

Article

Upcycling of Precipitated Silica from Bamboo Alkaline Black Liquor into a Mesoporous Silica-Based Adsorbent for Dye Removal

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Abstract

Dye wastewater pollution has become a critical environmental issue, while conventional silica adsorbents are often limited by high production costs and the use of chemical silicon sources. In this study, a black-liquor-derived silica-based adsorbent was prepared from bamboo alkaline black liquor through calcium hydroxide precipitation, acid leaching, washing, and calcination. The obtained product was systematically characterized by ICP-OES, XRD, SEM, and BET analysis. Phase analysis showed that the product was mainly composed of amorphous SiO₂, together with a small amount of residual CaSiO₃. The product was semi-quantitatively estimated to contain approximately 64.6 wt.% total SiO₂ and 14.7 wt.% total CaSiO₃, and the estimated SiO₂ yield was about 4.6 wt.% based on dry black liquor solids. The adsorbent exhibited a mesoporous structure with a specific surface area of 60.04 m²/g, a pore volume of 0.23 cm³/g, and an average pore diameter of 7.5 nm. The effects of adsorbent dosage, initial methylene blue concentration, solution pH, and temperature on adsorption performance were investigated. Under the selected conditions of 0.5 g adsorbent, 50 mg/L methylene blue, pH 7, and 20 °C, the removal efficiency reached 82.94%. Adsorption isotherm analysis showed that the Langmuir equation provided the best fit among the tested models over the studied concentration range, and the linear Langmuir fit gave an apparent capacity parameter of 840.3 mg/g. However, this fitted value should not be interpreted as a physically realizable ideal monolayer uptake. This work provides a feasible route for converting silicon-containing bamboo alkaline black liquor into a mesoporous silica-based adsorbent for dye removal.



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1. Introduction

Bamboo is an important non-wood raw material for pulping because of its rapid growth, wide availability, and high fiber yield. During NaOH-based bamboo cooking, a large amount of alkaline black liquor is generated, which contains dissolved lignin,

degraded carbohydrates, inorganic salts, and silicon-containing species. Compared with wood-based black liquor, non-wood black liquor usually contains a higher amount of silicon. Dissolved silicate in black liquor can increase liquor viscosity, promote scaling during evaporation, interfere with causticizing and alkali recovery, and reduce the combustion efficiency and heating value of the black liquor system. Therefore, silicon removal from bamboo alkaline black liquor is an important issue for the efficient utilization and chemical recovery of non-wood pulping black liquor [1,2].

Several desilication methods have been reported for non-wood pulping liquors, including acidification or carbonation, aluminum salt precipitation, sodium aluminate treatment, magnesium/aluminum compound precipitation, green liquor desilication, and lime- or calcium-based precipitation [3–6]. These methods mainly aim to transfer soluble silicate from the liquid phase into insoluble silicon-containing precipitates, thereby reducing the negative influence of silicon on evaporation, combustion, causticizing, and alkali recovery. Among them, calcium hydroxide precipitation is attractive because of its simple operation, low cost, and direct reaction with soluble silicate to form calcium silicate precipitates.

However, most previous studies on non-wood black liquor desilication have focused on improving desilication efficiency and protecting alkali-recovery operations, whereas the subsequent utilization of the silicon-rich precipitate has received much less attention. Previous work on bamboo and other non-wood pulping systems has mainly emphasized silicon removal during cooking, black liquor treatment, or green liquor desilication. Although recovery of silica from desilication sludge has been reported, the direct conversion of black-liquor-derived desilication precipitates into functional silica-based adsorbents remains limited [3,4,6].

Therefore, the novelty of the present work lies not merely in removing silicon from bamboo alkaline black liquor, but in converting the precipitated silicon-rich solid into a mesoporous silica-based adsorbent for dye removal. In addition, because the final product still contains residual CaSiO_3 , this study specifically discusses a silica-based material rather than fully purified SiO_2 .

Dye wastewater is another important environmental problem because of its strong color, toxicity, and poor biodegradability. Dye molecules can increase chemical oxygen demand (COD) and biochemical oxygen demand (BOD), reduce light penetration in water bodies, and disturb aquatic ecosystems [7–10]. Various technologies, including photocatalytic degradation, membrane filtration, biosorption, advanced oxidation, coagulation-flocculation, and adsorption, have been developed for dye removal [11–13]. Among these methods, adsorption is considered one of the most practical approaches because of its simple operation, flexible equipment design, mild treatment conditions, and relatively low sensitivity to toxic pollutants [14–16].

Silica-based adsorbents have attracted attention because of their porous structure, chemical stability, and abundant surface silanol (Si-OH) groups, which can interact with cationic dye molecules through electrostatic attraction and hydrogen bonding [17–19]. Compared with silica prepared from chemical silicon sources, black-liquor-derived silica-based materials may reduce preparation cost and improve the resource utilization of pulping waste. In addition, the residual calcium silicate phase formed during calcium hydroxide desilication may influence the pore structure and surface properties of the final adsorbent, although this role has been less discussed in black-liquor-derived systems [20].

In this work, NaOH -based bamboo black liquor was used as a silicon-containing waste stream to prepare a black-liquor-derived silica-based adsorbent through calcium hydroxide precipitation, acid leaching, washing, drying, and calcination. Considering that residual calcium silicate remained in the final product, the obtained material is described as a silica-based adsorbent rather than completely pure SiO_2 . The chemical composition,

phase structure, morphology, and pore characteristics of the product were characterized by ICP-OES, XRD, SEM, and BET analysis. Methylene blue was selected as a model cationic dye to evaluate the adsorption performance of the prepared adsorbent. This study provides a potential route for converting silicon-containing bamboo alkaline black liquor into a mesoporous silica-based adsorbent for dye wastewater treatment.

