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Synthesis of mesoporous SiO₂ derived from coal fly ash for methylene blue adsorption

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Abstract

Porous silica has been widely employed as an adsorbent owing to its high surface area, tunable pore structure, and abundant surface silanol groups. Owing to its abundant silicon content, coal fly ash (CFA) can serve as a low-cost silicon source for the preparation of porous silica materials, while enabling the upcycling of CFA. Therefore, this study proposed a synthesis strategy for a porous silica-rich adsorbent using CFA after a phase separation-acid leaching treatment as the silica source. The experimental results indicate that mesoporous silica synthesized under the optimal conditions (a Si/CTAB/NaOH molar ratio of 1:0.65:0.6, a crystallization temperature of 80 °C and a crystallization time of 1.5 h) exhibits a maximum specific surface area of 774.42 m²·g⁻¹, an average pore size of 7.27 nm, and a pore volume of 1.41 cm³·g⁻¹. Adsorption tests for methylene blue (MB) further verify that the synthesized mesoporous silica delivers a high MB adsorption capacity of 186.81 mg·g⁻¹ at pH 11 and 298.15 K, with an initial MB concentration of 200 mg·L⁻¹ and an adsorbent dosage of 1 g·L⁻¹. This study provided a potential pathway for the resource utilization of CFA and carries the typical significance of waste-to-treat-waste strategy.

Keywords: Mesoporous SiO₂; Coal fly ash; Methylene blue; Adsorption

1. Introduction

China is the largest energy consumer in the world, and the current energy consumption structure in China remains dominated by fossil fuels such as coal, oil, and

natural gas. Owing to abundant coal resources and relatively low cost, coal still accounts for more than half of total energy consumption in China^[1]. In 2020, coal consumption accounted for 56.80% of total energy consumption^[2]. According to the China Energy Statistical Yearbook, total coal consumption in China increased from 3.998 billion tons in 2015 to 4.019 billion tons in 2019, while the share of coal consumed by the production and supply of electric power, heat, gas and water increased from 41.50% to 50.60%^[3]. CFA is a solid by-product generated from coal combustion in thermal power plants and mainly consists of inorganic components such as silica (SiO_2) and alumina (Al_2O_3), along with small amounts of metal compounds such as iron oxide (Fe_2O_3) and calcium oxide (CaO). Its silica component can serve as an important secondary resource for the preparation of silicon-based functional materials. Recently, the high-value utilization of CFA has gradually expanded from traditional low-value-added applications, such as building fillers^[4] and road base materials^[5], to fields including silicon-based porous materials^[6], zeolites^[7], adsorbents^[8], and catalysts^[9].

The high SiO_2 content of CFA gave it considerable potential for the preparation of nanoporous materials, and materials derived from CFA with high specific surface area and large pore size could serve as supports and substrates for surface functionalization in applications involving waste-gas and wastewater adsorption and catalysis^[10]. Kumar obtained an aluminosilicate-containing supernatant from CFA via alkali fusion and used it to synthesize MCM-41 and SBA-15^[11]. The products varied under different hydrothermal conditions, and the synthesized MCM-41 and SBA-15 exhibited specific

surface areas of 842 and 483 $\text{m}^2\cdot\text{g}^{-1}$, respectively, with corresponding pore volumes of 0.75 and 0.53 $\text{cm}^3\cdot\text{g}^{-1}$. Compared with MCM-41 and SBA-15 prepared by conventional methods, these materials showed relatively lower specific surface areas and pore volumes, and pH adjustment during gel formation had a significant influence on the pore structure of mesoporous SiO_2 . Dhokte et al. synthesized MCM-41 with a particle size of 24 nm from CFA and applied it as a catalyst for organic transformation, where the product exhibited high catalytic activity in the Mannich reaction and afforded an ethanol yield of up to 90%^[12]. Zhou et al. synthesized a mesoporous material from fly ash in a one-step process and obtained spherical Al-containing mesoporous SiO_2 with a specific surface area of 525 $\text{m}^2\cdot\text{g}^{-1}$ and a pore volume of 0.71 $\text{cm}^3\cdot\text{g}^{-1}$ at an ethyl acetate dosage of 10 mL, and this material achieved a methylene blue adsorption capacity of 277 $\text{mg}\cdot\text{g}^{-1}$ ^[13].

In our previous work, we developed a phase separation-acid leaching method to purify silica from CFA, achieving a purity of over 98%^[14]. In this study, the resulting silica product was further converted into a mesoporous silica-rich adsorbent by a hydrothermal method to enhance its added value. The effects of the molar ratio of acid silica product/CTAB/NaOH, crystallization temperature, crystallization time, and ethyl acetate dosage on the pore-structure properties of the prepared materials were investigated through single-factor experiments. Using methylene blue as the adsorbate, the adsorption performance of the prepared mesoporous silica-rich materials was evaluated, and the effects of pH, temperature, initial methylene blue concentration, and adsorbent dosage on adsorption were examined through single-factor experiments,

followed by analyses of adsorption isotherms, adsorption kinetics, and adsorption thermodynamics.

2. Methodologies

2.1 Materials

The raw materials and chemical reagents used in the experiment included the silica-rich powder sourced from the phase separation-acid leaching treatment of CFA, NaOH, ethyl acetate (EA), cetyltrimethylammonium bromide (CTAB), HCl, and methylene blue. Details of the phase separation-acid leaching treatment of CFA could be found in our previous study. After washing and drying, the obtained high-silica powder appeared white and lightweight. As shown in Figure 1a-b, the powder was composed primarily of SiO₂, while it consisted of irregular block-like particles with non-uniform sizes and diameters ranging from 1 to 10 μm. SiO₂ existed in both amorphous and crystalline quartz forms, which is similar to the occurrence state of SiO₂ in fly ash. Besides, the high-silica product had a specific surface area of 364.21 m²·g⁻¹, an average pore diameter of 4.06 nm, and a pore volume of 0.24 cm³·g⁻¹, demonstrating its potential as an adsorbent material.

2.2 Experiment methods

2.2.1 Preparation method of the mesoporous high-silica adsorbent

A certain amount of CTAB and sodium hydroxide was dissolved in deionized water, followed by the addition of the silica-rich powder. The mixture was stirred uniformly

at 30 °C until CTAB was completely dissolved, and the solution was then transferred to a autoclave and subsequently subjected to heating at 125°C for 1 h in an oven. After cooling to room temperature, the mixture was centrifuged to remove impurities, yielding silica extraction solutions. Deionized water was added to the extraction solution, and after thorough stirring, ethyl acetate was rapidly introduced followed by vigorous stirring for 30 s. The precipitated white product and the solution were transferred to a hydrothermal reactor and reacted at a specified temperature. The precursor mesoporous silica was obtained after washing the resulting solid product. Furthermore, the precursor was calcined at 550 °C for 5 h to remove the template, producing the mesoporous high-silica adsorbent material.

2.2.2 Methylene blue adsorption experiments

The effects of pH, temperature, initial concentration of methylene blue solution, and adsorbent dosage on the adsorption performance of mesoporous silica toward methylene blue were investigated. First, different initial concentrations methylene blue solutions (100~800 mg·L⁻¹) were prepared, and pH was adjusted to 7~11. A certain amount of the mesoporous high-silica adsorbent (0.6~1.2 g·L⁻¹) was added to the solution for adsorption at different temperatures (298.15~328.15 K). After adsorption equilibrium was reached, the adsorption solution was filtered through a 0.45 µm syringe filter membrane, and the methylene blue concentration of the filtrate was measured using a UV-Vis spectrophotometer (Details of the MB standard calibration curve are provided in the Text S1). The removal efficiency (R) and adsorption capacity (q) of

mesoporous high-silica adsorbent were further calculated using the following equations to evaluate the adsorption performance.

