



Research article

BioMCM-41 mesoporous silica from agricultural waste for methylene blue removal and ANN-based prediction

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ABSTRACT

The development of sustainable mesoporous silica adsorbents from agricultural residues represents an important strategy for improving dye removal while reducing dependence on conventional silica precursors. However, the conversion of low-cost biomasses into ordered MCM-41-type materials and the prediction of their adsorption performance under variable conditions remain insufficiently explored. In this work, bio-silica-derived MCM-41 materials were synthesized from two abundant agricultural wastes, *Festuca arundinacea* and barley bran, using a cost-effective and environmentally friendly route. The extracted silicas were highly pure and amorphous, and were converted into sodium silicate precursors for mesoporous material synthesis and compared with commercial MCM-41. The materials were characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, X-ray fluorescence, N₂ adsorption-desorption, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and thermogravimetric-differential scanning calorimetry. The prepared materials exhibited ordered hexagonal mesoporosity, high specific surface areas of 1090, 1080, and 1030 m² g⁻¹ for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively, with pore diameters ranging from 2.9 to 3.9 nm. Their adsorption performance was evaluated using methylene blue as a model cationic dye. BioMCM-41FA and BioMCM-41BB achieved complete dye removal, while MCM-41C reached 95% under the same conditions. The corresponding adsorption capacities were 80.00, 80.00, and 77.29 mg g⁻¹. In addition, an artificial neural network model was developed to predict adsorption yield using eight input variables. After hyperparameter optimization, the ANN showed strong predictive performance, with R² = 0.941 for training, R² = 0.900 for external testing, Q² = 0.900, RMSE = 0.0526, MAE = 0.0354, and MAPE = 4.79%. These results confirm the potential of agricultural wastes for producing efficient mesoporous adsorbents and demonstrate the usefulness of ANN modeling for adsorption prediction.

1. Introduction

Agriculture produces a large amount of waste, and many regions of the world struggle to manage it effectively. Crop residues are often incinerated, which harms the environment and human health. This process releases fine particulate matter and toxic gases, polluting the atmosphere and endangering human health. This practice also exacerbates climate change by emitting harmful gases, including carbon monoxide and methane [1,2].

The reuse of agricultural waste, such as peanut shells [3], sugarcane bagasse [4], rice husks [5,6], corn cobs [7], and other plant residues, is a

promising solution to this problem. These silica-rich compounds have potential applications in the production of nanoparticles and water filtration materials. Developing methods to extract silica from these agricultural byproducts is a major research focus. This allows the silica (SiO₂) present in this waste to be exploited, a highly sought-after ingredient in many products. The unique properties of silica make it an attractive component in composite materials, thermal insulators, thixotropic agents, and a wide range of other industrial products. This offers new opportunities for environmentally friendly and technologically advanced solutions [8].

The sol-gel method is widely used to produce silica from agricultural

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waste. This process involves hydrolysis and condensation, in which biomass ash reacts with bases to produce sodium silicate. Subsequently, an acid is added to the sodium silicate to produce a silica gel. The quality of the biomass used significantly influences the purity of the silica obtained by this method [9–11]. Leaching before combustion is decisive, as it purifies the ash by increasing the SiO_2 content and reducing the amounts of other mineral elements, such as chloride (Cl), potassium oxide (K_2O), phosphorus oxide (P_2O_5), and magnesium oxide (MgO) [6].

The combination of pre-treatment, leaching, and alkaline attack enables the extraction of high-purity silica, which has numerous applications, particularly in nanotechnology and other industries [12,13].

Amorphous silica from agricultural by-products is particularly used to synthesize mesoporous silica-based materials [14]. Numerous studies have primarily concentrated on prevalent silica-rich agricultural byproducts. Liu et al. synthesized mesoporous PS-MCM-41 from peanut shell ash and exhibited its adsorption capabilities. Seroka et al. and September et al. investigated the conversion of sugarcane bagasse ash into silica and silicon-based products, proving the residue's usefulness as a renewable silica source. Other studies have reported silica extraction from rice husk and corn cob ashes, showing that alkaline extraction followed by acid precipitation can yield amorphous silica suitable for advanced material synthesis [3,4,10].

Since the discovery of the M41S family of ordered mesoporous materials in the early 1980s, MCM-41 has become one of the most extensively investigated members of this family [15].

MCM-41 is widely used across many fields due to several beneficial qualities, including a large specific surface area, a uniform porous structure, a narrow pore-size distribution, a large pore volume, and excellent thermal stability. It is frequently used as an adsorbent, catalyst support, and in the manufacture of sensors, among other applications [16–19].

Adsorption, an application of mesoporous materials, has proven particularly effective for treating industrial wastewater, especially that containing dyes. This wastewater comes from various sources, such as the textile, printing, dyeing, dye manufacturing, and food industries [20–22]. It contributes significantly to water pollution, as some dyes and their degradation products can be carcinogenic and harmful to mammals [23,24].

Adsorption offers several advantages for the treatment of dye-contaminated wastewater, including relatively simple process design, operational flexibility, high removal efficiency, and applicability over a broad range of pollutant concentrations. It may also enable adsorbent recovery and reuse, thereby improving the process's economic and environmental sustainability. Activated carbon is widely used because of its well-developed porous structure and high adsorption capacity. However, biomass-derived adsorbents and mesoporous silica materials have attracted increasing interest as potentially lower-cost and more sustainable alternatives. In particular, converting agricultural residues into adsorbent materials combines wastewater treatment with the valorization of plant waste. Despite these advantages, adsorption remains sensitive to the physicochemical properties of the adsorbent, the nature of the pollutant, and the operating conditions. Its practical application may also be limited by the progressive saturation of active sites and by constraints related to cost, regeneration, and adsorbent separation after treatment. These limitations justify the development of efficient, stable, and sustainable adsorbent materials, such as biomass-derived mesoporous silicas [25–27].

In a recent study, Celoria et al. synthesized nanosized MCM-41 from rice husk-derived biogenic silica and evaluated its use as a mesoporous adsorbent for the removal of rhodamine B from aqueous solution [28].

In another study, Barros et al. investigated the removal of rhodamine B from aqueous solution using MCM-41 and calcined MCM-41 mesoporous silica. Their study focused on the influence of pH, adsorption kinetics, and interaction mechanisms [29].

Recent work on EDTA-functionalized SBA-15 for Ni (II) adsorption has also illustrated the broader applicability of ordered mesoporous

silica materials to the removal of aqueous contaminants [30].

Artificial neural networks have recently attracted attention in adsorption research due to their ability to represent nonlinear relationships between experimental factors and adsorption performance. Unlike classical empirical models, ANN can simultaneously consider several operating parameters, such as pH, contact time, adsorbent dosage, ionic strength, temperature, and initial concentration, and predict adsorption efficiency with high accuracy.

In recent adsorption studies, artificial intelligence has been used to model and optimize dye removal processes. Mesutoğlu developed an ANN-based approach to predict methylene blue adsorption onto activated olive stone, while Kumari et al. compared several models, including ANN, for methylene blue adsorption using *Oryza sativa* straw biomass [31,32].

Beyond adsorption-specific applications, RSM has recently been used to optimize a crude-oil desalting process, while a combined RSM-ANN approach has been applied to model oil content in produced water [33, 34]. Comparative predictive studies have also evaluated model performance using complementary indicators such as R^2 , MAE, RMSE, and MAPE [35].

However, most previous studies on biomass-derived silica have focused on widely investigated agricultural residues, such as rice husk, sugarcane bagasse, peanut shells, and corn cobs. In comparison, *Festuca arundinacea* and barley bran remain insufficiently explored as alternative biosilica sources for the preparation of ordered mesoporous materials. To the best of our knowledge, no previous study has comparatively investigated these two biomasses under the same extraction and synthesis conditions for the production of BioMCM-41 materials. Furthermore, the influence of the biomass source on the physicochemical properties of the extracted bio-silica, the resulting mesoporous structure, and the adsorption performance remains insufficiently clarified.

Another important research gap is the limited integration of biomass-derived MCM-41 synthesis, systematic adsorption experiments, and data-driven prediction within a single study. Most reported works have focused separately on silica extraction, mesoporous material synthesis, adsorption performance, or predictive modeling. Therefore, an integrated approach that combines these aspects is needed to evaluate better both the material properties and their adsorption behavior under variable operating conditions.

Accordingly, the present study comparatively investigates *Festuca arundinacea* and barley bran as locally available and underutilized silica sources. Both biomasses were subjected to the same extraction and synthesis procedure to produce BioMCM-41FA and BioMCM-41BB, which were compared with MCM-41C synthesized from commercial sodium silicate. The materials were evaluated for their structural, morphological, chemical, and textural properties, and their adsorption performance toward methylene blue was investigated as a function of pH, contact time, adsorbent dosage, ionic strength, agitation speed, and temperature. Kinetic, equilibrium, and thermodynamic analyses were further combined with an artificial neural network model using eight input variables to predict the adsorption yield. The novelty of this work therefore lies in the comparative conversion of two less-explored biomasses into ordered BioMCM-41 materials and in the integration of material synthesis, systematic adsorption evaluation, and ANN-based prediction within the same study.

2. Material and methods

2.1. Raw materials and chemicals

The *Festuca arundinacea* plant and barley bran used in this study were collected in Algeria, specifically from the regions of Blida and Djelfa, respectively.

They were thoroughly washed with distilled water, naturally air-dried, subsequently cut into small fragments, and stored in a desiccator before synthesis.

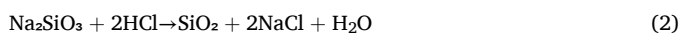
The chemicals used in this study are listed in Table 1, along with their chemical formulas, purities or concentrations, suppliers, and molecular weights. Distilled water was used throughout the extraction, synthesis, and adsorption experiments.

2.2. Extraction of silica

The extraction of silica from *Festuca arundinacea* (FA) and barley bran (BB) was carried out through a three-step process. Initially, 50 g of FA and BB were immersed in 500 mL of 3% (v/v) nitric acid solution and heated to 50 °C under stirring for two hours. Following the leaching process, the mixture was filtered, and the residue was repeatedly washed with distilled water until the pH reached neutrality. The treated FA and BB were then dried at 50 °C for 24 h, then calcinated at 600 °C for 8 h under air in a muffle furnace. Finally, an alkaline extraction method was employed to isolate silica from FA and BB, following the protocols established by Kalapathy et al. [36], Anuar et al. [37], and Nazriati et al. [38], with slight modifications. FA and BB ashes were mixed with a 4 M NaOH solution at a fixed solid-to-liquid ratio of 1:20 (w/v) in a round-bottom flask and subjected to reflux with continuous stirring at 80 °C for 4 h to dissolve the silica and form a sodium silicate solution. The reaction is represented as follows:



After cooling to room temperature, the mixture was filtered using Whatman No. 41 ashless filter paper. The resulting filtrate was then carefully titrated with HCl solution under continuous stirring until the pH reached 7, leading to the precipitation of silica gel, as described by the reaction:



The obtained silica gel was aged for 24 h, centrifuged at 4000 rpm for 10 min, and thoroughly rinsed with distilled water. Finally, the material was dried in an oven at 100 °C for 24 h, yielding silica powder.

2.3. Synthesis of bio-MCM-41 materials

A sodium silicate (Na_2SiO_3) solution was prepared using silica extracted from the two plants. The extracted silica was mixed with 1.6 g of NaOH pellets and 10 g of distilled water. The resulting mixture was continuously stirred and heated at 80 °C for 4 h, followed by natural cooling to ambient temperature.