2. Materials and Methods

2.1. Materials

The bamboo used in this experiment was Cizhu bamboo collected from Sichuan Province. The bamboo was wet-stored at the mill, air-dried after retrieval, and then packed in bags and equilibrated at 0–5 °C before use. Its dryness was 95.36%. A total of 5 kg of bamboo raw material was soaked in a barrel to soften the fibers and remove impurities, followed by steaming at an appropriate temperature for 15 min. Finally, the bamboo was processed into fibers using a fiber-twisting machine to obtain twisted bamboo fibers. All chemicals used were of analytical reagent (AR) grade and purchased from Nanjing Chemical Reagent Co., Ltd., Nanjing, China. The water used in all analyses was purified with an Upure water treatment system.

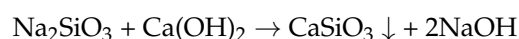
2.2. Bamboo Pulping and Black Liquor Procurement

The black liquor used in this study was prepared by two-cycle mild alkaline cooking of twisted bamboo fibers. In each cooking cycle, the NaOH charge was 8% based on the oven-dried bamboo fibers, and the solid-to-liquid ratio was maintained at 1:4. The cooking temperature and holding time were 100 °C and 60 min, respectively. After the first cooking cycle, the obtained liquor was reused as the cooking liquor for the second cycle, and the black liquor collected after the second cycle was used as the silicon-containing raw material for subsequent silica recovery.

This two-cycle cooking procedure was designed to obtain a silicon-enriched bamboo alkaline black liquor rather than to optimize pulp yield. Bamboo is a typical non-wood pulping raw material, and silicon-containing components in bamboo can be dissolved into alkaline liquor during cooking. Previous studies on wheat straw, bamboo, and other non-wood pulping systems have shown that dissolved silicon in black liquor or green liquor is one of the major factors causing scaling, high viscosity, causticizing difficulties, and poor alkali recovery performance [1,2,21]. Therefore, recycling the first-cycle liquor in the second cooking cycle can increase the concentration of dissolved lignin fragments, inorganic salts, and soluble silicate species in the liquor, providing a more suitable silicon-containing feedstock for calcium-based precipitation. The relatively mild cooking temperature and short holding time were selected to promote the dissolution of alkaline-soluble components while avoiding excessive carbohydrate degradation and unnecessary dilution of the black liquor system.

2.3. Preparation of Silica-Based Adsorbent

The preparation of the black-liquor-derived silica-based adsorbent was designed according to the desilication principle reported for non-wood pulping liquors and bamboo pulping systems [3,4]. In alkaline black liquor, dissolved silicon mainly exists as soluble silicate species. When $\text{Ca}(\text{OH})_2$ is introduced, Ca^{2+} can react with silicate to form insoluble calcium silicate precipitates, thereby transferring silicon from the liquid phase into the solid phase. The main reaction can be simplified as follows:



Based on this reaction pathway, the $\text{Ca}(\text{OH})_2$ dosage was estimated according to the approximate silicon content of the recycled bamboo black liquor and the Ca/Si stoichiometric relationship. Because bamboo black liquor contains lignin fragments, carbonate species, sodium salts, and other inorganic ions, a practical excess of $\text{Ca}(\text{OH})_2$ was used to ensure sufficient precipitation of silicon-containing species. Previous studies have also shown that lime-based desilication is effective for black liquor systems, and the required lime dosage may exceed the theoretical stoichiometric amount because of the formation of calcium silicate phases and side reactions with other inorganic components [5]. Therefore, the precipitation condition in this work was determined by combining the established lime-desilication mechanism, the estimated silicon content of the recycled black liquor, and the need to obtain enough silicon-rich precipitate for adsorbent preparation.

Because the Si content of the black liquor was not directly measured in this study, the $\text{Ca}(\text{OH})_2$ addition was determined by process estimation rather than direct elemental analysis. In a typical run, 200 g of recycled bamboo black liquor was placed in a beaker, and 0.44 g of $\text{Ca}(\text{OH})_2$ was slowly added under continuous stirring. The mixture was reacted at 70 °C and 500 r/min for 1.5 h to promote the formation and growth of calcium silicate precipitates. Temperature and reaction time are important factors affecting silica precipitation and solid–liquid separation in black liquor desilication [5]. Compared with more severe lime-treatment conditions reported in previous studies, the present condition used a moderate temperature and a longer residence time, which was favorable for sufficient precipitation while reducing energy consumption and limiting excessive organic co-precipitation from bamboo black liquor [3,4,6].

After precipitation, the mixture was centrifuged at 8000 r/min for 15 min to separate the solid precipitate. The obtained precipitate was dried at 105 °C to constant weight and then leached with 5% HCl at 60 °C for 1 h. The acid-leaching step was used to convert residual calcium-containing impurities into soluble salts and expose the silica-rich phase. During HCl leaching, residual calcium-containing phases such as calcium silicate and possible carbonate impurities can be partially converted into soluble calcium chloride and removed during washing, whereas the silica-rich framework remains in the solid phase [6]. During subsequent calcination, residual organics derived from black liquor are removed and neighboring silanol groups may partially condense to form a more stable silica network [17]. Similar acid-leaching and calcination strategies have been reported for recovering silica from black-liquor desilication sludge, where hydrochloric acid removes undesirable inorganic components and subsequent calcination removes residual organic matter [6]. After acid leaching, the solid was filtered and washed repeatedly with deionized water until the filtrate became neutral. Finally, the washed precipitate was dried again at 105 °C and calcined at 650 °C for 4 h to remove residual organics and obtain the black-liquor-derived silica-based adsorbent. The flow chart for the preparation of the black-liquor-derived silica-based adsorbent is illustrated in Figure 1.