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

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

where C_0 and C_t are the initial concentration of the methylene blue solution and the concentration at time t . V and m represent the volume of the adsorbate solution and the mass of the high-silica adsorbent. As for the adsorption isotherms, a total of 0.05 g of adsorbent was added to 50 mL of methylene blue solutions with different initial concentrations (100-800 mg·L⁻¹), at 298.15, 308.15, 318.15, and 328.15 K, respectively, while the pH was adjusted to 11. To investigate the adsorption kinetics, 0.05 g of adsorbent was separately dispersed in 50 mL of methylene blue solutions with different initial concentrations (100-300 mg·L⁻¹) at 298.15 K. During the adsorption process, samples were collected at fixed time intervals and the corresponding methylene blue concentration was determined.

2.3 Analysis method

Adsorption isotherm models are used to describe the relationship between the adsorption capacity and the equilibrium concentration of the adsorbate in solution at adsorption equilibrium under a given temperature. In this study, the experimental data were fitted and analyzed using the Langmuir (Equation 3) and Freundlich (Equation 4) adsorption isotherm models

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n_F} \quad (4)$$

Here, q_e and q_m are the equilibrium and saturated adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), respectively. K_L and K_F represent the constant value for Langmuir and Freundlich isotherm models, respectively. C_e is the equilibrium concentration of methylene blue solution ($\text{mg}\cdot\text{L}^{-1}$). Furthermore, n_F is a dimensionless constant describing the heterogeneity of the adsorbent or the adsorption intensity.

The pseudo-first-order kinetic model, pseudo-second-order kinetic model, and Elovich kinetic model were employed to investigate the adsorption rate. In term of the pseudo-first-order kinetic model, the adsorption rate is linearly related to the adsorbate concentration and that the adsorption process is controlled by the diffusion step. The equation was as following.

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (5)$$

where, q_t and q_e are the adsorption capacity at time t and adsorption equilibrium ($\text{mg}\cdot\text{g}^{-1}$), respectively, while k_1 is the first-order adsorption rate constant (min^{-1}). As for pseudo-second-order kinetic model (equation 6), the adsorption rate and the driving force of adsorption are determined by the adsorbate concentration and the number of active sites on the adsorbent.

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

where, k_2 is the second-order adsorption rate constant (min^{-1}). The Elovich kinetic model is an empirical equation that describes heterogeneous chemisorption with two

different activation energy values.

$$q_t = \frac{\ln(1 + \alpha\beta t)}{\beta} \quad (7)$$

thereinto, α is the initial adsorption rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) and β is the desorption constant ($\text{mg} \cdot \text{g}^{-1}$), which is affected by the extent to which the surface is covered by solute molecules and the activation energy of chemisorption. The equations used to calculate the changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) during adsorption were as follows.

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

$$K_c = \frac{q_e}{C_e} \quad (10)$$

where, K_c is the thermodynamic equilibrium constant and R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), while T is the absolute temperature in Kelvin (K).

3. Results and discussion

3.1 Effect of synthesis conditions on the pore structure of mesoporous SiO_2 adsorbents

Mesoporous SiO_2 with different SiO_2/CTAB molar ratios were prepared to investigate its effect on the pore structure of mesoporous SiO_2 . As shown in Figure 1a, when the SiO_2/CTAB molar ratio was 0.5:0.65 or 1:0.65, the isotherms exhibited H3-type hysteresis loops, indicating the presence of slit-like plate pores, cracks, and wedge-shaped structures, as well as a layered material structure with a relatively disordered

pore distribution. At a SiO₂/CTAB molar ratio of 2.0:0.65, the N₂ adsorption-desorption isotherm displayed a type IV isotherm accompanied by an H1-type hysteresis loop, which was caused by capillary condensation. This indicated that the synthesized adsorbent possessed a typical mesoporous structure with a relatively narrow pore size distribution and more uniform pore dimensions. The adsorption capacity increased rapidly when p/p_0 ranged from 0.7 to 1.0, indicating that the sample had relatively large pores, which was consistent with the corresponding pore size distribution curve. As shown in Figure 1b, a SiO₂/CTAB molar ratio of 2:0.65 gave the highest specific surface area, reaching 437.02 m²·g⁻¹, together with the largest pore volume of 1.34 cm³·g⁻¹. With increasing SiO₂/CTAB ratio, the specific surface area showed an upward trend, whereas the pore diameter and pore volume first decreased and then increased. An increase in the SiO₂/CTAB ratio favored the formation of mesoporous SiO₂ with higher specific surface area, whereas an excessively high relative CTAB content tended to produce unstable layered meso-structures^[15].

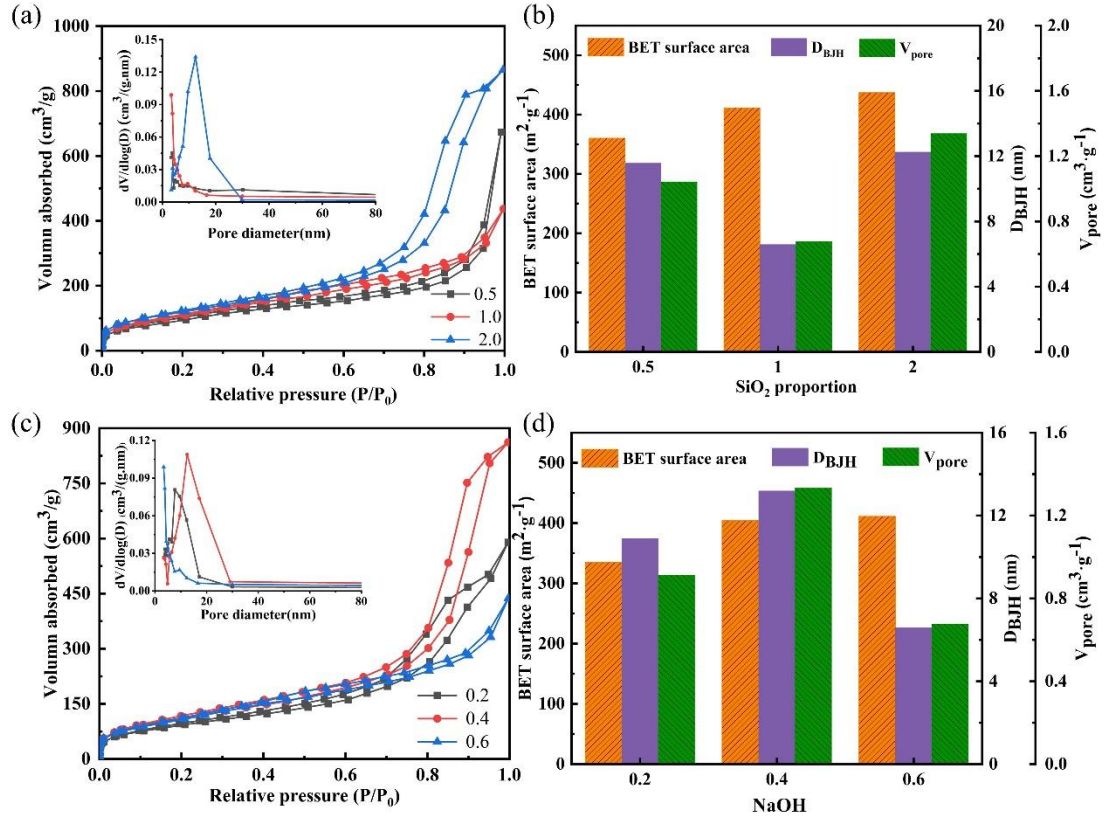


Figure 1 N₂ adsorption-desorption isotherms (a, c) and corresponding pore structure properties (b, d) of mesoporous silica with different Si/CTAB (a-b) and concentrations of NaOH(c-d)