A homogeneous precursor solution was prepared by dissolving 2.4 g of cetyltrimethylammonium bromide (CTAB) in 120 g of deionized water under continuous stirring at 35 °C. Subsequently, 8 mL of ammonium hydroxide was added to the solution and stirred for 10 min. Then 10 mL of sodium silicate solution was added dropwise under stirring for an additional two hours. The pH was adjusted to 10 using a dilute HCl solution. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 100 °C for 72 h. The obtained white precipitate was collected by filtration, then washed sequentially and dried at 100 °C for 24 h. The removal of the organic template was achieved through calcination in a muffle

furnace at 550 °C for 5 h under air. This protocol follows a modified procedure based on the methodology reported by D. Kumar et al. [39]. It gives BioMCM-41FA and BioMCM-41BB depending on the source of SiO_2 extracted (FA or BB) and gives BioMCM-41FA and BioMCM-41BB depending on the source of SiO_2 extracted (FA or BB).

For comparison purposes, MCM-41C was synthesized following the same protocol, except that commercial sodium silicate was used instead of natural sodium silicate obtained from FA or BB.

The silica extraction and BioMCM-41 synthesis procedures were repeated 3 times to assess the reproducibility of the yields. The silica extraction yield was higher for *Festuca arundinacea* than for barley bran under the applied extraction conditions. For BioMCM-41 synthesis, the yield was estimated from the mass of recovered material relative to the initial mass of bio-silica used as a precursor. The average synthesis yield was estimated to be $74.29 \pm 2.86\%$, indicating a satisfactory and reproducible conversion of bio-silica into BioMCM-41 materials.

2.4. Characterization

The chemical analysis of the produced silica and MCM41 samples was performed by wavelength-dispersive X-ray fluorescence (WDXRF) using a Rigaku Supermini200 spectrometer (Rigaku Corporation, Japan). The structure of the produced silica and synthesized MCM-41 samples was examined using a Rigaku SmartLab X-ray diffractometer. Nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was used; the diffraction patterns were recorded in the 2θ range of $3^\circ - 80^\circ$ for silica and 1° to 10° [20] for MCM-41 at a scan rate of $1^\circ/\text{min}$. The functional groups on the extracted silica and MCM-41 surfaces were identified using Fourier Transform Infrared Spectroscopy (FTIR) (FT/IR-6700, Jasco 4x) over the spectral range of $450 - 4000 \text{ cm}^{-1}$. A field-emission scanning electron microscope (FEG-SEM), JEOL JSM-7610F Plus (Tokyo, Japan), was used to investigate the morphology of the samples. Their chemical composition was determined using an Energy-Dispersive X-Ray Spectroscopy (EDS) system, Quantax200 (Bruker, Germany), equipped with an XFlash6/10 silicon drift detector (SDD) mounted in the microscope chamber. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out using a Simultaneous Thermal Analyzer (TGA/DSC) by METTLER TOLEDO. The samples were heated at $10^\circ\text{C}/\text{min}$ from 25°C to 950°C . Nitrogen adsorption-desorption isotherms were recorded at 77 K using a QUANTACROM ASIQUV 0000-6 instrument after degassing the samples under vacuum to around 10^{-6} at 250°C . The pore size distributions were calculated from the desorption isotherms using the BJH method. Transmission Electron Microscopy (TEM) images were obtained using an EM-F200 microscope.

2.5. Batch adsorption experiments

Adsorption experiments were conducted at controlled pH, temperature, and initial dye concentration, with equilibrium time determined experimentally. A fixed dose of MCM-41 material was added to 50 mL of methylene blue (BM) aqueous solution at an initial concentration of $20 \text{ mg}\cdot\text{L}^{-1}$. The mixture was placed in a 100 mL amber glass flask and maintained at a pH of 6.42. The suspension was then agitated using an orbital shaker at 210 rpm and room temperature for 2 h to ensure

Table 1
List of chemicals used.

Chemical reagent	Chemical formula	Purity	Supplier	Molecular weight (g mol^{-1})
Nitric acid	HNO_3	65% w/w in water	Fluka	63.01
Hydrochloric acid	HCl	37% w/w in water	Fluka	36.46
Sodium hydroxide	NaOH	97% w/w	Biochem	40.00
Ammonium hydroxide	NH_4OH	25% w/w in water	Sigma-Aldrich	35.05
Hexadecyltrimethylammonium bromide (CTAB)	$\text{C}_{16}\text{H}_{33}\text{BrN}$	99% w/w	Sigma-Aldrich	364.45
Sodium silicate	Na_2SiO_3	Not specified	Sigma-Aldrich	122.06
Methylene blue (MB)	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$	95–101%	Biochem	319.85

equilibrium was reached.

Before analysis, the suspensions were filtered through a 0.45 µm membrane microfilter to remove any remaining particulate matter. The supernatant was collected and analyzed using a UV-Vis spectrophotometer at the maximum absorbance wavelength of 664 nm of BM. The equilibrium adsorption capacity (q_e , mg·g⁻¹) and the removal efficiency (R%) of BM were determined according to Eqs. (3) and (4), respectively.

$$q_e = (C_o - C_e) * V/m \quad (3)$$

$$R\% = (C_o - C_e)/C_o * 100 \quad (4)$$

In these equations, C_o and C_e (mg·L⁻¹) refer to the initial and equilibrium concentrations of BM in solution, respectively. V (L) is the volume of the solution, and m (g) is the weight of the adsorbent employed in the batch system [40].

Under carefully controlled experimental settings, the adsorption behavior was systematically evaluated by changing important operational factors such as solution pH (2–11), contact period (0–120 min), adsorbent dosage (2–15 mg), salts concentrations (50–200 mg/L) and agitation speed (100–300 rpm) For the thermodynamic study, experiments were conducted at temperature intervals ranging from 20 to 75 °C.

2.6. Kinetics study

The experimental kinetic data were analyzed using the nonlinear forms of the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models to investigate the adsorption kinetics of MB onto the MCM-41 materials. The corresponding model equations are presented in Eqs. (5–8) [40].

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$q_t = (k_2 q_e^2 t) / (1 + k_2 q_e t) \quad (6)$$

$$q_t = K_{diff} t^{0.5} + C \quad (7)$$

$$q_t = 1/\beta * \ln(1 + \alpha \beta t) \quad (8)$$

Where q_t and q_e are the adsorbed amount in mg·g⁻¹ at time t and at equilibrium, K_1 is the

first-order kinetic rate constant (min⁻¹), t (min) is the contact time, K_2 is the pseudo-second-order kinetic rate constant (g·mg⁻¹·min⁻¹), K_{diff} (mg·g⁻¹·min^{-1/2}) and C (mg·g⁻¹) are the rate constant of intraparticle diffusion and the constant varied directly with the boundary layer thickness, respectively, α (mg·g⁻¹·min⁻¹) is the initial adsorption rate, and β (g·mg⁻¹) is the extent of surface.

2.7. Isotherm models

The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherm models were applied to describe the adsorption equilibrium of MB onto the MCM-41 materials. The corresponding nonlinear equations are presented in Eqs. (9–12) [40].

$$q_e = k_l q_m C_e / (1 + k_l C_e) \quad (9)$$

$$q_e = K_f (C_e)^{1/n} \quad (10)$$

$$q_e = RT/b_t * \ln(K_t C_e) \quad (11)$$

$$q_e = q_m * \exp(-\beta \epsilon^2) \quad (12)$$

Where C_e (mg·L⁻¹) is the BM concentration at equilibrium, and q_e (mg·g⁻¹) represents the adsorption capacity of the adsorbent. q_m (mg·g⁻¹) represents the maximal adsorption capacity, and K_l (l·mg⁻¹) represents the Langmuir constant. $1/n$ and K_f and K_T represent the adsorption

intensity coefficient and the Freundlich Temkin constant, respectively. $RT/b_t = B$ is associated with the heat of adsorption. q_{D-R} represents the maximal adsorption capacity. E represents the average sorption energy in (kJ mol⁻¹), while β denotes the activity coefficient and ϵ , representing the Polanyi potential (kJ mol⁻¹), are defined by Eqs. (13) and (14), respectively [40].

$$\epsilon = RT \ln(1 + \frac{1}{C_e}) \quad (13)$$

$$E = 1 / \sqrt{2\beta} \quad (14)$$

2.8. Thermodynamic study

Thermodynamic parameters must be determined at different temperatures to understand how temperature affects the adsorption process. Consequently, three fundamental thermodynamic parameters were examined: the Gibbs free energy of adsorption (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS). The variation in Gibbs free energy during the adsorption process is associated with the equilibrium constant (K_c). All these parameters were either obtained or calculated using the following Eqs. (15–17) [40].

$$\Delta G = -RT \ln K_d \quad (15)$$

$$= q_e / C_e \quad (16)$$

$$\ln K_d = \Delta S^0 / R - \Delta H^0 / RT \quad (17)$$

In this context, T (K) represents the absolute temperature, R denotes the gas constant, and the values of ΔS^0 and ΔH^0 are derived from Van't Hoff's equation (Eq17). [40]

All adsorption experiments were performed in triplicate under identical experimental conditions. The experimental results are reported as mean ± standard deviation. Error bars shown in the adsorption figures represent the standard deviation of three independent measurements

2.9. Artificial neural network modeling

An artificial neural network (ANN) model was developed to predict the adsorption yield based on eight experimental input variables: pH, adsorbent mass, initial BM concentration, silica percentage, temperature, agitation speed, NaCl concentration, and contact time. The output variable was the experimental yield. Prior to modeling, the dataset was cleaned by removing missing, non-numeric, and infinite values. All input and output variables were converted to numerical format, and the data were divided into training and external test subsets using an 80:20 split.

To improve model stability, the input variables and target values were standardized using StandardScaler. The ANN was implemented using a feed-forward multilayer perceptron architecture in TensorFlow/Keras. The network consisted of an input layer, one to three hidden dense layers, and one linear output neuron for regression. The number of hidden layers, number of neurons, activation function, dropout rate, learning rate, optimizer, batch size, L2 regularization strength, and batch normalization option were optimized using the Optuna algorithm.

Hyperparameter optimization was performed only on the training set using 5-fold cross-validation in order to avoid data leakage. The external test set was kept independent and used only for final model evaluation. Early stopping and learning-rate reduction were applied during training to reduce overfitting and improve generalization. The model performance was evaluated using the coefficient of determination (R^2), root mean square error (RMSE), mean absolute error (MAE), mean squared error (MSE), mean absolute percentage error (MAPE), and predictive Q^2 (Figs. 1–5).