2.4. Chemical Characterization of the Silica-Based Adsorbent

To clarify the phase composition of the calcined samples, X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with a scanning range of $2\theta = 5\text{--}80^\circ$ and a scanning speed of $0.02^\circ/\text{min}$, and the XRD patterns of the samples were finally obtained; the pore structure characteristics including specific surface area, porosity and pore size distribution of the samples were systematically investigated through Brunauer–Emmett–Teller (BET) specific surface area analysis (Micromeritics, Norcross, GA, USA); the micromorphology of the calcined samples was observed using a Hitachi SU8600 scanning electron microscope (SEM, Hitachi, Tokyo, Japan). The elemental composition of the obtained silica sample was determined

by inductively coupled plasma optical emission spectroscopy (ICP-OES) after appropriate acid digestion (Thermo Scientific, Dreieich, Germany).

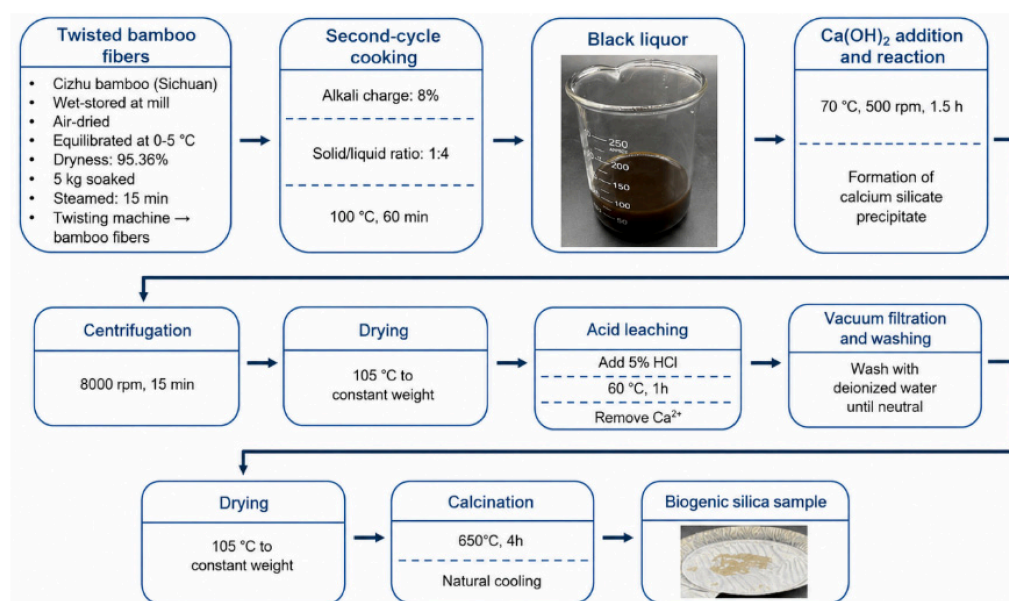


Figure 1. Flow chart for the preparation of the black-liquor-derived silica-based adsorbent.

2.5. Adsorption of Methylene Blue by the Silica-Based Adsorbent

Methylene blue was selected as the target dye pollutant to evaluate the adsorption performance of the silica-based adsorbent prepared from bamboo alkaline black liquor. Batch adsorption experiments were carried out to investigate the effects of key operating factors, including adsorbent dosage, initial methylene blue concentration, solution pH, and reaction temperature, on the adsorption efficiency.

For the adsorbent dosage experiment, the dosage was varied from 0.05 to 0.6 g, while the initial methylene blue concentration, solution pH, reaction temperature, and adsorption time were fixed at 50 mg/L, pH 7, 20 °C, and 2 h, respectively. For the initial concentration experiment, the methylene blue concentration was adjusted from 50 to 500 mg/L, with the adsorbent dosage, pH, temperature, and adsorption time maintained at 0.5 g, pH 7, 20 °C, and 2 h, respectively. The effect of solution pH was studied over the pH range of 2–10, under fixed conditions of 50 mg/L methylene blue, 0.5 g adsorbent, 20 °C, and 2 h. The effect of reaction temperature was investigated from 10 to 50 °C, with the initial methylene blue concentration, adsorbent dosage, pH, and adsorption time fixed at 50 mg/L, 0.5 g, pH 7, and 2 h, respectively.

To further analyze the adsorption behavior and estimate the maximum adsorption capacity of the adsorbent, the experimental equilibrium data were fitted using several adsorption isotherm models, including the linear and nonlinear Langmuir models, Freundlich model, Temkin model, Dubinin–Radushkevich (D–R) model, and Redlich–Peterson (R–P) model. The fitting analysis was used to clarify the adsorption mechanism, surface heterogeneity, adsorption affinity, and whether the adsorption process was dominated by monolayer or multilayer adsorption behavior. The adsorption isotherm models used in this work are expressed as follows:

$$\text{Langmuir (nonlinear)} : q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$

$$\text{Langmuir (linear)} : \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{C_e}$$

$$\text{Freundlich : } q_e = K_F C_e^{\frac{1}{n}}$$

$$\text{Temkin : } q_e = \frac{RT}{b_T} \ln(K_T C_e)$$

$$\text{Dubinin–Radushkevich : } \ln q_e = \ln q_{\text{m}} - k \epsilon^2$$

$$\text{Redlich–Peterson : } q_e = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e^\beta}$$

3. Results

3.1. Phase Composition and Elemental Analysis

The elemental composition and phase characteristics of the silica-based product recovered from bamboo alkaline black liquor were analyzed by ICP-OES and XRD, respectively. Because the silicon content of the original recycled black liquor was not directly measured, the $\text{Ca}(\text{OH})_2$ dosage used during precipitation was based on process estimation, and the phase composition of the final product was interpreted in a semi-quantitative manner. The final product yield was approximately 7.0 wt.% based on dry black liquor solids.