Mesoporous SiO₂ prepared with different NaOH molar ratios were used to investigate the effect of NaOH dosage on the pore structure of mesoporous adsorbents. With increasing NaOH content, the maximum adsorption capacity in the adsorption-desorption isotherms first increased and then decreased, indicating that the pore volume of the resulting mesoporous SiO₂ initially increased and then declined (Figure 1c). A similar trend was also observed in the pore-size distribution. The three adsorbent materials exhibited specific surface areas of 335.02, 404.38, and 411.12 m²·g⁻¹, respectively, showing a gradual increase, while the corresponding pore volumes were

0.91, 1.33, and $0.68 \text{ cm}^3 \cdot \text{g}^{-1}$ and the average pore diameters were 10.89, 13.19, and 6.58 nm, respectively (Figure 1d). These results suggested that increasing the NaOH content favored the formation of mesoporous SiO_2 with a higher specific surface area. An appropriate Na^+ concentration was beneficial for enlarging the pore volume, although it also leads to a broader pore size distribution. At higher Na^+ concentrations, electrostatic repulsion between like charges hindered mesopore formation, while an increased NaOH proportion raised the solution pH and promoted the dissolution and reprecipitation of Si-O-Si bonds, thereby reducing the stability of SiO_2 during aging and ultimately causing mesopore collapse during subsequent heat treatment or drying, which affected the pore volume and pore size of the material^[11].

Different amounts of ethyl acetate were introduced during the synthesis process to investigate their effect on the pore structure of mesoporous SiO_2 . The adsorption isotherms of the samples were characteristic type IV isotherms and exhibited both H2- and H3-type hysteresis loops (Figure 2a), suggesting that increasing the ethyl acetate content might transform the mesoporous structure of the material from an ink-bottle-type pore system to a more irregular structure. As shown in Figure 2b, the specific surface area of mesoporous SiO_2 first increased and then decreased with increasing ethyl acetate content, reaching a maximum of $461.70 \text{ m}^2 \cdot \text{g}^{-1}$ at 3 mL of ethyl acetate. Under static conditions, ethyl acetate enabled slow and homogeneous acidification, which favored the formation of a bimodal pore structure during the self-assembly of SiO_2 ^[16]. The hydrolysis of ethyl acetate provided protons to promote SiO_2 condensation and regulated its polycondensation rate. As the pH decreased, the hydrolysis rate of the

silica source was altered, and the micelles formed by CTAB were coated with continuously polymerizing silicate anions, leading to the development of the pore structure. Therefore, the addition of ethyl acetate reduced the meso-structural order and specific surface area, altered the mode of mesopore formation, and promoted the generation of a bimodal structure with a broader distribution of pore size. Previous study stated that the addition of ethyl acetate affected the morphology of mesoporous SiO₂, enabling the formation of worm-like, spherical, and popcorn-like mesoporous SiO₂^[17].

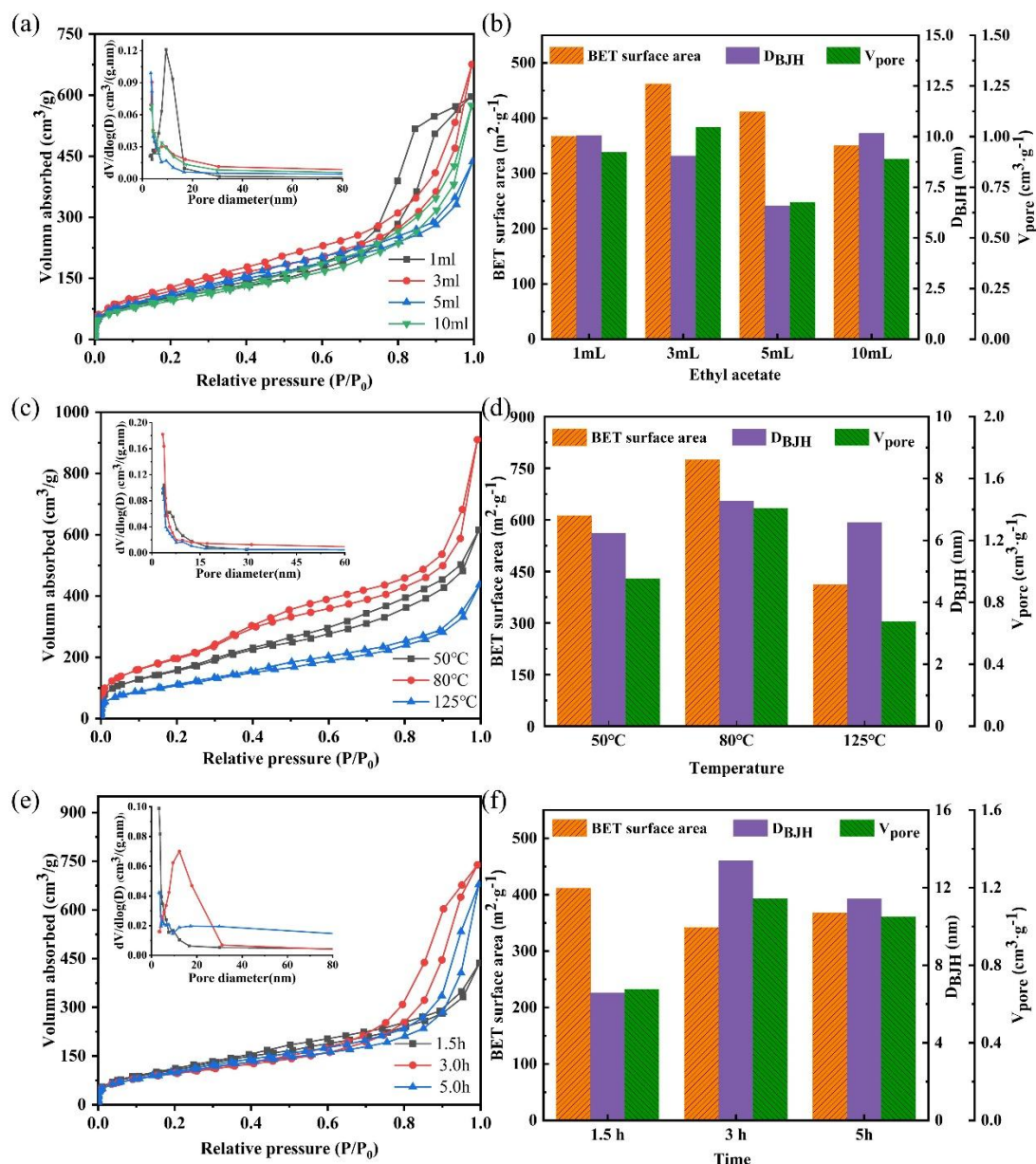


Figure 2 N₂ adsorption-desorption isotherms (a, c, e) and corresponding pore structure properties (b, d, f) of mesoporous silica with different amounts of ethyl acetate (a-b), temperatures (c-d) and times (e-f).