The robustness of the ANN model was further assessed by comparing

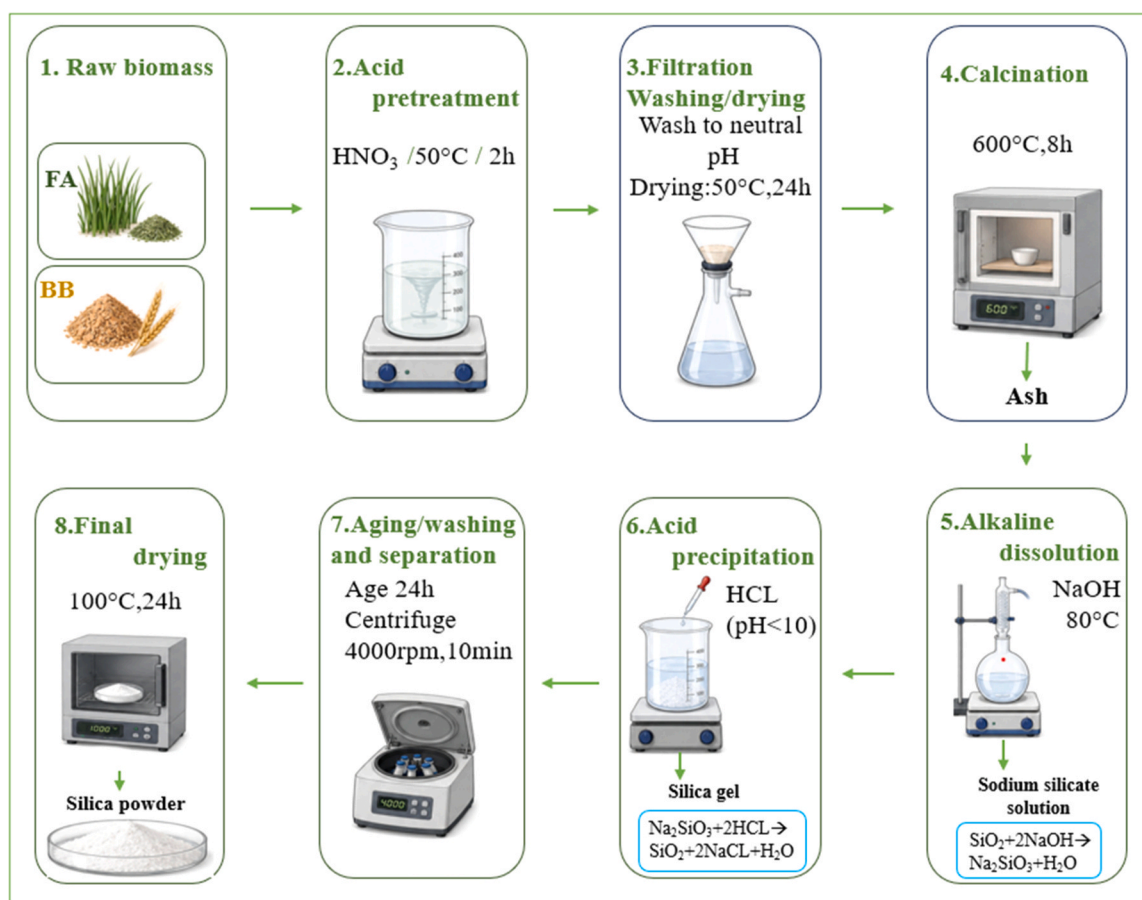


Fig. 1. Schematic diagram of silica extraction from biomass residues.

training and external test performances, as well as by internal cross-validation and leave-one-out validation. Feature importance and sensitivity analyses were performed using permutation importance, Garson's algorithm, Olden's connection-weight method, Pearson/Spearman correlation analysis, and one-at-a-time sensitivity analysis. Finally, an applicability domain was defined using a distance-based approach on the standardized training data to identify whether new predictions were located inside or outside the model's reliable prediction space.

The overall experimental and modeling workflow adopted in this study is summarized in Fig. 6.

3. Results and discussions

3.1. Characterization of silica

Tables 2 and 3 display the elemental compositions of *Festuca arundinacea* (FA) and barley bran (BB) prior to and following acid treatment, calcination, and alkali treatment. Following these operations, the SiO_2 concentration rises to 99.2% for FA and 98.8% for BB, while the proportions of the other components decrease significantly. These results demonstrate the effectiveness of the chemical treatment approach for extracting silica from *Festuca arundinacea* and barley bran [41].

The silica content before acid treatment (untreated samples) was 25.9% for FA and 12.9 for BB. After pretreatment with nitric acid (HNO_3), the SiO_2 content increased to 62.8% for FA and 29% for BB, confirming that acid leaching effectively removes metallic impurities [42].

According to numerous studies, most metallic impurities can be effectively removed by boiling the plant in an acid solution during

preliminary leaching, prior to thermal treatment for varying durations [13,31].

During the calcination stage, the silica content increases from 62.8% to 80.7% for FA and from 29% to 80.1% for BB as a result of the elimination of volatile components.

The alkaline treatment using sodium hydroxide (NaOH), followed by precipitation with hydrochloric acid (HCl), was effective in obtaining silica with high purity, reaching 99.2% for FA and 98.8% for BB. Chemical composition analysis by X-ray fluorescence (XRF) spectroscopy shows that *Festuca arundinacea* and barley bran possess a high silica content, indicating that these agricultural wastes can serve as highly pure alternative sources to commercial silica for the synthesis of bio-derived MCM-41 mesoporous material [43].

Silica purity obtained from both biomasses was compared with other studies (Table 4), which present the percentage of silica extracted from various agricultural and industrial waste using different synthesis methods.

Fig. 7(a) shows the X-ray diffractometry (XRD) patterns of FA and BB derived silica. The XRD results indicate that the silica powders primarily exhibit an amorphous structure, as evidenced by the broad and intense peak centered around $2\theta = 22^\circ$. A similar result was reported by Puja Priyadarshini Nayak, [47] who extracted silica from rice husks (RH) using pretreatment with acid, calcination, and an alkaline treatment with NaOH. This is due to the fact that sodium hydroxide only dissolves amorphous silica, which then precipitates [48]. This broad halo is typical of amorphous material and indicates the absence of long-range crystalline order, in agreement with [49].

The primary functional groups in the amorphous silica prepared by alkaline extraction of *Festuca arundinacea* and barley bran were

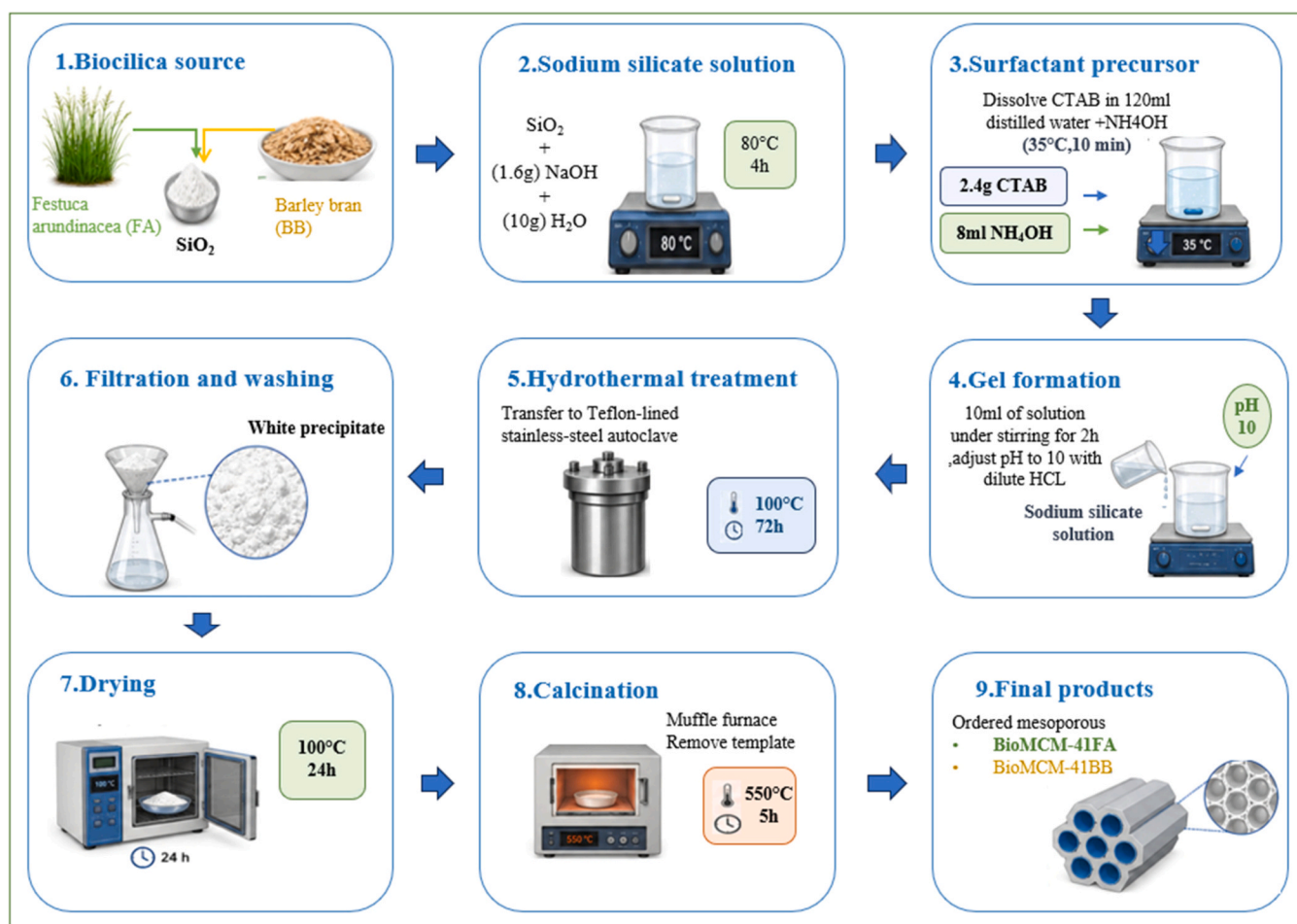


Fig. 2. Schematic illustration of the synthesis route of BioMCM-41 materials.

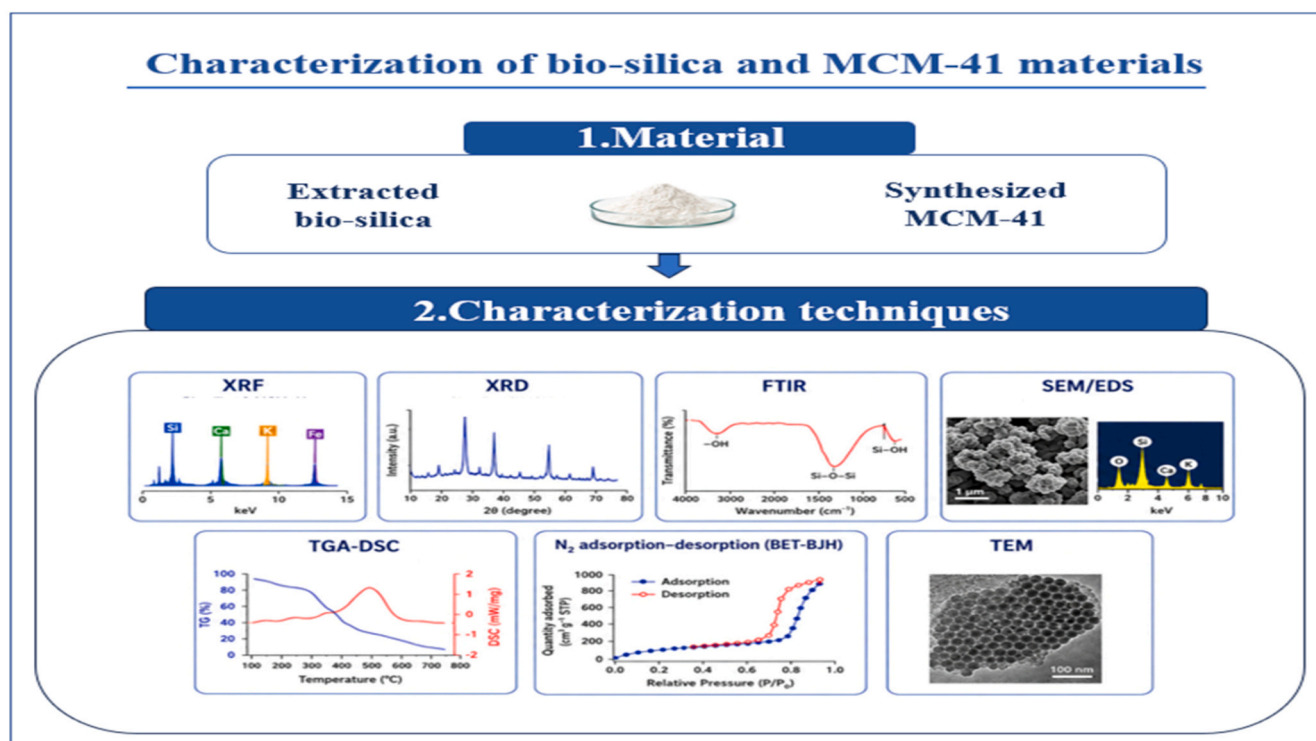


Fig. 3. Schematic summary of the physicochemical characterization of bio-silica and MCM-41-based materials.