ICP-OES analysis showed that the product contained 33.7 ± 0.3 wt.% Si and 5.1 ± 0.2 wt.% Ca (Table 1). Based on the simplified assumption that the major Si- and Ca-bearing phases in the product were SiO_2 and CaSiO_3 , respectively, and combined with the XRD identification of amorphous silica and minor calcium silicate, the product was semi-quantitatively estimated to contain approximately 64.6 wt.% total SiO_2 and 14.7 wt.% total CaSiO_3 . These values should be regarded as approximate compositional estimates rather than exact quantitative phase fractions.

Table 1. Si and Ca contents of the silica-based product determined by ICP-OES.

Element	Percentage (wt.%)	Component Mass (mg)
Si	33.7 ± 0.3	166.8
Ca	5.1 ± 0.2	25.0

The XRD pattern (Figure 2) exhibited a broad halo at approximately $2\theta = 21.8\text{--}26.6^\circ$, indicating that the product was predominantly amorphous. Several weak peaks assignable to CaSiO_3 were also observed, confirming that a small amount of crystalline calcium silicate remained after acid leaching and calcination. Because the overall crystallinity was only about 4.1%, quantitative phase analysis based on XRD alone would carry substantial uncertainty. Therefore, the XRD result is interpreted here mainly in a qualitative or semi-quantitative manner (Table 2).

Table 2. Semi-quantitative estimation of the major phases in the silica-based product based on ICP-OES and XRD interpretation.

Composition	Percentage (wt.%)	Component Mass (mg)
Total SiO_2 phase	64.6	319.3
Total CaSiO_3 phase	14.7	72.5
Overall crystallinity from XRD is 4.1%		

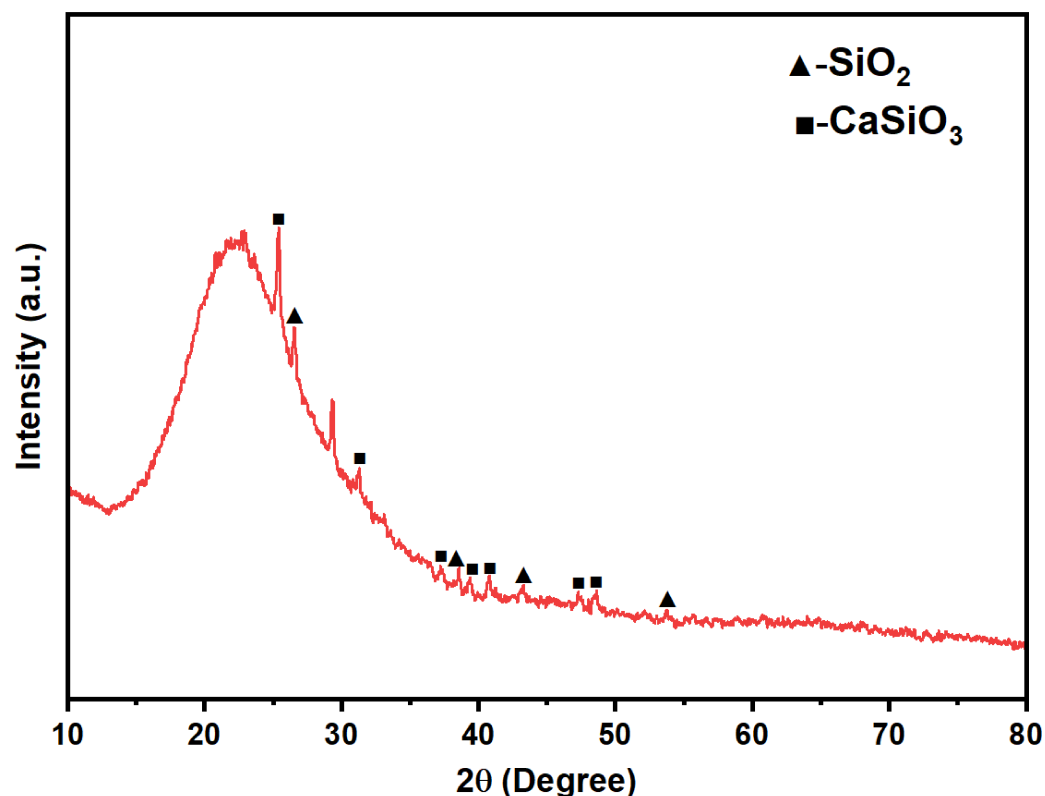


Figure 2. XRD pattern of the silica-based product recovered from bamboo alkaline black liquor. The pattern shows a dominant amorphous halo with weak peaks assignable to minor crystalline calcium silicate and silica phases.

3.2. Microstructure Analysis

The micromorphology of the silica adsorbent extracted from black liquor was observed by scanning electron microscopy (SEM) at different magnifications, and the results are shown in Figure 3.

The morphological features from low to high magnifications clearly reveal the overall structure, surface details, and impurity distribution of the adsorbent, providing intuitive evidence for understanding the correlation between its pore formation mechanism and adsorption performance. At low magnification, the adsorbent exhibits an irregular agglomerate structure with rounded particles and loose packing, without obvious dense massive agglomerates, indicating no excessive aggregation during preparation. These agglomerates form via weak interactions between silica particles during calcination at 650 °C, which not only avoids separation difficulties caused by excessive particle dispersion but also provides sufficient channels for dye molecule diffusion. As magnification increases, the porous characteristics become more prominent, showing a typical loose porous morphology with numerous pores and grooves of varying sizes and no dense regions. This porous structure originates from the preparation process: the loose flocculent calcium silicate formed in the precipitation stage generates initial pores after hydrochloric acid decalcification where Ca^{2+} originally occupied spaces, and subsequent thermal decomposition of trace organic residues during 650 °C calcination further expands the pore space. At high magnification, the sample shows a uniform loose texture without obvious regular crystalline morphology, which is consistent with the predominantly amorphous character indicated by the XRD result. A small number of dispersed dense micron-sized particles are observed, identified as incompletely removed CaSiO_3 impurities. Some fine impurities embed in mesoporous channels or form thin surface layers, consistent with ICP results. This may help explain the lower Si content than the theoretical value. Residual calcium-containing impurities

dilute the Si proportion and may partially cover some adsorption sites, although the overall porous structure is still retained. The adsorbent's micromorphology is logically consistent with its preparation process and properties: the loose porous agglomerate structure ensures high specific surface area, sufficient mesoporous channels, and certain mechanical stability, while the amorphous structure and uniform pores provide structural adaptability for methylene blue adsorption.