Under the synthesis conditions of SiO₂: CTAB: H₂O: ethyl acetate: NaOH=1:0.65:225:3.69:0.6, with a crystallization temperature of 125 °C and a crystallization time of 1.5 h, mesoporous SiO₂ could be efficiently prepared with a

specific surface area of $411.12 \text{ m}^2\cdot\text{g}^{-1}$, a pore volume of $0.68 \text{ cm}^3\cdot\text{g}^{-1}$, and a pore diameter of 6.58 nm. To further increase the specific surface area of mesoporous SiO_2 , the crystallization parameters were optimized by preparing the materials at crystallization temperatures of 50, 80, and 125°C and crystallization times of 1.5, 3, and 5 h. The N_2 adsorption-desorption isotherms of mesoporous silica obtained at different crystallization temperatures were all type IV isotherms accompanied by H3-type hysteresis loops (Figure 2c). With increasing crystallization temperature, the maximum adsorption capacity first increased and then decreased. The specific surface area of mesoporous SiO_2 increased from 611.69 to $774.42 \text{ m}^2\cdot\text{g}^{-1}$ and then dropped sharply to $411.12 \text{ m}^2\cdot\text{g}^{-1}$. The effect of crystallization temperature on pore size was less pronounced, as shown in Figure 2d. The above results indicated that an increase in temperature tended to concentrate the distribution of pore size and markedly enhanced the specific surface area and pore volume. However, excessively high temperatures may interfere with the re-hydrolysis, crosslinking, and homogeneous distribution of the silica species, thereby undermining the stability of the meso-structure and resulting in a pore collapse^[18].

The effect of crystallization time on the properties of pore structure is shown in Figure 2e. The isotherm obtained at a crystallization time of 3 h exhibited a typical type IV adsorption-desorption profile with a distinct hysteresis loop. Extending the crystallization time from 1.5 to 3 h improved both the pore size distribution and the structural ordering of the material, whereas further prolongation to 5 h resulted in a deterioration of the distribution of pore size. The materials prepared with crystallization

times of 1.5, 3, and 5 h exhibited specific surface areas of 411.12, 341.80, and 367.52 $\text{m}^2\cdot\text{g}^{-1}$, respectively. As shown in Figure 2f, increasing the crystallization time from 1.5 to 3 h increased the average pore diameter of mesoporous SiO_2 from 6.58 to 13.38 nm and the pore volume from 0.68 to $1.14 \text{ cm}^3\cdot\text{g}^{-1}$, which indicating that an appropriate extension of crystallization time could effectively promote mesopore formation. With further prolongation of the crystallization time, the pore volume decreased from $1.14 \text{ cm}^3\cdot\text{g}^{-1}$ at 3 h to $1.049 \text{ cm}^3\cdot\text{g}^{-1}$, and the average pore diameter also declined from 13.38 to 11.85 nm. This may be attributed to the fact that prolonged crystallization at 125°C could disturb the charge-matching equilibrium and cooperative assembly between silicate species and CTAB micelles. Such changes may weaken the surfactant–silicate mesophase, leading to partial loss of the internal liquid-crystalline ordering and deterioration of the mesoporous structure^[19].

Based on the above analysis, the mesoporous silica prepared at a Si/CTAB/NaOH molar ratio of 1:0.65:0.6, with 5 mL of ethyl acetate, a crystallization temperature of 80°C , and a crystallization time of 1.5 h exhibited the highest specific surface area of $774.42 \text{ m}^2\cdot\text{g}^{-1}$, together with an average pore diameter of 7.27 nm and a pore volume of $1.41 \text{ cm}^3\cdot\text{g}^{-1}$. In addition, this material was subjected to further structural characterization, which was presented in Figure 3.

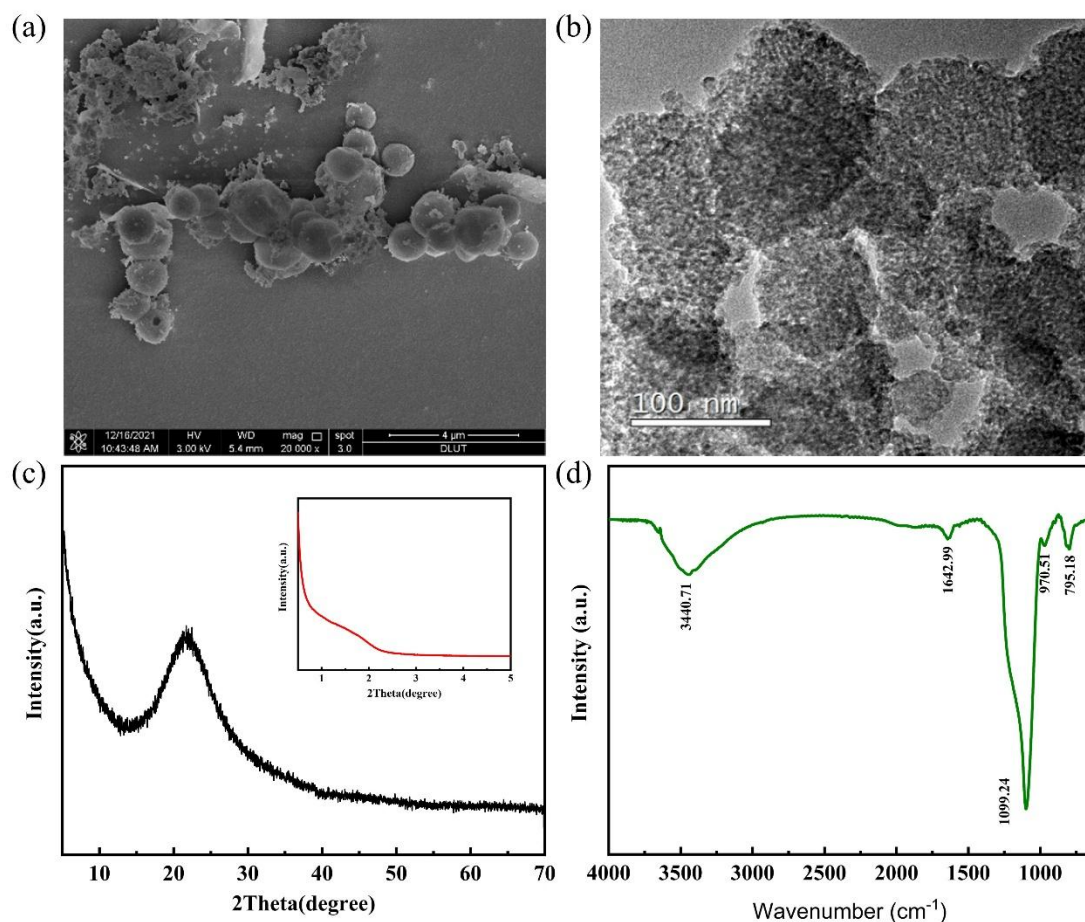


Figure 3 SEM (a), TEM (b), XRD (c), and FTIR spectrum (d) of mesoporous SiO₂

The microstructure and morphology of the prepared mesoporous SiO₂ are shown in Figure 3a-b. The mesoporous SiO₂ exhibited a spherical morphology, with particle diameters ranging from 0.5 to 2 μm . TEM observations revealed a honeycomb-like porous structure with local ordered domains. The XRD pattern exhibited a broad diffraction peak at around 22°, indicating the presence of an amorphous phase and confirming that the prepared mesoporous SiO₂ existed predominantly in the form of amorphous silica. Small-angle XRD showed no diffraction peaks in the range of 0.5°-5°, suggesting that the mesoporous structure lacked long-range order. The FTIR spectrum showed that the peak near 795 cm⁻¹ is assigned to the symmetric stretching

vibration of Si-O-Si in the silica tetrahedral framework. The peaks at 970 and around 1099 cm^{-1} were attributed to the vibration of Si-OH groups and the asymmetric stretching vibration of Si-O-Si, respectively. The absorption bands at 1642 and around 3440 cm^{-1} were assigned to the bending vibration of hydroxyl groups and the stretching vibration of water molecules, respectively.