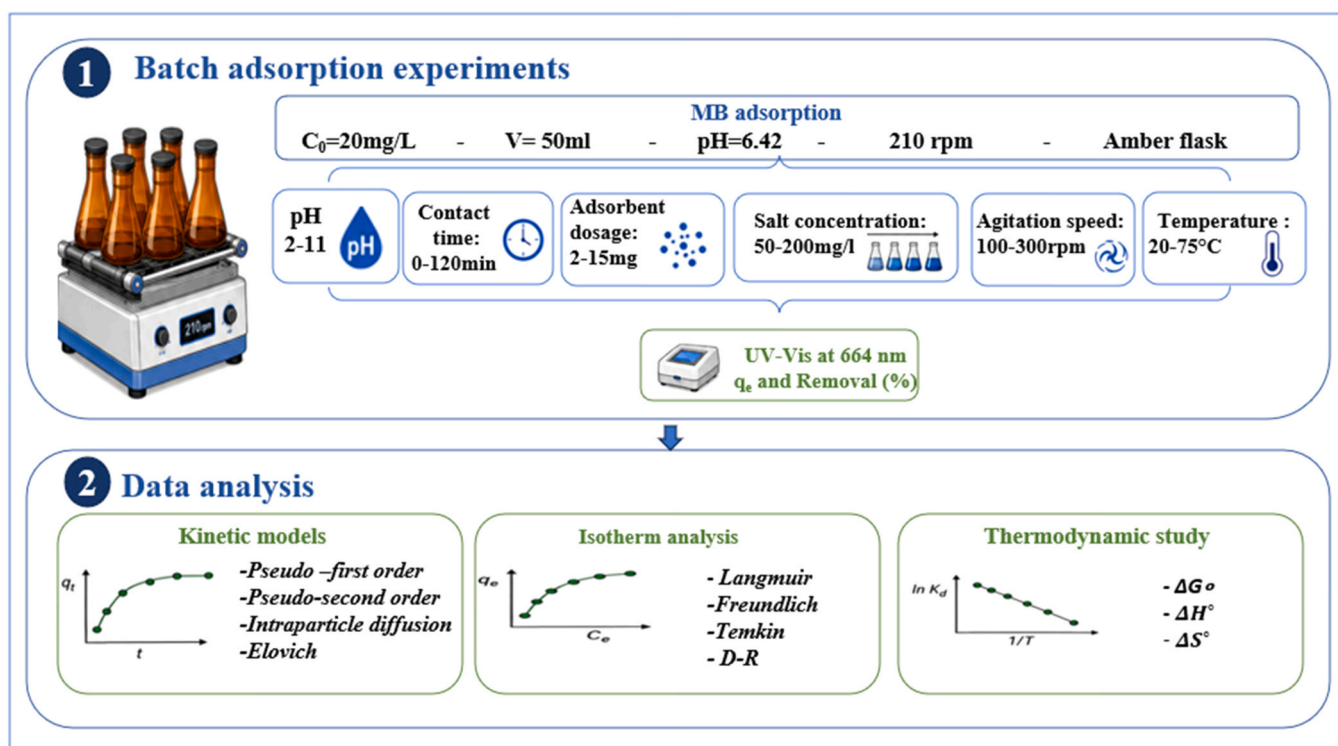


Fig. 4. Experimental workflow for methylene blue adsorption and data analysis using MCM-41-based adsorbents.

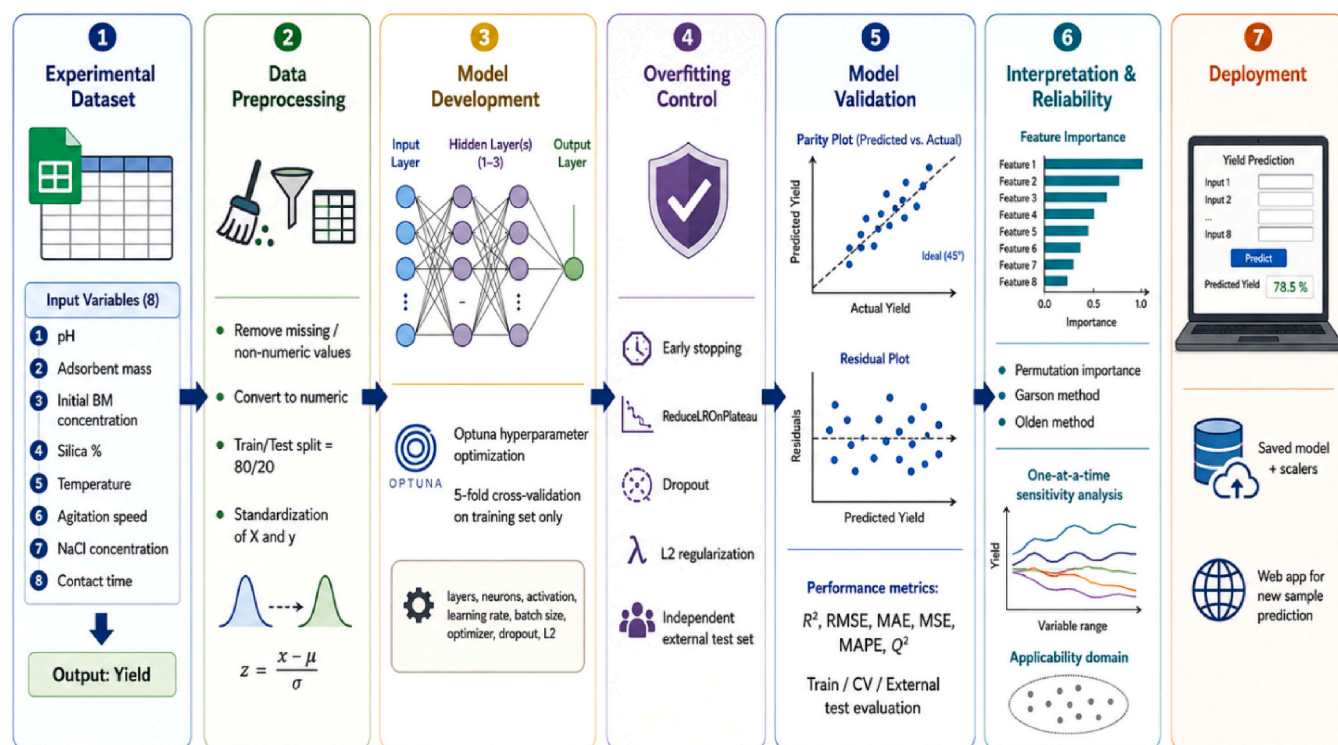


Fig. 5. Modeling methodology.

characterized by Fourier transform infrared spectroscopy (FT-IR). The absorption bands in Fig. 7(b), provide information on the chemical bonds present in the extracted silica. Similar peaks were observed for both biomass sources.

The intense band at 1060 cm^{-1} corresponds to asymmetrical

stretching of Si–O–Si [50]. Similar to this study, Suman Mor et al. (2017) and Xiao et al. (2015) also found a band at 794 cm^{-1} , which is caused by the stretching of the Si–O–Si bond, and a band at 473 cm^{-1} , which is caused by bending waves [51].

A band at 956 cm^{-1} is associated with the absorption of bending

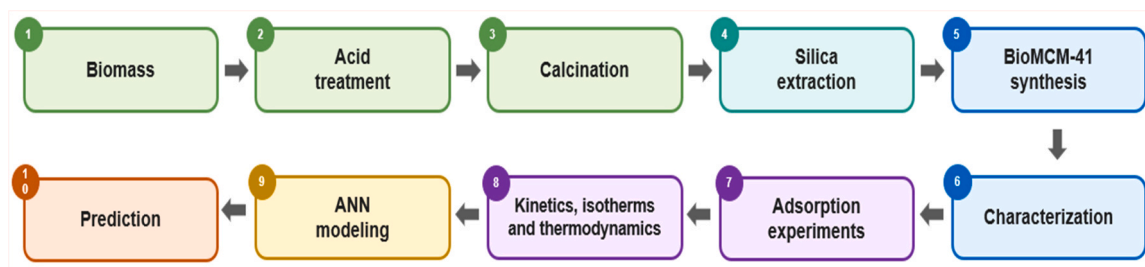


Fig. 6. Experimental and modeling workflow.

Table 2

Chemical composition of *Festuca arundinacea* (FA) before and after treatment (acid leaching, calcination and alkali extraction).

Component	Mass %			
	Before acid treatment	After acid treatment	After calcination	After alkali treatment
SiO ₂	25.90	62.80	80.70	99.20
K ₂ O	31.70	7.75	0.66	0.13
SO ₃	2.77	4.80	3.15	0
CaO	16.50	15.70	10.30	0.02
Fe ₂ O ₃	3.46	2.57	0.21	0.07
Al ₂ O ₃	2.82	0.99	0.44	0.40
Cl	10.40	2.92	0.09	0.03
ZnO	0.16	0.46	0.08	0.15
P ₂ O ₅	4.11	1.94	2.25	0
MgO	2.28	0	2.05	0
Others	5.21	5.26	5.28	0.15

Table 3

Chemical composition of barley bran (BB) before and after treatment (acid leaching, calcination and alkali extraction).

Component	Mass %			
	Before acid treatment (untreated)	After acid treatment	After calcination	After alkali treatment
SiO ₂	12.90	29.00	80.10	98.8
K ₂ O	28.80	11.60	3.27	0
SO ₃	13.10	18.70	0.53	0
CaO	11.10	14.80	2.79	0.03
Fe ₂ O ₃	4.88	10.70	0.15	0.11
Al ₂ O ₃	0	0	0	0.49
Cl	6.53	4.82	0	0.48
ZnO	0	0.86	0.02	0
P ₂ O ₅	14.60	9.56	11.90	0
MgO	8.10	0	1.26	0
Others	0	0	0.02	0.07

Table 4

Percentage of silica extracted from various agricultural and industrial waste using different synthesis methods.