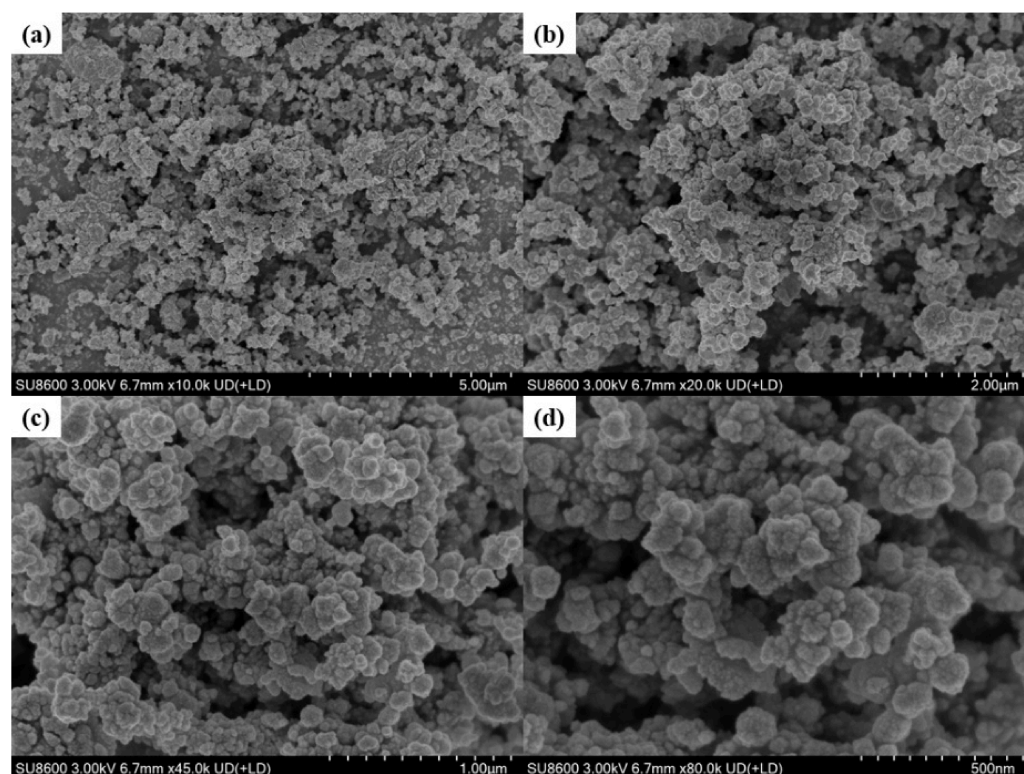


Figure 3. Microstructure of silica sample from black liquor at different magnification: (a) 10k; (b) 20k; (c) 45k; (d) 80k.

3.3. Analysis of Pore Structure Characteristics and Formation Mechanism

Pore structure is a critical parameter governing adsorbent performance, directly determining the accessibility of active sites, dye diffusion pathways, and maximum adsorption capacity. In this study, BET nitrogen adsorption–desorption tests were performed to systematically analyze the specific surface area, total pore volume (V_{tol}), and pore size distribution of the sample, accurately characterizing its pore properties and elucidating the structural basis for adsorption performance. The BET results (Figure 4) show a typical Type IV isotherm with an H1-type hysteresis loop, characteristic of mesoporous materials. The H1-type loop indicates a relatively narrow pore size distribution dominated by cylindrical interparticle pores, which facilitates rapid dye diffusion and adsorption. The sample has a specific surface area of $60.04 \text{ m}^2/\text{g}$, a total pore volume of $0.23 \text{ cm}^3/\text{g}$, and an average pore diameter of 7.5 nm , with pores predominantly concentrated in the $2\text{--}10 \text{ nm}$ range. The unimodal pore size distribution curve shows no distinct micropore or macropore peaks, demonstrating good pore structure uniformity.

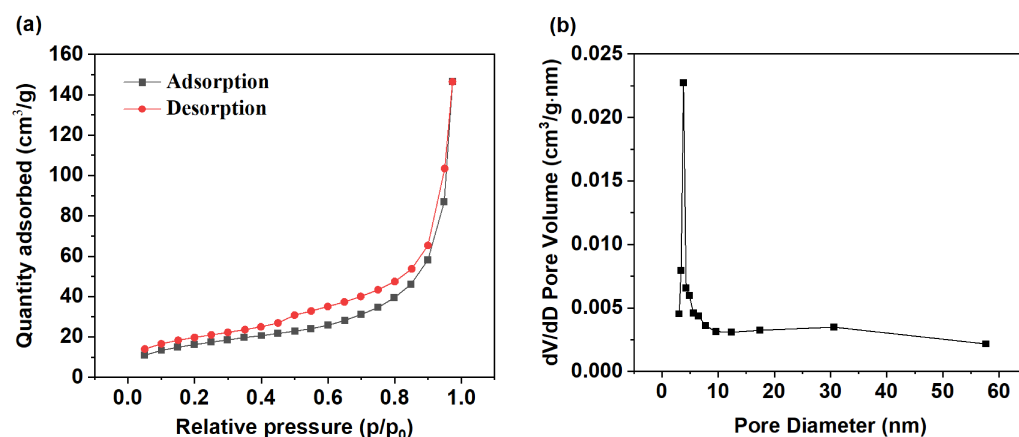


Figure 4. BET specific surface area analysis: (a) adsorption-desorption isotherm; (b) BJH pore size distribution.