3.2 Adsorption performance of mesoporous SiO_2

The effect of pH on the adsorption performance of MB by the mesoporous SiO_2 adsorbent was investigated at an initial MB concentration of 200 $\text{mg}\cdot\text{L}^{-1}$, an adsorption temperature of 298.15 K, and a mesoporous SiO_2 dosage of 1 $\text{g}\cdot\text{L}^{-1}$ (Figure 4a). As the pH increased from 7 to 11, the adsorption capacities rose to 85.44, 104.20, 144.59, 153.62, and 177.31 $\text{mg}\cdot\text{g}^{-1}$, respectively, showing an overall upward trend. The corresponding MB removal efficiencies were 45.24%, 56.60%, 76.55%, 98.24%, and 99.54%, respectively, also showing a continuous increase. Both the adsorption capacity and removal efficiency reached their maximum values of 177.31 $\text{mg}\cdot\text{g}^{-1}$ and 99.54%, respectively, at pH 11. pH had a pronounced effect on adsorption performance because pH influenced the surface charge of the adsorbent and thus affects the adsorption process. Since MB is a cationic dye with a positively charged surface, the acidic Si-OH groups on the surface of the mesoporous material tended to lose H^+ under alkaline conditions to be negatively charged, thereby providing adsorption sites for MB. As the pH increased, the negative charge density on the adsorbent surface also increased, resulting in a marked enhancement in the adsorption capacity of mesoporous SiO_2 .

toward MB at higher pH value^[20].

The effect of temperature on the adsorption performance of MB by mesoporous SiO₂ was investigated at an initial MB concentration of 200 mg·L⁻¹, pH 11, and a mesoporous SiO₂ dosage of 1 g·L⁻¹(Figure 4b). As the temperature increased from 298.15 to 328.15 K, the adsorption capacities decreased from 186.81 to 129.23 mg·g⁻¹. The corresponding MB removal efficiencies were 98.84%, 99.70%, 75.66%, and 69.95%, respectively, showing an overall downward trend. The highest adsorption capacity and removal efficiency were obtained at 298.15 K, reaching 186.81 mg·g⁻¹ and 98.84%, respectively. Comparison of the adsorption capacities at different temperatures indicated that adsorption decreased with increasing temperature, suggesting that heating adversely affected the adsorption of MB. This might be attributed to the enhanced mobility of the adsorbed MB molecules at elevated temperatures, causing desorption to exceed adsorption and thus lowering the adsorption capacity at higher temperatures^[21].

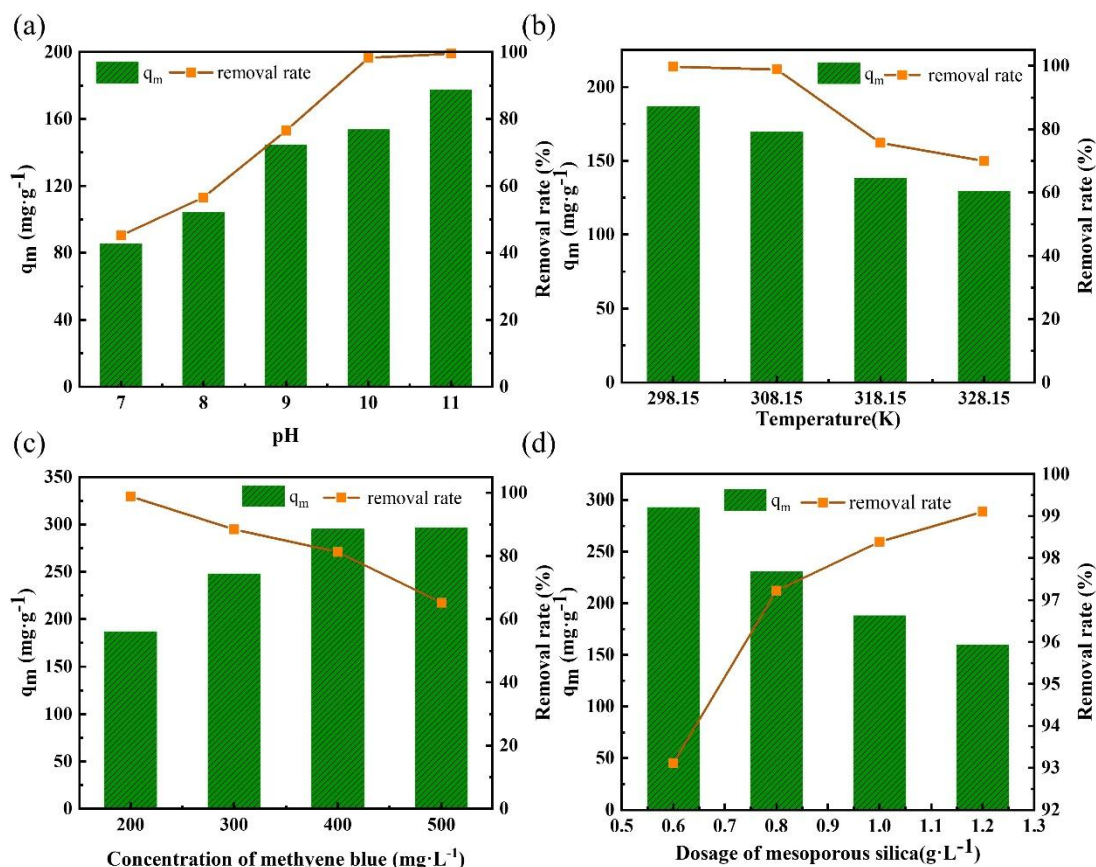


Figure 4 Effect of pH (a), temperatures (b), initial concentration (c), and adsorbent dosage (d) on adsorption properties of MB

The effect of the initial adsorbate concentration on the adsorption performance of MB by mesoporous SiO₂ was investigated at pH 11, 298.15 K, and a mesoporous SiO₂ dosage of 1 g·L⁻¹(Figure 4c). As the initial adsorbate concentration increased from 200 to 500 mg·L⁻¹, the adsorption capacities rose from 186.81 to 296.39 mg·g⁻¹. The corresponding MB removal efficiencies were 98.84%, 88.43%, 81.25%, and 65.21%, respectively, exhibiting an overall decline. The maximum adsorption capacity of 296.39 mg·g⁻¹ was obtained at an initial adsorbate concentration of 500 mg·L⁻¹, whereas the highest removal efficiency of 98.84% was achieved at an initial adsorbate concentration

of 200 mg·L⁻¹. Comparison of the adsorption capacities at different initial adsorbate concentrations indicated that increasing the initial concentration enhanced the adsorption capacity for MB but reduced the removal efficiency. As the concentration increased, the concentration gradient of MB between the mesoporous material and the solution became larger, thereby increasing the mass transfer driving force and promoting adsorption. However, at excessively high initial concentrations, the active sites on the adsorbent surface became insufficient, leaving more adsorbate molecules unabsorbed and thus leading to a lower removal efficiency.

The effect of mesoporous silica dosage on the adsorption of MB was investigated at an initial MB concentration of 200 mg·L⁻¹, pH 11, and 298.15 K (Figure 4d). As the adsorbent dosage increased from 0.6 to 1.2 g·L⁻¹, the adsorption capacities decreased from 292.76 to 159.63 mg·g⁻¹. The corresponding removal efficiencies of MB were 93.12%, 97.22%, 98.34%, and 99.11%, respectively, showing an overall increasing trend. The maximum adsorption capacity, 292.76 mg·g⁻¹, was obtained at an adsorbent dosage of 0.6 g·L⁻¹, whereas the highest removal efficiency, 99.11%, was achieved at 1.2 g·L⁻¹. Comparison of the adsorption capacities under different adsorbent dosages indicated that increasing the dosage reduced the adsorption capacity. This was because a higher adsorbent dosage provided more adsorption sites, thereby increasing the number of MB molecules removed and improving the removal efficiency, while the limited amount of MB in solution restricted the amount adsorbed per unit mass of the material.