Type of waste	Corn Cob [44]	Sugarcane Bagasse [45]	Rice Husk [46]	coconut husk [37]
SiO ₂	97.13	88.13	99.08	90.01
Al ₂ O ₃	0.00	0.24	0.06	3.17
CaO	0.89	0.57	0.04	1.47
Fe ₂ O ₃	0.48	0.94	0.04	0.21
MgO	0.92	3.04	0.06	-
K ₂ O	0.58	0.50	0.01	1.01
Cl	-	-	-	0.51
P ₂ O ₅	-	1.15	-	0.73
Others	0.00	5.43	0.01	2.89

vibrations by Si-OH. The broad band observed between 3000 and

3600 cm⁻¹ is attributed to Si-OH bonding stretching from surface silanol groups (Si-OH) and observed water. The bending vibrations of H-O-H (water molecules) are responsible for the little band at 1633 cm⁻¹, as stated by Rafiee [52]. No bands in the 1700–2800 cm⁻¹ region were detected, indicating the absence of residual organic species.

These findings demonstrate the efficiency of the alkaline extraction approach in obtaining silica from *Festuca arundinacea* and barley bran ashes.

Additionally, it implies that the process of preparation and washing effectively removes all contaminants, including alkali and alkaline earth metals, and that there is no sodium chloride present [51].

Fig. 8(a) shows SEM images of silica extracted from *Festuca arundinacea*, while Fig. 8(b) presents silica derived from barley bran. Each set of images, taken at different magnifications, reveals the detailed structural features of the materials at the microscopic level.

These figures clearly show that the particles are predominantly spherical shape, with a relatively uniform size of less than 176 nm for FA and less than 488 nm for BB. Furthermore, the lack of agglomeration and the absence of an ordered particle arrangement suggest that the extracted silica is amorphous. EDX analysis revealed that the main elements in the particles were silicon and oxygen, as depicted in Fig. 7(c). The analysis confirmed the high purity of the obtained particles, with only Si and O peaks detected with only negligible peak of sodium (Na) [53].

To study the thermal behavior of amorphous silica extracted from FA and BB, thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) was carried out. The results obtained are shown in Fig. 7(d). These curves provide detailed information on silica mass variations with temperature and its thermal properties, enabling an in-depth assessment of silica's thermal behavior. According to the results of the DSC and TGA thermograms, there were three distinct thermal transitions for both biomasses:

At the beginning of heating, the TGA curve reveals a considerable mass loss, especially in the temperature range of 0–200°C. This loss is likely attributable to the evaporation of adsorbed water, characterized by the elimination of water not chemically associated to the silica, without causing any substantial alteration to the silica structure, this is accompanied by an endothermic peak on the DSC curve, which represents the heat absorbed when water evaporates [54].

During the second phase, which occurs between 200°C and 650°C, the mass loss is approximately 2% lower than in the first phase and is associated with the dehydroxylation of amorphous silica. The mass loss that occurs within this temperature range is due in part to the elimination of hydroxyl groups (Si-OH) from the silica surface during calcination, which occurs as water vapor. An endothermic peak, indicating heat absorption, appears in the differential scanning calorimetry (DSC) curve and is often most pronounced between 400 and 500 °C. [55,56].

During the third phase of heat treatment (650°C–916°C), mass stabilization is observed, suggesting that dehydration/dihydroxylation was completed before this temperature range. In the high-temperature range, a weak exothermic peak is observed while the mass loss remains stable in the TGA curve. This indicates that no decomposition or volatilization occurs in this region. The exothermic event is therefore

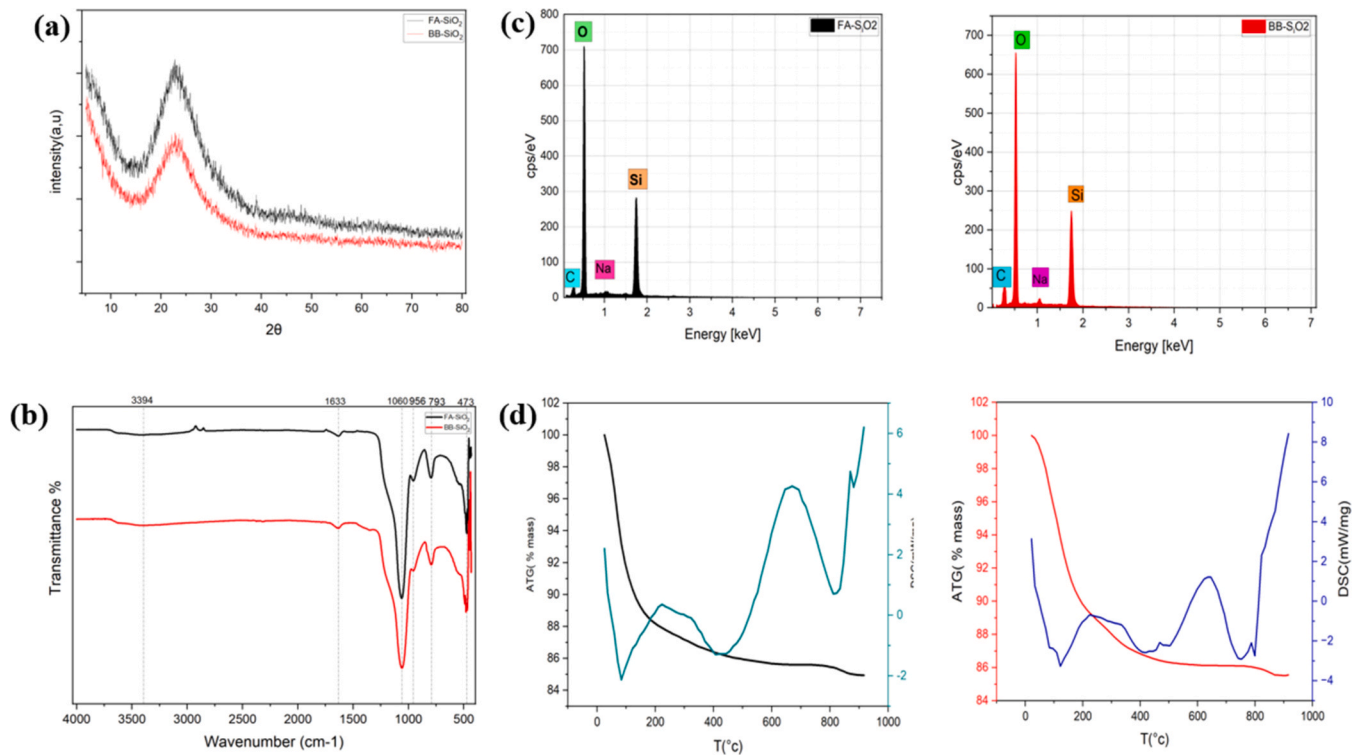


Fig. 7. Characterization of Bio-Silicas Extracted from FA and BB (a): XRD, (b): FTIR, (c) EDX, (d): TG-DSC Analysis.

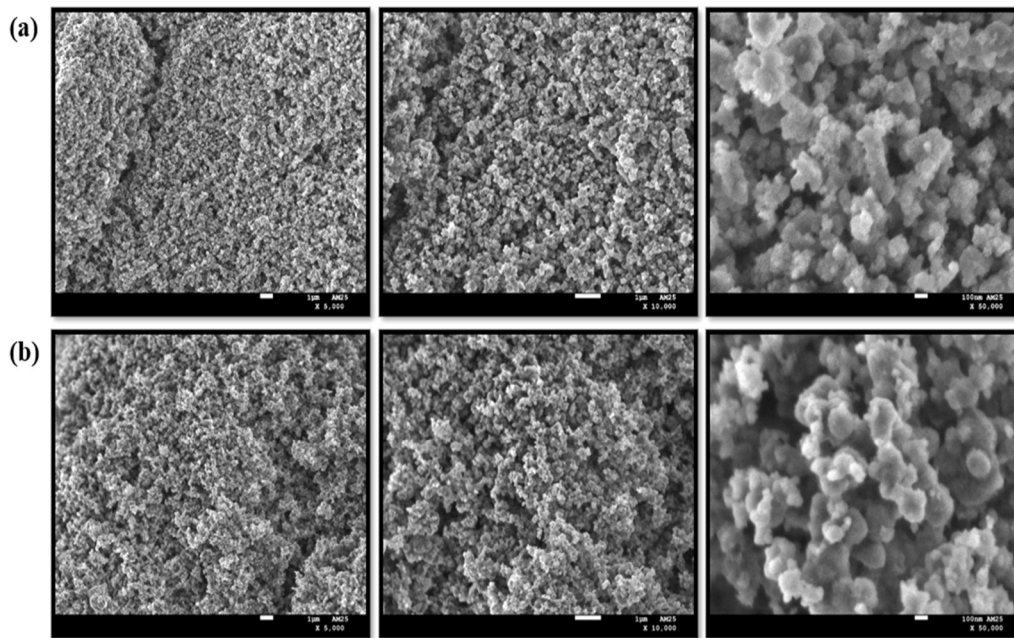


Fig. 8. SEM images of extracted silica from (a): *Festuca arundinacea* (b): barley bran.

attributed to a structural rearrangement and densification of the amorphous silica network, rather than to a crystallization process, as commonly reported for amorphous materials undergoing enthalpy release without phase transition [57].

3.2. Structural and textural properties of BioMCM-41 and MCM-41C

The mesoporous silica materials BioMCM-41FA, BioMCM-41BB, and MCM-41C demonstrate a well-ordered silica structure, as indicated by

their X-ray diffraction (XRD) patterns at low 2θ angles (1° – 10°) in Fig. 9 (a), which show the characteristic diffraction profiles of these materials, with four distinct peaks at approximately 2.3° , 4.3° , 4.6° , and 6° . The primary peak at $2\theta \approx 2.3^\circ$ is associated with the (100) reflection plane, while the peaks at 4.4° , 4.6° , and 6° correspond to the (110), (200), and (210) planes, respectively.

This pattern displays a hexagonal mesoporous structure, consistent with the findings conducted by Beck et al. [15].