Compared with literature data on black liquor-derived silica, the pore parameters of this sample fall within the reasonable range of 50–80 m²/g specific surface area and 0.15–0.30 cm³/g total pore volume reported for similar materials [22,23], providing a solid structural foundation for adsorption applications. Specifically, the 60.04 m²/g surface area provides accessible adsorption sites, and the 2–10 nm mesopores are expected to facilitate the diffusion of methylene blue to the internal surface of the adsorbent [24,25]. The pore volume of 0.23 cm³/g indicates that the material possesses sufficient mesoporous space for adsorption. However, because N₂ adsorption-desorption analysis after methylene blue adsorption was not performed, the present BET data do not directly demonstrate pore filling by methylene blue. The porous structure forms through three key mechanisms: initial pores from Ca²⁺ removal during decalcification, additional pores from soluble impurity washing, and further pore expansion from organic residue decomposition during 650 °C calcination, with interparticle voids from mild silica agglomeration also contributing to mesoporosity [21]. Calcination also enhances structural stability to prevent pore collapse during subsequent adsorption processes.

Notably, no significant micropores are observed because amorphous black liquor-derived silica forms pores via particle packing and impurity removal rather than crystalline lattice pores, differing fundamentally from crystalline silicon materials [26]. The absence of macropores indicates dense particle packing without excessive dispersion, improving mechanical stability and avoiding separation difficulties in practical applications. The mesoporous structure may facilitate methylene blue diffusion and provide accessible space for adsorption.

3.4. Analysis of Influencing Factors and Mechanism of Adsorption Performance

Methylene blue (MB) is a cationic thiazine dye and exists predominantly in cationic form under typical aqueous conditions. Therefore, electrostatic interactions between MB and the silica-based adsorbent are expected to depend strongly on the pH-dependent surface charge of the adsorbent [27]. Using methylene blue as the target pollutant, this study systematically investigated the effects of adsorbent dosage, initial methylene blue concentration, solution pH, and reaction temperature on adsorption performance, as shown in Figure 5a–d. The core control mechanisms of the adsorption process combined with the structural characteristics obtained from previous characterizations were therefore revealed.

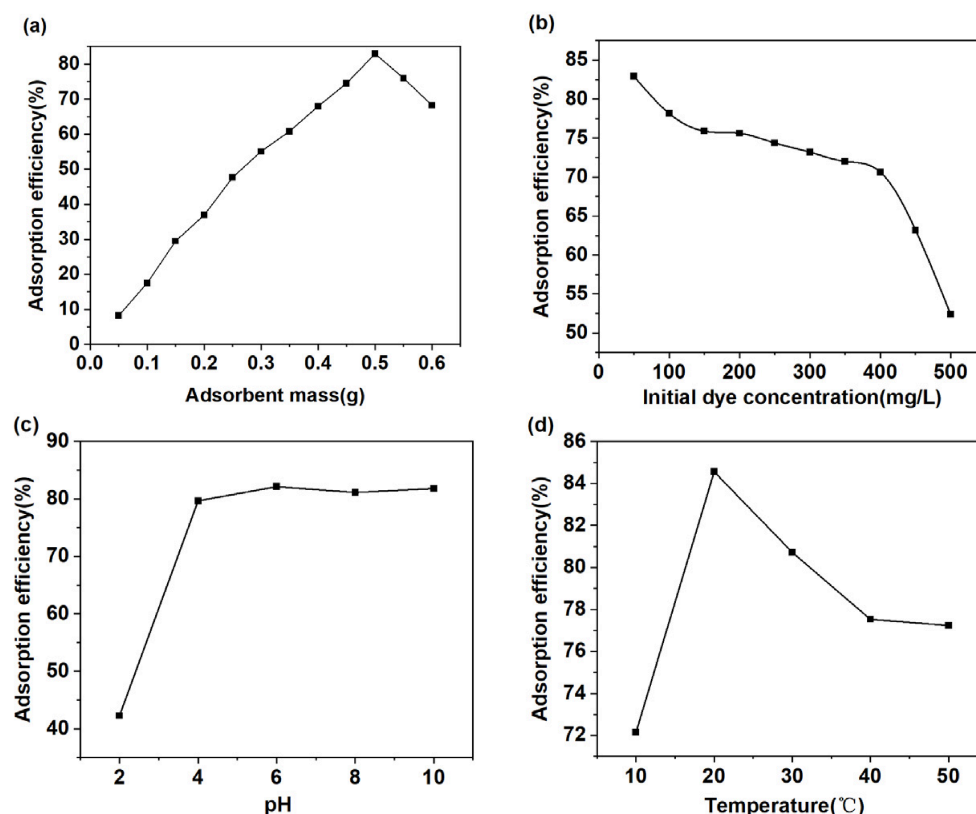


Figure 5. Effects of (a) adsorbent dosage, (b) initial methylene blue concentration, (c) pH, and (d) temperature on adsorption efficiency.

Adsorbent dosage is a key parameter affecting treatment efficiency and cost, which directly determines the total number of active sites. The results showed that the removal rate increased linearly from 8.2% to 82.94% as dosage increased from 0.05 g to 0.5 g, but decreased to 68.24% at 0.6 g. Because no replicate tests or error bars were provided for the 0.4–0.7 g dosage range, this decline should be interpreted cautiously. A possible explanation is that a higher solids loading may promote particle aggregation, reduce effective mixing, and increase external mass-transfer limitations. Therefore, 0.5 g is reported here as the best dosage within the tested range, while the reproducibility of the decrease at 0.6 g remains to be verified [28]. The dosage of 0.5 g was selected as the optimal condition in this study because it achieved a removal efficiency higher than 80% under the tested conditions [29,30]. Notably, a minimum effective dosage threshold exists: below 0.05 g, particle agglomeration caused by hydrophobic interactions significantly reduces exposed active sites [31].