To elucidate the distribution of adsorbate molecules between the solution and the

adsorbent surface, as well as the nature of their interactions under adsorption equilibrium, the experimental data for MB adsorption on mesoporous SiO₂ at 298.15, 308.15, 318.25, and 328.15 K were fitted using the Langmuir and Freundlich adsorption isotherm equations, and the results are presented in Figure 5 and Table 1. As shown in Table 1, the Langmuir model gave higher fitting coefficients than the Freundlich model at all four temperatures, indicating that the Langmuir equation provides a better description of MB adsorption on mesoporous SiO₂. According to the assumptions of the Langmuir isotherm model, the surface of mesoporous SiO₂ was homogeneous, the adsorption sites were uniformly distributed, and MB adsorption occurred as monolayer adsorption without intermolecular interactions between MB molecules. As the adsorption temperature increased from 298.15 to 328.15 K, the maximum adsorption capacities ($q_{\max}$) calculated from the Langmuir equation were 831.59, 473.03, 359.33, and 396.91 mg·g⁻¹, respectively, showing an overall decreasing trend. These results indicated that increasing temperature was unfavorable for MB adsorption, suggesting that the adsorption of MB on mesoporous SiO₂ was an exothermic process and was more favorable at lower temperatures, in agreement with the upon results.

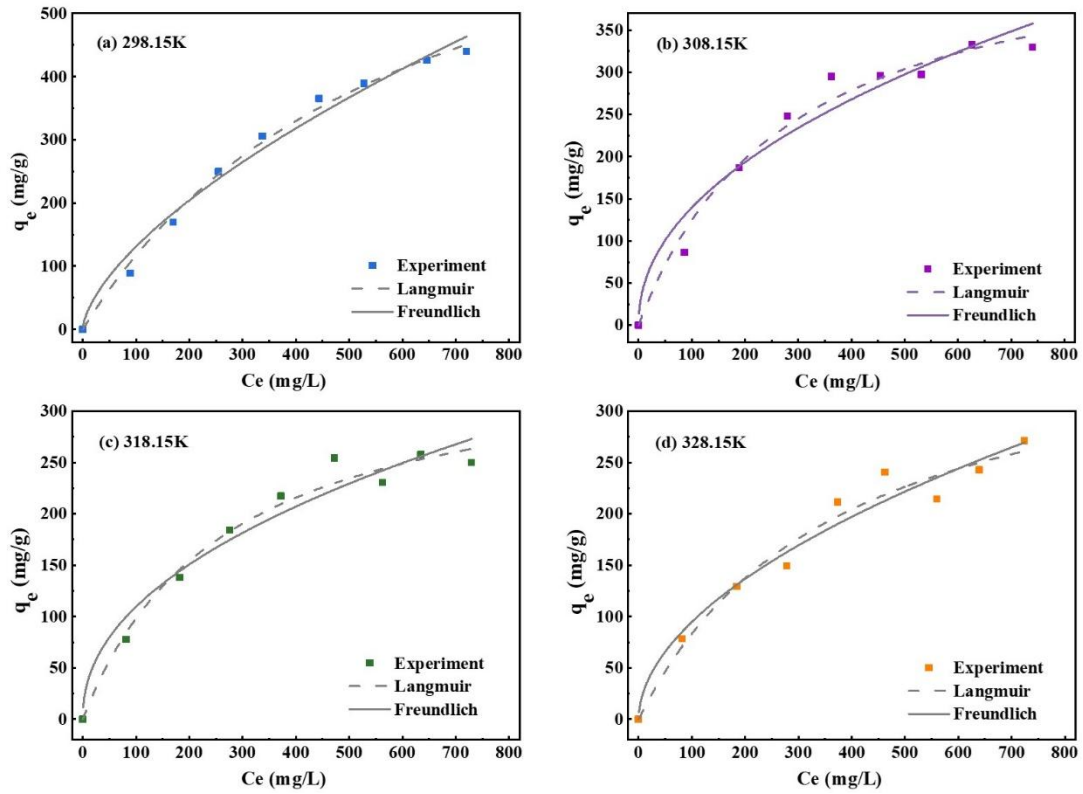


Figure 5 Langmuir and Freundlich plots for the adsorption of MB with different temperatures

Table 1 Langmuir and Freundlich isotherm parameters and correlation coefficients

Model	Parameters	Temperature (K)			
		298.15	308.15	318.15	328.15
Langmuir	$q_{\max}(\text{mg} \cdot \text{g}^{-1})$	831.59	474.03	359.33	396.91
	$K_L(\text{L} \cdot \text{mg}^{-1})$	0.0016	0.0036	0.0038	0.0027
	R^2	0.9947	0.9799	0.9795	0.9685
	$KF(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	6.89	15.98	13.27	8.38
Freundlich	$n(\text{mg} \cdot \text{L}^{-1})$	1.5632	2.1254	2.1805	1.8972
	R^2	0.9669	0.8848	0.8977	0.9251

3.3 Adsorption kinetics and thermodynamic analysis

In this study, the experimental data collected over an adsorption time range of 0-360 min at different initial MB concentrations (100, 200, and 300 mg·L⁻¹) were linearly fitted using the pseudo-first-order, pseudo-second-order, and Elovich kinetic models, and the fitting results are shown in Figure 6 and Table 2.

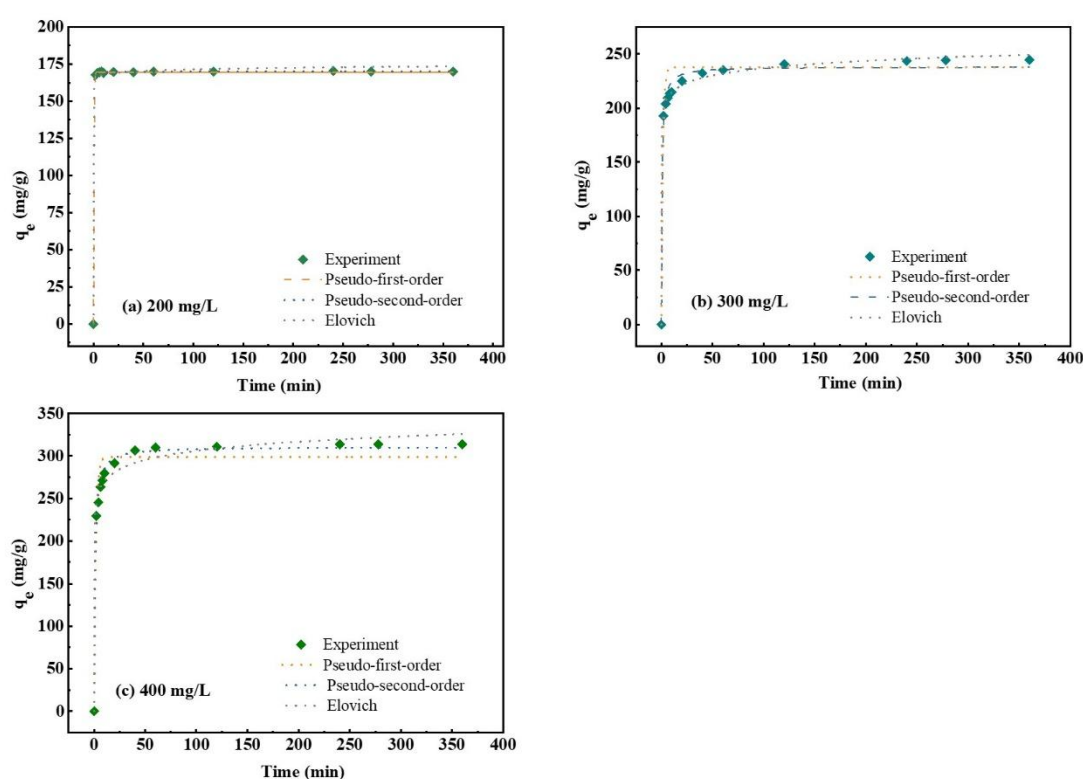


Figure 6 Pseudo-first-order, Pseudo-second-order, Elovich kinetic plots for the adsorption of MB with different concentrations