The unit cell parameter (a_0) of the produced materials is obtained

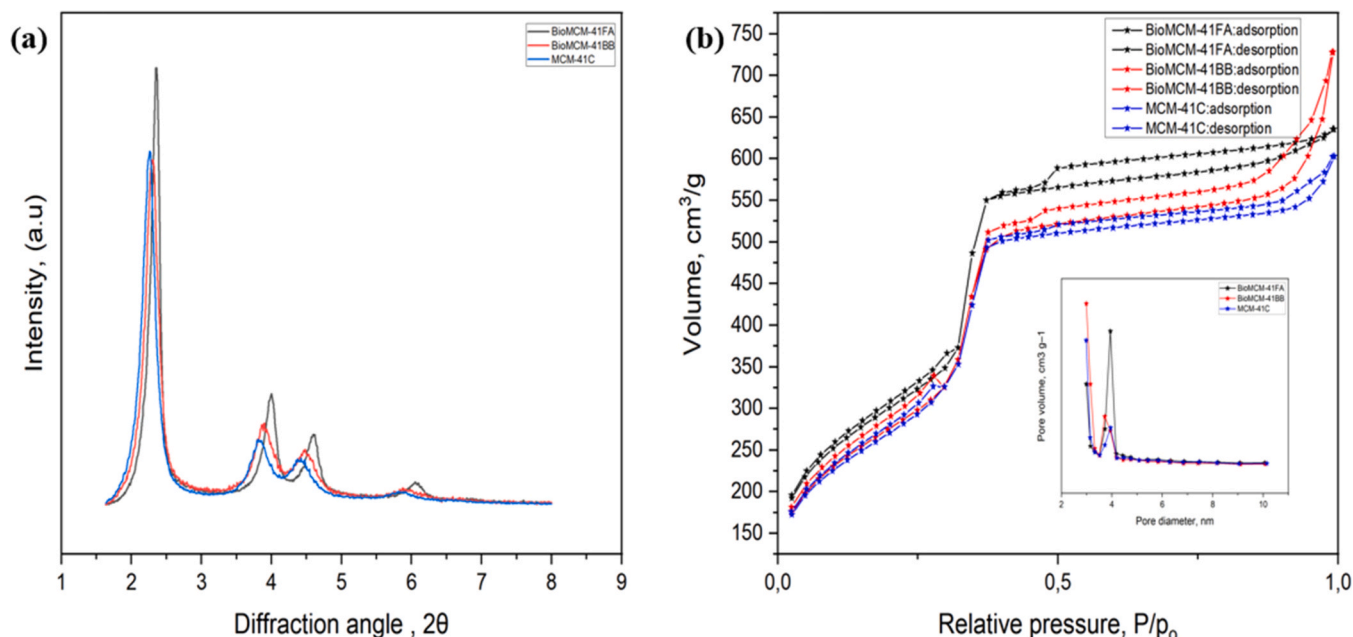


Fig. 9. Characterization of both BioMCM-41 and MCM-41C: (a): XRD, (b): N_2 adsorption-desorption, and Pore size distribution.

using Eq. (18): [58]

$$a_0 = 2d_{100} / \sqrt{3} \quad (18)$$

where a_0 is the unit cell parameter in nanometers and d_{100} is the nanometer-scale distance of the (100) plane in the hexagonal network. The unit cell measure (a_0) for BioMCM-41FA, BioMCM-41BB and MCM-41C were found to be 4.33 nm, 4.36 nm, 4.45 nm respectively (Table 3). The pore sizes can be calculated from the X-ray diffraction interplanar spacing (Fig. 6) and nitrogen isotherms (Fig. 7) using Eq. (19), as follow:

$$S = b \cdot d \sqrt{\rho V_p / (1 + V_p)} \quad (19)$$

where S is the pore size, b is a constant dependent on the assumed pore geometry and equal to 1.155 for hexagonal models, d is the XRD interplanar spacing (100), V_p is the mesoporous volume, and is the pore wall density (ca. 2.2 cm³ g⁻¹ for siliceous materials) [59]. The pore sizes of the synthesized BioMCM-41FA, BioMCM-41BB, and MCM-41C were 3.08 nm, 3.83 nm, and 2.95 nm, respectively, as determined by Eq. (19).

The mesoporous structure of the synthesized materials was also confirmed by N_2 adsorption measurements. Fig. 9(b) illustrates the N_2 adsorption-desorption isotherm and pore size distribution for the BioMCM-41FA, BioMCM-41BB and MCM-41C. The samples have a characteristic type IV isotherm and the hysteresis loops correspond to type H1, indicating that the created materials are mesoporous according to IUPAC classification [60,61].

The isotherms of the BioMCM-41FA show three distinct stages, with inflection points at $P/P_0 = 0.34$ and 0.39 .

The first stage involves monolayer and multilayer nitrogen adsorption on the mesoporous walls at low relative pressures ($P/P_0 < 0.34$). The second stage shows a significant increase in adsorption ($0.34 < P/P_0 < 0.4$). As the relative pressure increases, the isotherms indicate a rapid, sharp rise in adsorption due to capillary condensation within uniform pores. This verifies the presence of a mesoporous structure in produced silicas [62]. The third stage of the adsorption isotherm shows a progressive increase at high P/P_0 values ($0.4-0.99$) due to multilayer adsorption on particle surfaces. BioMCM-41BB exhibits three-stage adsorption at $P/P_0 < 0.321$, $0.321 < P/P_0 < 0.375$ and $0.375 < P/P_0 < 0.99$. MCM-41C displays a similar pattern with stages at $P/P_0 < 0.322$, $0.322 < P/P_0 < 0.375$, and $0.375 < P/P_0 < 0.99$. The small differences

observed in the relative pressure intervals between samples can be explained by differences in pore size and textural properties, while the adsorption mechanism remains the same. These results clearly show that well-ordered mesoporous silica structures form in all synthesized MCM-41 samples.

The BioMCM-41FA sample had a specific surface area of 1090 m²·g⁻¹, a total pore volume of 0.30 cm³·g⁻¹, and an average pore diameter of 3.9 nm. BioMCM-41BB had a specific surface area of 1081 m²·g⁻¹, a total pore volume of 0.54 cm³·g⁻¹, and an average pore diameter of 3.0 nm. MCM-41C had a specific surface area of 1042 m²·g⁻¹, a total pore volume of 0.25 cm³·g⁻¹, and an average pore diameter of 3.0 nm.

The wall thickness of the manufactured material was determined using Equation (20) [63].

$$\text{Wall thickness} = 2d_{100} / \sqrt{3} - D_{BJH} \quad (20)$$

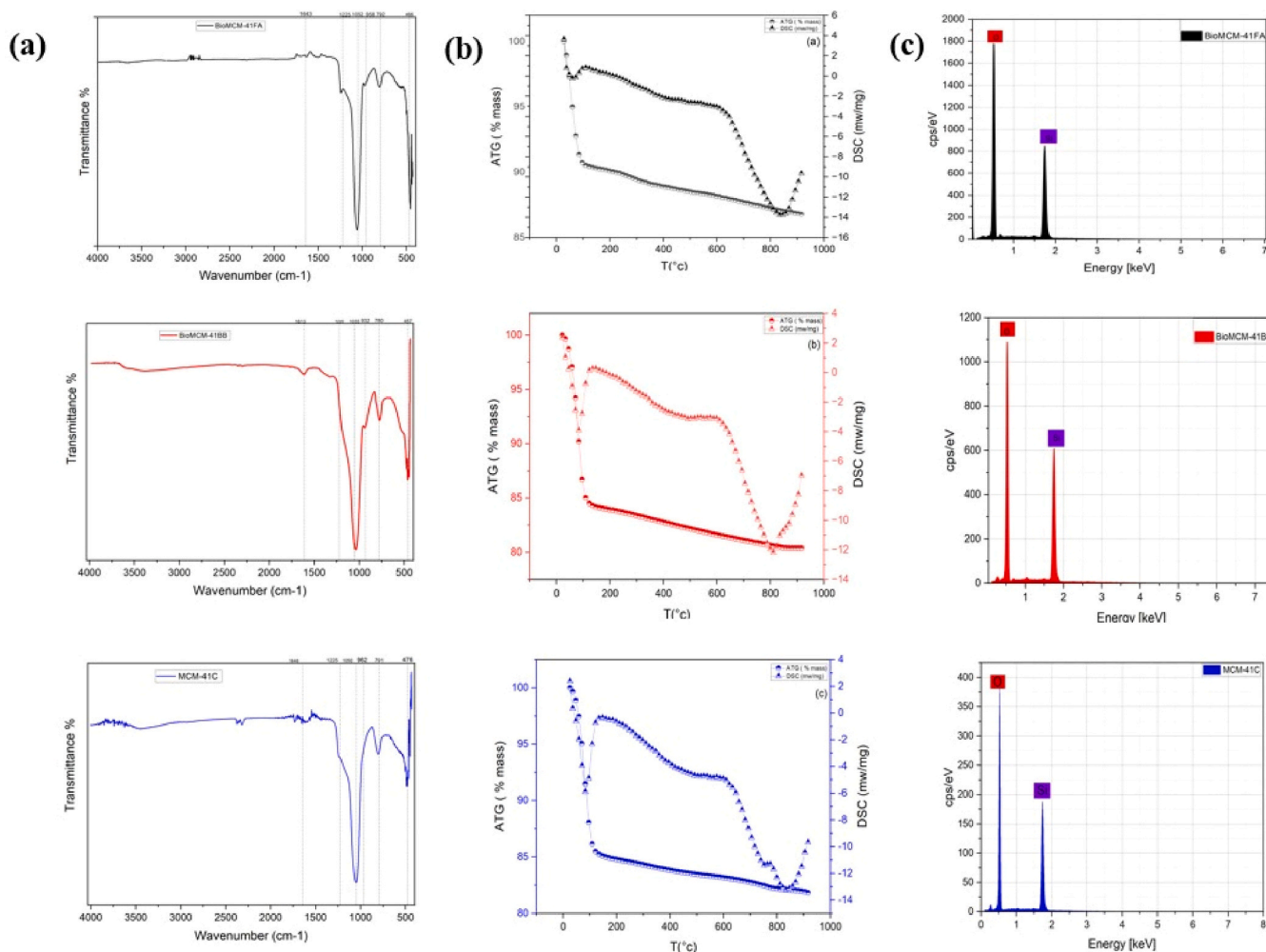
which the wall thickness of the BioMCM-41FA, BioMCM-41BB and MCM-41C were 0.43 nm 1.36, 1.45 respectively. Table 5 summarizes the physical parameters of nitrogen isotherms for the Barret-Joyner-Halenda average pore diameter (D_{BJH}), the Brunauer-Emmett-Teller surface area (S_{BET}), and the total pore volumes (V_{total}) of Bio MCM-41 with a selection of the published literature.

Fig. 10(a) shows the FTIR spectra of BioMCM-41FA, BioMCM-41BB, and MCM-41C in the wavenumber area 450–4000 cm⁻¹. The structures of these materials appear identical based on FTIR spectra, although the peaks show slight shifts in position across the different samples. However, the minor variations in band position indicate that no significant structural differences are present among the examined materials. The samples spectra showed bands typical of the symmetric and asymmetric stretching vibrations of the (Si-O-Si) groups, with frequencies in the ranges of approximately 806 cm⁻¹, 1055 cm⁻¹, and 1243 cm⁻¹. These bridges are the patterns of silicate polymers produced during hydrothermal treatment [68]. In the range of 1629 cm⁻¹, there was a minor transmittance peak caused by the vibration of H-O-H bonds [61]. The bending mode of Si-O-Si is attributed to the band at around 456 cm⁻¹ [69]. A weak band close to 958 cm⁻¹ likely arises from Si-OH stretching. The disappearance of the organic bands confirms the complete removal of surfactants after calcination. Furthermore, the thermal stability and structural integrity of the samples are confirmed by the

Table 5

Textural properties of BioMCM-41FA, BioMCM-41BB and MCM-41C.

Sample	N ₂ adsorption–desorption			XRD			TEM	Ref
	S _{BET} (m ² g ^{−1})	V _{total} (cm ³ g ^{−1})	Pore diameter (nm)	d ₁₀₀ (Å)	a ₀ (nm)	Wall thickness (nm)	pore diameter (nm)	
BioMCM-41FA	1090	0.30	3.9	3.75	4.33	0.43	4.0	This study
BioMCM-41BB	1081	0.54	3.0	3.78	4.36	1.36	3.1	This study
MCM-41C	1042	0.25	3.0	3.86	4.45	1.45	2.6	This study
MCM-41	973	0.87	2.7	-	3.11	1.66	2.3	[55]
MCM-41	901	0.72	3.2	-	4.30	1.09	-	[64]
MCM-41	848	0.84	3.2	4.39	5.07	1.66	3.2	[65]
MCM-41	1028	1.69	2.4	-	4.4	1.92	-	[66]
MCM-41	856	0.56	2.9	3.8	-	1.80	-	[67]

**Fig. 10.** Characterization of BioMCM-41FA, BioMCM-41BB and MCM-41C, using (a) FTIR, (b) TGA-DSC, and (c) EDX analysis.

continued presence of the characteristic silica bands, even after the calcination process.