Initial methylene blue concentration reflects wastewater pollution degree. The removal rate decreased from 82.94% to 52.37% as concentration increased from 50 mg/L to 500 mg/L, consistent with equilibrium diffusion theory. At low concentrations, sufficient active sites and large concentration gradients ensure high removal efficiency; at medium concentrations, active sites are gradually occupied and diffusion paths are extended; at high concentrations, adsorption reaches saturation, and pore blockage by dye aggregates further reduces efficiency [32]. This adsorbent is suitable for treating low-to-medium concentration methylene blue wastewater, and multi-stage adsorption can be used for high-concentration wastewater.

Solution pH significantly affects adsorption by altering the surface charge of the adsorbent. The low removal efficiency at pH 2 is consistent with the low point of zero charge/isoelectric point of silica, which is commonly reported to be around pH 2.0. Near this pH, the silica surface is weakly charged, and electrostatic attraction toward cationic

methylene blue is limited. At pH values above this range, deprotonation of surface silanol groups generates a more negatively charged surface, thereby favoring the adsorption of cationic MB through electrostatic attraction and hydrogen bonding. This explains the marked increase in removal efficiency from pH 2 to pH 4 and the relatively stable adsorption behavior at pH 4–10 [17,33–35].

Reaction temperature affects adsorption thermodynamics and kinetics. The removal rate increased from 72.14% to 84.56% as temperature rose from 10 °C to 20 °C, then decreased to 77.24% at 50 °C, indicating an exothermic physical adsorption process [36]. At low temperatures, increased temperature enhances dye diffusion; at high temperatures, desorption dominates and Si-OH active sites are partially dehydrated [37]. The optimal temperature of 20 °C provides significant energy-saving advantages compared to modified nano-SiO₂ that requires 30 °C for optimal performance.

3.5. Adsorption Model

To quantitatively characterize the maximum adsorption capacity of black liquor-derived silica for methylene blue, linear and nonlinear Langmuir models, Freundlich, Temkin, Dubinin–Radushkevich (D–R), and Redlich–Peterson (R–P) models were employed for fitting analysis at 20 °C and pH = 7. The fitting parameters are presented in Table 3, and the fitting curves are shown in Figure 6.

Table 3. Fitting constant of adsorption model.

Model	Parameter	Value
Langmuir (Linear)	Q_m (mg/g)	840.3361
	K_L (L/mg)	0.0125
	R^2	0.9956
Langmuir (Nonlinear)	Q_m (mg/g)	960.2990
	K_L (L/mg)	0.0104
	R^2	0.9875
Freundlich	K_F (L/mg) $1/n$ (mg/g)	42.1752
	$1/n$	0.5193
	R^2	0.9435
Temkin	B (mg/g)	204.0960
	K_T (L/mg)	0.1113
	R^2	0.9574
D–R	Q_m (mg/g)	426.0347
	β (mol ² /J ²)	-
	E (kJ/mol)	0.1447
R–P	K_R (L/g)	9.9371
	a_R (L/mg) β	0.0103
	β	1.0000
	R^2	0.9889

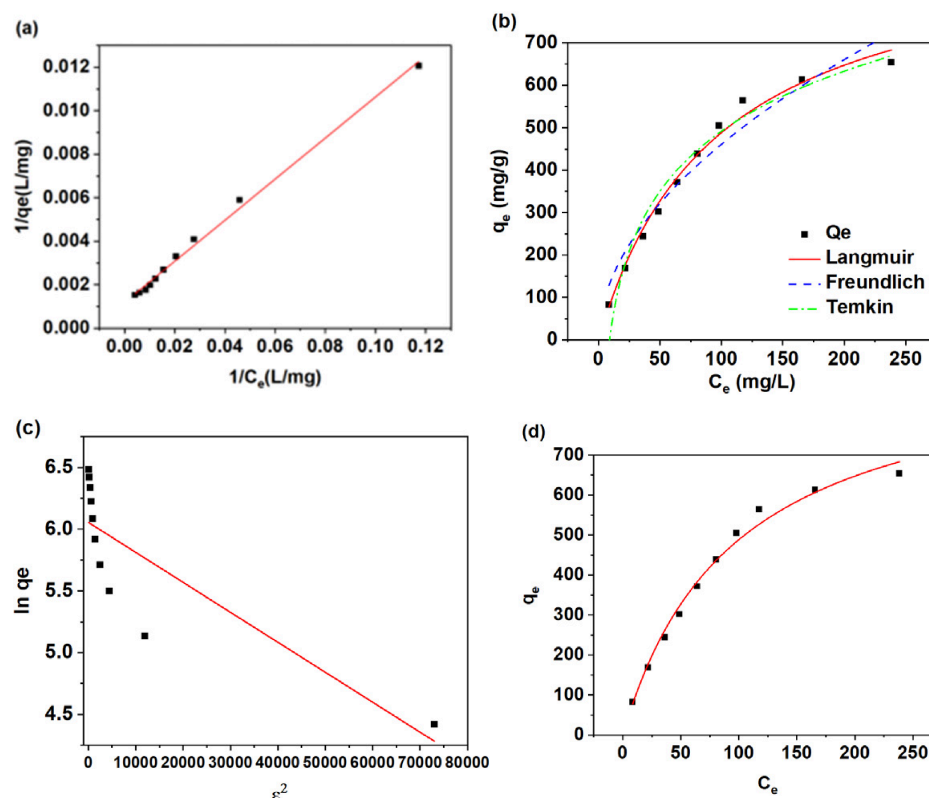


Figure 6. Adsorption model fitting diagrams: (a) Langmuir linear fitting diagram; (b) Langmuir nonlinear, Freundlich, Temkin fitting diagram; (c) fitting diagram of Dubinin–Radushkevich (D–R) model; (d) Redlich–Peterson (R–P) model fitting diagram.