Table 2 Parameters and correlation coefficients of Pseudo-first-order, Pseudo-second-order and Elovich kinetic

Model	Parameters	Initial MB concentrations (mg·L ⁻¹)
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		200	300	400
Pseudo-first-order	$q_e(\text{mg}\cdot\text{g}^{-1})$	169.68	237.64	298.66
	$K_1(\text{min}^{-1})$	2.2404	0.6807	0.5684
	R^2	0.9999	0.9493	0.9515
Pseudo-second-order	$q_e(\text{mg}\cdot\text{g}^{-1})$	169.94	238.09	310.71
	$K_2(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	0.245	0.0068	0.00358
	R^2	0.9999	0.9892	0.9932
Elovich	$\alpha(\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1})$	3.8884E44	3.20726E9	6.47875E7
	$\beta(\text{mg}\cdot\text{g}^{-1})$	0.6231	0.1023	0.0649
	R^2	0.9976	0.9975	0.9847
	Q_e	169.74	244.69	313.60

408

409 As shown in Table 2, all three models provided a good fit for the adsorption process
410 of MB on mesoporous SiO₂ at the three different initial MB concentrations. At an initial
411 MB concentration of 200 mg·L⁻¹, the fitted R² values of all three models were greater
412 than 0.99, which may be attributed to the relatively high initial adsorption rate. Based
413 on the correlation coefficients of the fitted results, the adsorption of MB on the
414 mesoporous material was better described by the pseudo-second-order kinetic model.
415 In addition, the theoretical equilibrium adsorption capacity (q_e) calculated from the
416 pseudo-second-order model was closer to the experimental value (Q_e). These results
417 indicated that the adsorption behavior of MB on the mesoporous material was more
418 consistent with the pseudo-second-order kinetic model. The reaction rate constant
419 decreased with increasing initial adsorbate concentration, whereas the equilibrium

adsorption capacity gradually increased. The pseudo-second-order model assumed that the adsorption rate depends on the adsorbate concentration and the number of active sites on the adsorbent, and that the adsorption capacity is proportional to the number of active sites on the material surface. In this model, the driving force for adsorption arises from the availability of active sites. As shown in the Figure 6, the adsorption capacity increased rapidly during the initial stage of adsorption within 0-10 min. As the adsorption time increased, the adsorption rate gradually decreased over the period from 10 to 120 min. Adsorption equilibrium was reached at around 120 min, indicating a rapid adsorption process. The mesoporous material possessed uniformly distributed active sites on its surface, and the relatively high solute concentration gradient enabled rapid mass transfer and adsorption at the initial stage of the process. With increasing adsorption time, the number of available active sites decreased, while adsorbate molecules began to diffuse into the pores of the material, leading to a gradual decline in the adsorption rate.

To examine the effect of temperature on methylene blue adsorption, adsorption isotherms of $\ln(q_e/C_e)$ versus T^{-1} were constructed using the equilibrium adsorption concentration C_e and temperature under different initial MB concentrations, followed by linear regression fitting, as shown in Figure 7 and Table 3.

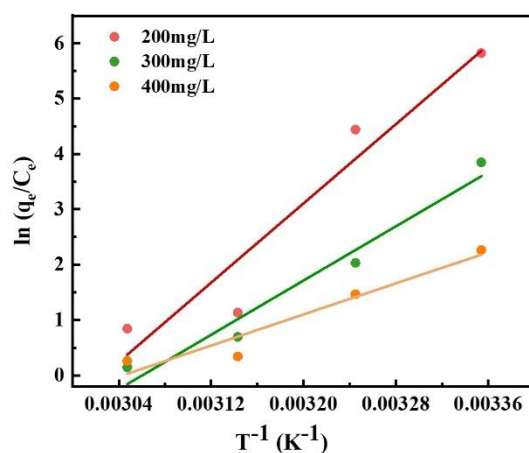


Figure 7 Thermodynamic plots for the adsorption of MB with different concentrations

Table 3 Thermodynamic paraments of MD absorption

Initial MB concentrations (mg·L ⁻¹)	Temperature (K)	ΔG (KJ·mol ⁻¹)	ΔH (KJ·mol ⁻¹)	ΔS (KJ·mol ⁻¹ ·K ⁻¹)	T Δ S(KJ·mol ⁻¹)
200	298.15	-14.53	-148.81	-0.4504	-134.27
	308.15	-10.03			-138.78
	318.15	-5.53			-143.28
300	298.15	-8.92	-101.81	0.3116	-92.89
	308.15	-5.80			-96.01
	318.15	-2.69			-99.13
400	298.15	-5.41	-58.35	-0.1776	-52.94
	308.15	-3.63			-54.72
	318.15	-1.86			-56.49

All ΔG values were negative, indicating that the adsorption of MB by the mesoporous material proceeded spontaneously (Table 3). At initial MB concentrations of 200, 300, and 400 mg·L⁻¹, the ΔH were -148.81, -101.81, and -58.35 kJ·mol⁻¹,

respectively, all of which were negative, indicating that the adsorption process was exothermic. The fact that $|\Delta H|$ exceeded $20 \text{ kJ}\cdot\text{mol}^{-1}$ suggested that the adsorption process involved both physical adsorption and chemical adsorption. At initial MB concentrations of 200, 300, and $400 \text{ mg}\cdot\text{L}^{-1}$, the ΔS values were -0.4504, -0.3116, and $-0.1776 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, all of which were negative, indicating a decrease in disorder at the solid-liquid interface during adsorption due to the reduced freedom of the adsorbate molecules after adsorption. Comparison of $|\Delta H|$ and $|T\Delta S|$ under different conditions showed that $|\Delta H|$ was consistently greater than $|T\Delta S|$, indicating that the adsorption of methylene blue on mesoporous SiO_2 was governed primarily by enthalpy change.

Furthermore, using MB as the adsorbate, the adsorption performances of the fly ash after heat and acid-leaching treatment, the modified product, and other mesoporous SiO_2 materials were compared, as shown in Table 4.

Table 4 Comparison of adsorption properties

Material	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{pore} ($\text{cm}^3\cdot\text{g}^{-1}$)	D_{BJH} (nm)	C_0 ($\text{mg}\cdot\text{L}^{-1}$)	D_{SiO_2} ($\text{g}\cdot\text{L}^{-1}$)	q_m ($\text{mg}\cdot\text{g}^{-1}$)	R (%)
Raw	364.21	0.24	4.06	200.00	1.00	116.95	61.62
Improved	774.42	1.41	7.23	200.00	1.00	186.81	98.84
[22]	1207.00	1.03	3.60	50.00	2.00	24.50	97.50
[23]	1014.60	0.81	3.36	20.00	2.00	9.40	99.94

C_0 represents the initial methylene blue concentration, D_{SiO_2} denotes the adsorbent

dosage, and R is the methylene blue removal efficiency. Compared with the original fly ash product after heat and acid-leaching treatment, the modified SiO_2 exhibited a twofold increase in specific surface area, a sixfold increase in pore volume, and a marked improvement in adsorption performance. In comparison with the mesoporous SiO_2 adsorbents reported in other studies, it also demonstrated favorable adsorption performance.