The thermal stability of MCM41 mesoporous materials was investigated using a TGA-DSC analysis (Fig. 10(b)).

The TGA curve revealed two distinct weight-loss stages at 25–150 °C and 150–950 °C [16,70], corresponding to the removal of adsorbed water and the condensation of silanol groups, respectively. Weight loss (9.4%) in the first stage is due to the desorption of adsorbed water molecules and is accompanied by a small exothermic peak.

Weight loss (3.7%) in the second stage is due to the loss of water molecules produced by silanol group condensation. Thus, a thermally stable silica network forms, indicating the absence of decomposition of

Table 6

Chemical composition of BioMCM-41FA, BioMCM-41BB, and MCM-41C.

Component	BioMCM-41FA	BioMCM-41BB	MCM-41C
(%)			
SiO ₂	99.4	98.5	98.8
Al ₂ O ₃	0.26	0.94	0.79
K ₂ O	0.08	0.08	-
CaO	0.06	0.05	0.06
Fe ₂ O ₃	0.05	0.15	0.13
ZnO	0.03	0.04	0.02
P ₂ O ₅	0.13	-	-
Cl	-	0.18	0.09
Others	0.02	0.05	0.03

significant residual organic at these temperatures, so confirming the surfactant successful removal [56,71].

Table 6 presents the chemical composition of the three MCM-41 samples, namely the two bio-MCM-41 materials and the commercial MCM-41. The composition is reported in terms of the contents of the major oxides (SiO_2 , Al_2O_3 , K_2O , CaO , Fe_2O_3 , ZnO , and P_2O_5) together with Cl content.

According to XRF analysis (Table 6), the BioMCM-41FA, BioMCM-41BB, and MCM-41C materials are mostly composed of silica (SiO_2), with trace amounts of iron oxide (Fe_2O_3), potassium oxide (K_2O), calcium oxide (CaO), zinc oxide (ZnO), phosphorus pentoxide (P_2O_5), b, and alumina (Al_2O_3). These elements, which are common in plant-derived materials, are present at trace levels and are unlikely to affect MCM-41 fundamental characteristics, such as its adsorption capacity or mesoporous structure.

SEM images (Fig. 11(a-c)) of BioMCM-41FA and BioMCM-41BB and MCM-41C exhibited spherical particle morphology, consistent with the characteristics of MCM-41 mesoporous materials [72], with diameters ranging from 350 nm to 1300 nm.

The EDX results (Fig. 10(c)) showed that oxygen and silicon were the primary elements present, as expected, since they are the main components of the MCM-41 framework. The studies did not reveal potassium (K) or iron (Fe) from K_2O and Fe_2O_3 , which XRF had detected in the silica taken from the biomasses. These elements were removed during washing with distilled water, so they did not participate in the formation of the bioMCM-41 structure [73].

To complement the XRD and N_2 physisorption analyses and to examine the internal morphology and structural features of our BioMCM-41FA, BioMCM-41BB, and MCM-41C, transmission electron microscopy (TEM) characterization was performed. Figs. 12(a-c) and 13 shows standard TEM pictures of the bioMCM-41 from both plants and MCM-41C.

The images clearly reveal the well-defined hexagonal ordering of the mesopores, indicative of a uniform, highly organized porous structure. The results of this study are very similar to those of another study on MCM-41 [74,75], with well-defined pores, with average pore sizes of

approximately 4 nm for BioMCM-41FA, 3.1 nm for BioMCM-41BB, and 2.6 nm for MCM-41C. This value is in close agreement with pore sizes determined by XRD and N_2 adsorption measurements, confirming the successful formation of high-quality MCM-41 from *Festuca arundinacea* and barley bran [64]. XRD, N_2 adsorption, and TEM analyses confirm a mesoporous structure consistent with the IUPAC definition of mesopores (2–50 nm) as observed in porosimetry measurements. The figures demonstrate a highly ordered mesoporous structure typical of M41S-type materials.

The structural and surface characterization results provide important information for anticipating the potential adsorption behavior of the synthesized materials. FTIR analysis confirmed the presence of abundant surface silanol groups (Si-OH), while XRF and EDX analyses demonstrated the high purity of the silica framework. In addition, XRD, TEM and N_2 adsorption–desorption analyses showed a highly ordered hexagonal mesoporous structure associated with very high specific surface areas exceeding $1000 \text{ m}^2 \text{ g}^{-1}$. Such characteristics are generally recognized as favorable for adsorption applications, as they can facilitate the diffusion of adsorbate molecules within the pore network and increase the availability of accessible surface sites. Based on these structural and chemical features, BioMCM-41 materials are expected to exhibit promising adsorption properties. The influence of these characteristics on methylene blue removal is examined in the following section.

3.3. Sustainability comparison of silica precursors

To better contextualize the sustainability potential of the proposed approach, a qualitative comparison between conventional silica precursors and FA/BB-derived bio-silica is presented in Table 7. This comparison considers the silica source, raw material cost, waste valorization potential, renewability of the feedstock, silica purity, and environmental benefit. It should be noted that this comparison is not intended to replace a comprehensive techno-economic or life-cycle assessment, which was beyond the scope of this study. Rather, it provides an indicative evaluation showing that using *Festuca arundinacea*

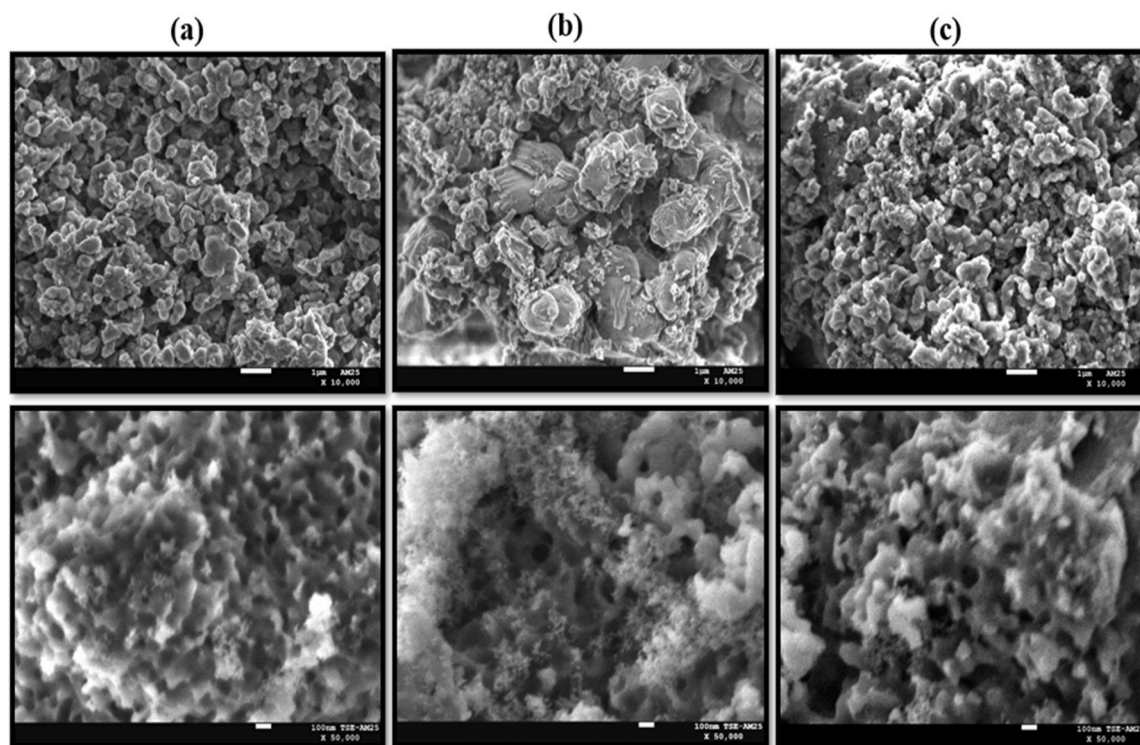


Fig. 11. SEM images of (a). BioMCM-41FA (b). BioMCM-41BB (c). MCM-41C.

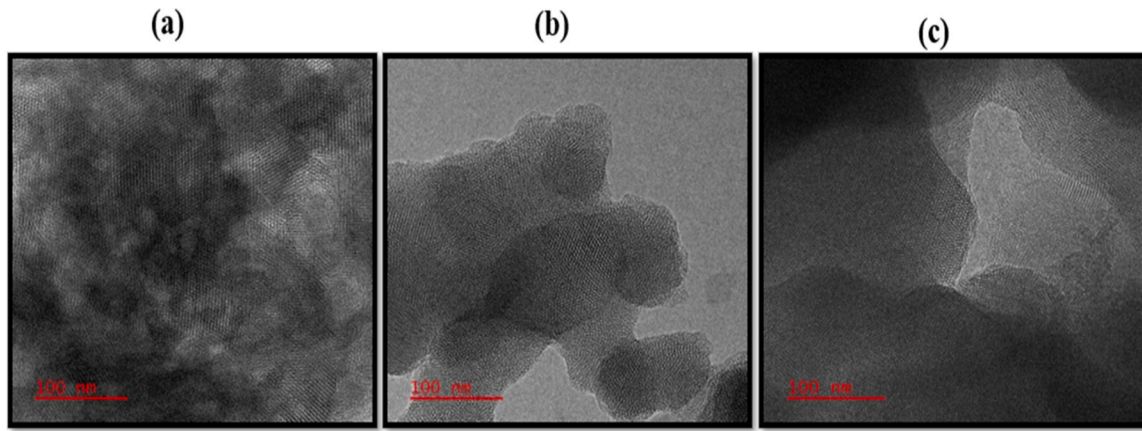


Fig. 12. TEM images of (a). BioMCM-41FA (b). BioMCM-41BB (c). MCM-41C.