Both linear and nonlinear Langmuir equations described the adsorption data reasonably well, but they yielded different fitted q_m values. The linear model gave an apparent q_m of 840.3 mg/g, whereas the nonlinear model gave a higher q_m of 960.3 mg/g, indicating that the fitted capacity is sensitive to the fitting method. Considering the relatively modest BET surface area of 60.04 m²/g, these q_m values should not be interpreted as physically realizable ideal monolayer coverages on the adsorbent surface [38,39]. In the present system, the Langmuir equation is therefore used as an empirical fitting equation over the studied concentration range rather than as direct evidence of a true monolayer adsorption mechanism.

A more cautious interpretation is that methylene blue uptake in this silica-based material mainly involves electrostatic attraction to negatively charged silica surfaces together with adsorption on accessible external and internal surfaces of the adsorbent. The mesoporous structure may facilitate mass transfer and provide adsorption space. Possible contributions from pore filling by methylene blue or dye–dye aggregation/stacking under confined pore conditions cannot be excluded [40,41], but these effects were not directly demonstrated in the present study because post-adsorption N₂ adsorption–desorption analysis and direct spectroscopic evidence were not available. Residual Ca-containing sites may also influence the local surface chemistry and adsorption behavior. Therefore, the comparatively high fitted q_m more likely reflects the overall uptake behavior of this mesoporous system than a simple one-site-one-molecule monolayer mechanism. The Freundlich, Temkin, D–R, and R–P models were also examined to provide complementary information on adsorption heterogeneity and interaction strength. Because the β value of the R–P model approached 1, the adsorption data may still be described as Langmuir-type in an empirical fitting sense within the tested concentration range [42,43]. It should also be noted that the present mechanistic discussion is based on indirect evidence from adsorption

behavior, pore structure, and silica surface chemistry, rather than direct post-adsorption structural characterization.

Compared with previously reported silica-based adsorbents (Table 4), the present material exhibited a relatively modest BET surface area but a comparatively high Langmuir-fitted q_m . This again indicates that the fitted q_m in this system should not be interpreted as a true ideal monolayer capacity determined only by BET surface area. Instead, the comparatively high fitted q_m likely reflects the combined contribution of accessible adsorption sites, mesoporous transport pathways, and the surface chemistry of the silica-based material. Possible contributions from pore filling, dye aggregation/stacking, and residual Ca-containing sites cannot be excluded, but they were not directly demonstrated in this study. Similar behavior has been reported for mesoporous silica-based adsorbents, in which pore accessibility and surface functional groups play important roles in dye uptake [18,19,41].

Table 4. Performance comparison of different kinds of silica as methylene blue adsorbent.

Adsorbent	Parameter					Ref.
	Si Source	S BET (m ² /g)	Vp (cm ³ ·g ^{−1})	Dp (nm)	Q _m (mg/g)	
BL-SiO ₂ /CaSiO ₃	Bamboo BL	60.04	0.23	7.52	840.34	This work
LT-SiO ₂	TEOS	276.00	-	2–25	516.92	[44]
m-SiO ₂	TEOS	-	-	-	17.73	[45]
Gel-SiO ₂	TEOS	510.00	0.72	6.00	168.00	[19]
Sago-g-SiO ₂	Rice husk	227.74	-	-	10.31	[46]
MW-RH-SiO ₂	Rice husk	84.56	-	-	679.92	[47]

4. Conclusions

In this study, a silica-based adsorbent was successfully prepared from bamboo pulping black liquor through calcium hydroxide precipitation, acid leaching, washing, drying, and calcination. The recovered product was not completely pure SiO₂, but a black-liquor-derived silica-based material mainly composed of amorphous SiO₂ with a small amount of residual CaSiO₃. Based on the combined interpretation of ICP-OES and XRD, the product was semi-quantitatively estimated to contain approximately 64.6 wt.% total SiO₂ and 14.7 wt.% total CaSiO₃, and the estimated SiO₂ yield was about 4.6 wt.% based on dry black liquor solids.

The adsorbent exhibited a mesoporous structure with a specific surface area of 60.04 m²/g, a pore volume of 0.23 cm³/g, and an average pore diameter of 7.5 nm. The pores were mainly distributed in the range of 2–10 nm, which was favorable for methylene blue diffusion and adsorption. Under the selected adsorption conditions of 0.5 g adsorbent, 50 mg/L methylene blue, pH 7, and 20 °C, the removal efficiency reached 82.94%. The adsorption data were best fitted by the Langmuir equation within the studied concentration range, and the linear Langmuir fitting gave an apparent capacity parameter of 840.3 mg/g. However, this fitted value should not be interpreted as a true ideal monolayer capacity. Instead, the adsorption behavior is more reasonably attributed to surface adsorption on the silica-based material together with the facilitation of mass transfer by the mesoporous structure. Possible contributions from pore filling, dye aggregation/association in confined pores, and residual CaSiO₃-related surface effects cannot be excluded, but they were not directly demonstrated in this study. Accordingly, these factors should be regarded as tentative interpretations rather than confirmed adsorption mechanisms.

This work provides a feasible approach for the resource utilization of silicon-containing bamboo pulping black liquor and its conversion into a waste-derived adsorbent for dye

removal. Further studies on adsorption kinetics, regeneration performance, continuous adsorption, and real dye wastewater systems are still needed to evaluate its practical application potential.

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