4. Conclusions

In this study, the fly ash after heat and acid-leached treatment was used as the silica source to prepare mesoporous SiO_2 materials via a hydrothermal method, and the effects of synthesis conditions on pore structure and MB adsorption performance were systematically investigated. The results showed that the mesoporous SiO_2 obtained under the conditions of a Si/CTAB/NaOH molar ratio of 1:0.65:0.6, an ethyl acetate dosage of 5 mL, a crystallization temperature of 80 °C, and a crystallization time of 1.5 h exhibited the optimal pore structure, with a specific surface area, average pore diameter, and pore volume of 774.42 $\text{m}^2\cdot\text{g}^{-1}$, 7.27 nm, and 1.41 $\text{cm}^3\cdot\text{g}^{-1}$, respectively. The adsorption experiments demonstrated that the solution pH had a significant effect on the adsorption of MB by mesoporous SiO_2 . As the pH increased, both the adsorption capacity and removal efficiency of MB increased markedly. Under the conditions of pH 11, an adsorption temperature of 298.15 K, an initial MB concentration of 200 $\text{mg}\cdot\text{L}^{-1}$, and an adsorbent dosage of 1 $\text{g}\cdot\text{L}^{-1}$, the adsorption capacity of mesoporous SiO_2 reached 186.81 $\text{mg}\cdot\text{g}^{-1}$, with a removal efficiency of 98.84%, demonstrating excellent capability

for cationic dye removal. Analysis of the adsorption mechanism showed that the adsorption behavior of MB on the surface of mesoporous SiO₂ was better described by the Langmuir isotherm model, indicating that the process was dominated by monolayer adsorption on a homogeneous surface. The adsorption kinetics were better fitted by the pseudo-second-order kinetic model, suggesting that the adsorption process was closely associated with surface active sites. The thermodynamic results indicated that the adsorption was a spontaneous and exothermic process, and that lower temperatures were more favorable for the removal of MB. Overall, the fly ash-derived mesoporous SiO₂ exhibited a well pore structure and high MB adsorption performance, highlighting its potential for application in dye wastewater treatment.

CRedit authorship contribution statement

Chen Zhan: Writing–review & editing, Writing-original draft. **Jingwen Wu:** Methodology, Investigation, Writing-original draft. **Jun Yang:** Writing-review & editing, Supervision, Software. **Zegang Fu:** Writing-review & editing, Supervision, Software, Funding acquisition, Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

References

1. Dong KY, Sun RJ, Li H, Jiang HD. A review of China's energy consumption structure and outlook based on a long-range energy alternatives modeling tool. **Pet Sci** **2017**, 14(1): 214-227.
2. China NBOS. Statistical Communiqué of the People's Republic of China on the 2020 National Economic and Social Development; 2021. Report.
3. China NBOS. China Energy Statistical Yearbook 2020; 2020. Report.
4. Ahmaruzzaman M. A review on the utilization of fly ash. **Prog Energy Combust Sci** **2010**, 36(3): 327-363.
5. Hui Y, Zhang R, Men G, Yuan H, Gu S, Ma L, et al. Fly ash for sustainable roads: A comprehensive review on mechanisms and performance optimization. **Journal of Road Engineering** **2025**, 5(4): 618-638.
6. Lee YR, Soe JT, Zhang S, Ahn JW, Park MB, Ahn WS. Synthesis of nanoporous materials via recycling coal fly ash and other solid wastes: A mini review. **Chem Eng J** **2017**, 317: 821-843.
7. Aldahri T, Behin J, Kazemian H, Rohani S. Synthesis of zeolite Na-P from coal fly ash by thermo-sonochemical treatment. **Fuel (Lond)** **2016**, 182: 494-501.
8. Aigbe UO, Ukhurebor KE, Onyancha RB, Osibote OA, Darmokoesoemo H, Kusuma HS. Fly ash-based adsorbent for adsorption of heavy metals and dyes from aqueous solution: a review. **J Mater Res Technol-JMRT** **2021**, 14: 2751-2774.
9. Shen Z, Yu X, Yu D. Preparation and applications of coal fly ash-based catalysts: A comprehensive review. **Journal of Environmental Chemical Engineering** **2025**, 13(3): 116782.
10. Miricioiu MG, Niculescu VC. Fly Ash, from Recycling to Potential Raw Material for Mesoporous Silica Synthesis. *Nanomaterials*; 2020. p. 474.
11. Kumar P, Mal N, Oumi Y, Yamana K, Sano T. Mesoporous materials prepared using coal fly ash as the silicon and aluminium source. **Journal of Materials Chemistry** **2001**, 11(12): 3285-3290.
12. Dhokte AO, Khillare SL, Lande MK, Arbad BR. Synthesis, characterization of mesoporous silica materials from waste coal fly ash for the classical Mannich reaction. **J Ind Eng Chem** **2011**, 17(4): 742-746.
13. Zhou C, Gao Q, Luo W, Zhou Q, Wang H, Yan C, et al. Preparation, characterization and adsorption evaluation of spherical mesoporous Al-MCM-41 from coal fly ash. **J Taiwan Inst Chem Eng** **2015**, 52: 147-157.
14. Jiang A, Wu J, Qu B, Fu Z, Wang T, Ji G. Metals removal and high-silica powder production from coal fly ash via phase separation process. **Waste Manag** **2026**, 214: 115411.
15. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. **Nature** **1992**, 359(6397): 710-712.
16. Rathousky J, Zukalova M, Kooyman PJ, Zukal A. Synthesis and characterization of colloidal MCM-41. **Colloids Surf A Physicochem Eng Asp** **2004**, 241(1): 81-86.
17. Zhou C, Yan C, Zhao J, Wang H, Zhou Q, Luo W. Rapid synthesis of morphology-controlled mesoporous silica nanoparticles from silica fume. **J Taiwan Inst Chem Eng** **2016**, 62: 307-312.
18. Bai K, Hao J, Yang Y, Qian A. The effect of hydrothermal temperature on the properties of SBA-

- 553 15 materials. **Heliyon** **2020**, 6(8): e04436.
- 554 19. Lin HP, Mou CY. Structural and Morphological Control of Cationic Surfactant-Templated
555 Mesoporous Silica. **Acc Chem Res** **2002**, 35(11): 927-935.
- 556 20. Yuan N, Cai H, Liu T, Huang Q, Zhang X. Adsorptive removal of methylene blue from aqueous
557 solution using coal fly ash-derived mesoporous silica material. **Adsorp Sci Technol** **2019**, 37(3-4):
558 333-348.
- 559 21. Gao Q, Zhu H, Luo WJ, Wang S, Zhou CG. Preparation, characterization, and adsorption evaluation
560 of chitosan-functionalized mesoporous composites. **Microporous Mesoporous Mat** **2014**, 193: 15-
561 26.
- 562 22. An QL. Study of methylene blue adsorption on mesoporus molecular sieve from aqueous solution.
563 **Advanced Materials Research** **2012**, 549: 207-211.
- 564 23. Thome AG, Harms C, Roessner F. Synthesis of Macro-Mesoporous MCM-41 and Its Use in
565 Methylene Blue Adsorption. **Chem Ing Tech** **2017**, 89(7): 944-948.
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