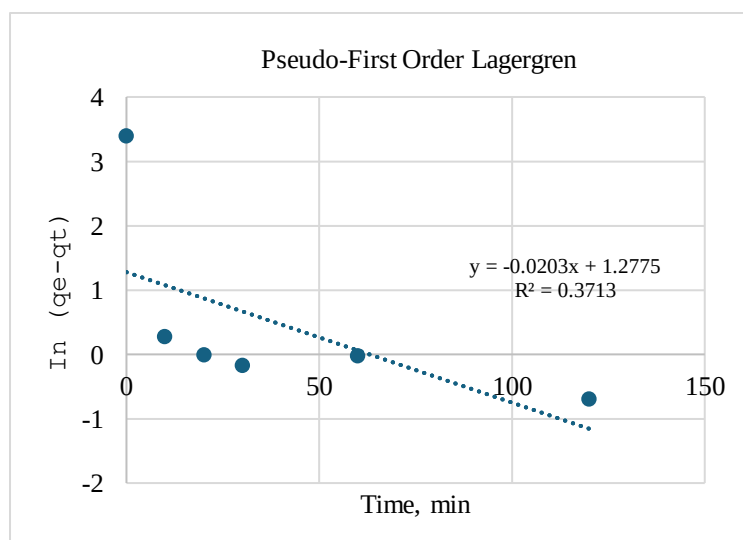


Figure 5. Linear curve of the Lagergren first-order kinetic model

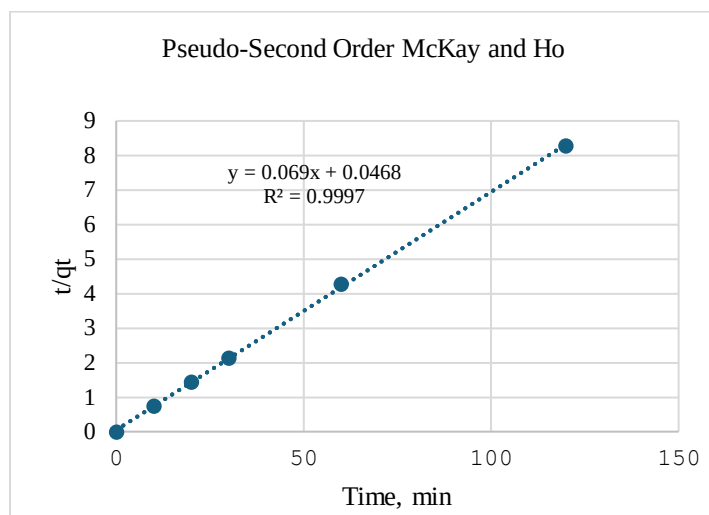


Figure 6. Linear curve of the McKay & Ho second-order kinetic model

CONCLUSION

This research proves that sugarcane bagasse (SCB), a readily available crop by-product, can be successfully converted into biochar and used as a cheap adsorbent to remove methylene blue (MB) dye from water solutions. Characterization analyses verified that pyrolysis at 500°C improved the carbon content, surface porosity, and functional group composition of SCB biochar, which are fundamental parameters responsible for its adsorption capability. Kinetics study revealed that MB adsorption onto SCB biochar followed a pseudo-second-order kinetic model ($R^2 > 0.999$), indicating chemisorption as the predominant mechanism, where there is exchange or sharing of electrons among MB molecules and surface functional groups. The rate constant of adsorption from this model was significantly higher than for Langmuir Hinshelwood and pseudo-first-order models, which reflects the fast and effective process of adsorption. The higher adsorption rate and equilibrium capacity acceptable indicate that SCB biochar is an effective alternative to commercial adsorbents with environmental as well as economic benefits. The contribution of this work to circular economic practices comes in the form of upcycling agricultural waste into useful product for the treatment of wastewater. Pilot-scale tests under real wastewater conditions, reusability, and regeneration efficiency are avenues that should be explored in future studies to further establish its suitability in the environment.

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