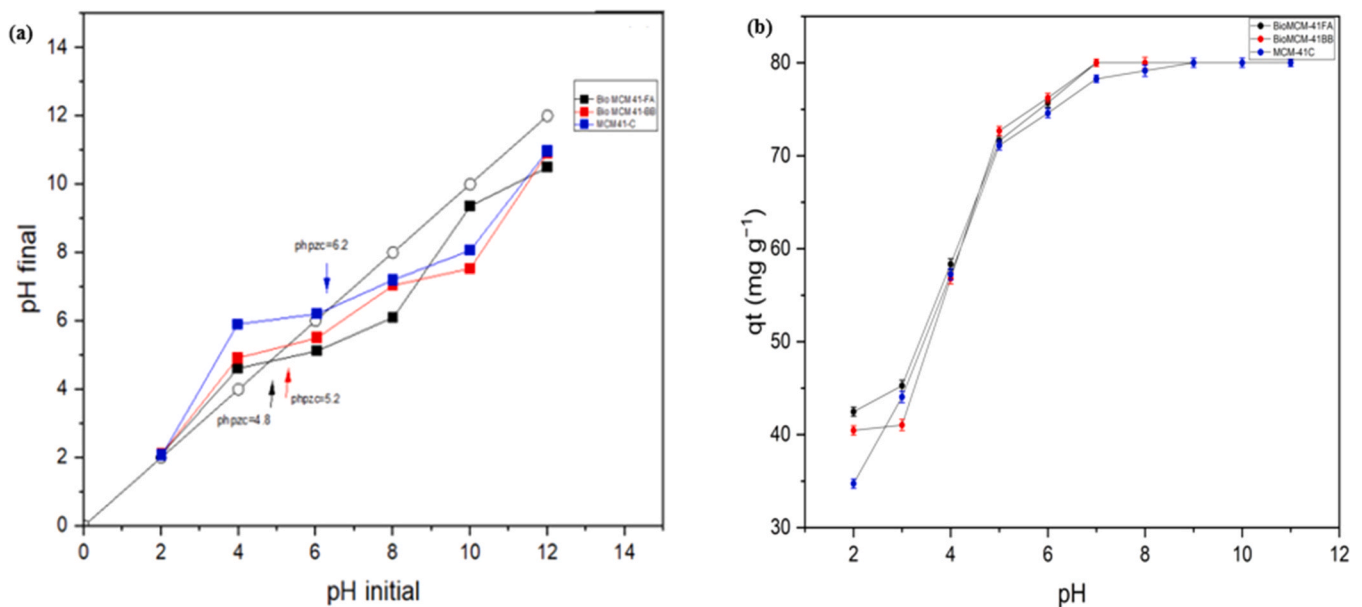


Fig. 13. (a) Determination of the point of zero charge (pH_{pzc}) of the MCM-41 materials and (b) effect of initial pH on MB adsorption capacity onto BioMCM-41FA, BioMCM-41BB, and MCM-41C. Conditions for (b): $pH = 2-11$, $C_0 = 20 \text{ mg L}^{-1}$, $m = 12.5 \text{ mg}$, $V = 50 \text{ mL}$, $v = 210 \text{ rpm}$, and $T = 25^\circ \text{C}$.

Table 7
Sustainability comparison of conventional silica precursors and FA/BB-derived bio-silica.

Parameter	TEOS route	Commercial sodium silicate	Bio-silica FA/BB
Silica source	Synthetic	Industrial	Agricultural waste
Raw material cost	High	Moderate	Very low
Waste valorization	No	No	Yes
Renewable feedstock	No	No	Yes
Silica purity / Si-O content	100.% Si + O by EDX [76]	100.% Si + O by EDX [76]	98.8–99.2% SiO ₂ by XRF
Additional environmental benefit	None	Limited	Agricultural waste recycling

and barley bran as bio-silica sources offers a means to recover value from agricultural residues while reducing dependence on conventional synthetic or industrial silica precursors.

3.4. Effect of operational parameters on MB adsorption

The pH of the sample influences all adsorption processes, particularly for dyes, as it determines the strength of electrostatic interactions at the adsorbent surface. When the pH is optimal, the adsorbent can sequester a greater quantity of dye molecules, as its surface possesses the appropriate electrostatic charge to interact with charged dye molecules, which may exhibit negative and positive charges, when dissolved and partially ionized in water [77].

The effect of initial pH on the equilibrium adsorption capacity of MB using three adsorbents, BioMCM-41FA, BioMCM-41BB, and MCM-41C, was examined across a pH range of 2–11 (Fig. 12 (b)).

At pH 2, the removal efficiency of MB was very low, but it gradually increased as pH increased. This low adsorption of MB at acidic pH is likely due to the competition between H^+ ions and the positively charged dye molecules for adsorption sites. The increase in MB adsorption capacity with increasing pH suggests the formation of more Si–O[−], resulting from the deprotonation of silanol groups, which leads to a strong electrostatic interaction between the MB dye ion and the adsorbent [78].

Additionally, the pH_{pzc} corresponds to the pH at which the net

charge on the material surface is zero. This parameter is very important for understanding the adsorbate–adsorbent interactions in a solution of a given pH. According to Fig. 12(a), the values of pH_{PZC} are 6.2, 5.2, and 4.8 for MCM-41C, BioMCM-41BB, and BioMCM-41FA, respectively.

These values indicate that when the pH was lower than the point of zero charge ($pH < 6.2, 5.2, 4.8$), the overall surface charge on BioMCM-41 was positive, thereby decreasing the removal efficiency of cationic dyes such as MB. On the other hand, when the pH was above the point of zero charge ($pH > 6.2, 5.2, \text{ or } 4.8$), the surface became negatively charged, thereby enhancing the removal efficiency of cationic dyes.

The superior adsorption performance of BioMCM-41 materials can be explained by the combined effect of their surface chemistry and textural properties. FTIR spectra revealed the presence of abundant silanol groups (Si–OH) on the silica surface. When the solution pH exceeds the pH_{PZC} , these groups become progressively deprotonated, generating negatively charged siloxide species (Si–O[−]) that act as active adsorption sites for cationic methylene blue molecules via electrostatic attraction. Furthermore, the very high specific surface areas of BioMCM-41FA ($1090 \text{ m}^2 \text{ g}^{-1}$) and BioMCM-41BB ($1081 \text{ m}^2 \text{ g}^{-1}$), together with their ordered mesoporous channels confirmed by XRD and TEM analyses, facilitate the diffusion of dye molecules and increase the accessibility of adsorption sites. Consequently, the adsorption process results from the synergistic contribution of surface functional groups, favorable surface charge and well-developed mesoporosity, leading to the near-complete removal of methylene blue.

To study the effect of the adsorbent dose of mesoporous silica materials on the adsorption of methylene blue (MB), different doses ranging from 2.5 mg to 15 mg were tested. The results (Fig. 14(a)) show that the adsorption efficiency exhibited a linear rise with the augmentation of the adsorbent quantity, reaching maximum efficiency at 12.5 mg. As the amount of adsorbent rises, the number of binding sites also increases, which means that the adsorption capacity increase [79]. However, increasing the adsorbent dosage beyond 12.5 mg did not lead to any significant improvement in dye removal, indicating that this amount is sufficient to adsorb nearly all the methylene blue present in the solution. Therefore, the adsorption process becomes limited by the initial dye concentration rather than the availability of adsorption sites.

The effect of the ionic strength on the adsorption capacity (q_e) of BioMCM-41FA BioMCM-41BB, MCM-41C was investigated.

Fig. 14(b) shows that increasing the ionic strength from 0 to 200 mg/

L results in only a slight decrease in the adsorption capacity of the three MCM-41 materials. This small variation can be attributed to the low NaCl concentration, which does not generate significant ionic competition between Na⁺ ions and the adsorbate for active sites, nor an electrostatic screening effect large enough to significantly affect the adsorption process.

Stirring speed was varied from 100 to 300 rpm. Adsorption capacity increases between 100 and 210 rpm (Fig. 14(c)), indicating improved external mass transfer from a thinner boundary layer around the MCM-41 particles.

No significant improvement in adsorption occurs above 210 rpm, indicating that mass transfer equilibrium has been reached and higher stirring speeds do not enhance process efficiency. Therefore, 210 rpm is considered optimal, providing adequate mixing without causing excessive hydrodynamic disturbances or desorption.

3.5. Adsorption kinetics

Kinetic experiments were performed to investigate the effect of contact time on MB adsorption over 0–180 min at a fixed solution pH, with an initial MB concentration of 20 mg L^{-1} and an adsorbent mass of 12.5 mg. Contact time is a critical factor in adsorption kinetics, as it influences both the removal efficiency and the interactions between the adsorbent and the adsorbate [80]. Optimizing this parameter helps to understand the adsorption mechanism of methylene blue better and to assess the adsorption performance of BioMCM-41-based materials.

Fig. 15(a) presents the evolution of MB removal efficiency (%) as a function of contact time. The experimental data were fitted using conventional kinetic models, namely pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models. The corresponding kinetic parameters are summarized in Table 5, while the fitting curves are illustrated in Fig. 15 (b–d).

As shown in Fig. 15(a), MB removal efficiency increased rapidly during the first few minutes of contact, particularly within the first 15 min, and reached its maximum after approximately 45 min. The adsorption process can be divided into three distinct phases. The first phase, from 0 to 15 min, corresponds to a rapid adsorption stage, mainly due to the availability of numerous vacant active sites on the BioMCM-41 and MCM-41C surface. In addition, the ordered mesoporous structure of the material facilitates the rapid diffusion of MB molecules into the

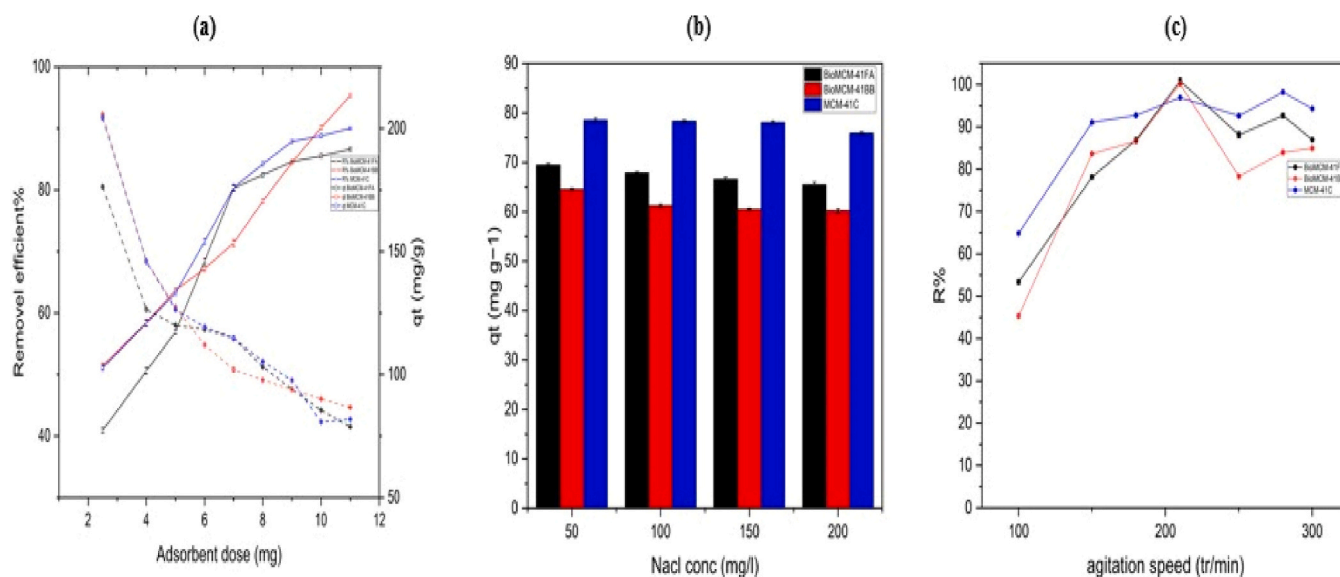


Fig. 14. Effects of (a) adsorbent dosage, (b) ionic strength, and (c) agitation speed on MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C. Common conditions: $C_0 = 20 \text{ mg L}^{-1}$, $V = 50 \text{ mL}$, $pH = 6.42$, and $T = 25^\circ \text{C}$; (a) $m = 2.5\text{--}15 \text{ mg}$ and $v = 210 \text{ rpm}$; (b) $\text{NaCl} = 50\text{--}200 \text{ mg L}^{-1}$, $m = 12.5 \text{ mg}$, and $v = 210 \text{ rpm}$; (c) $v = 100\text{--}300 \text{ rpm}$ and $m = 12.5 \text{ mg}$.

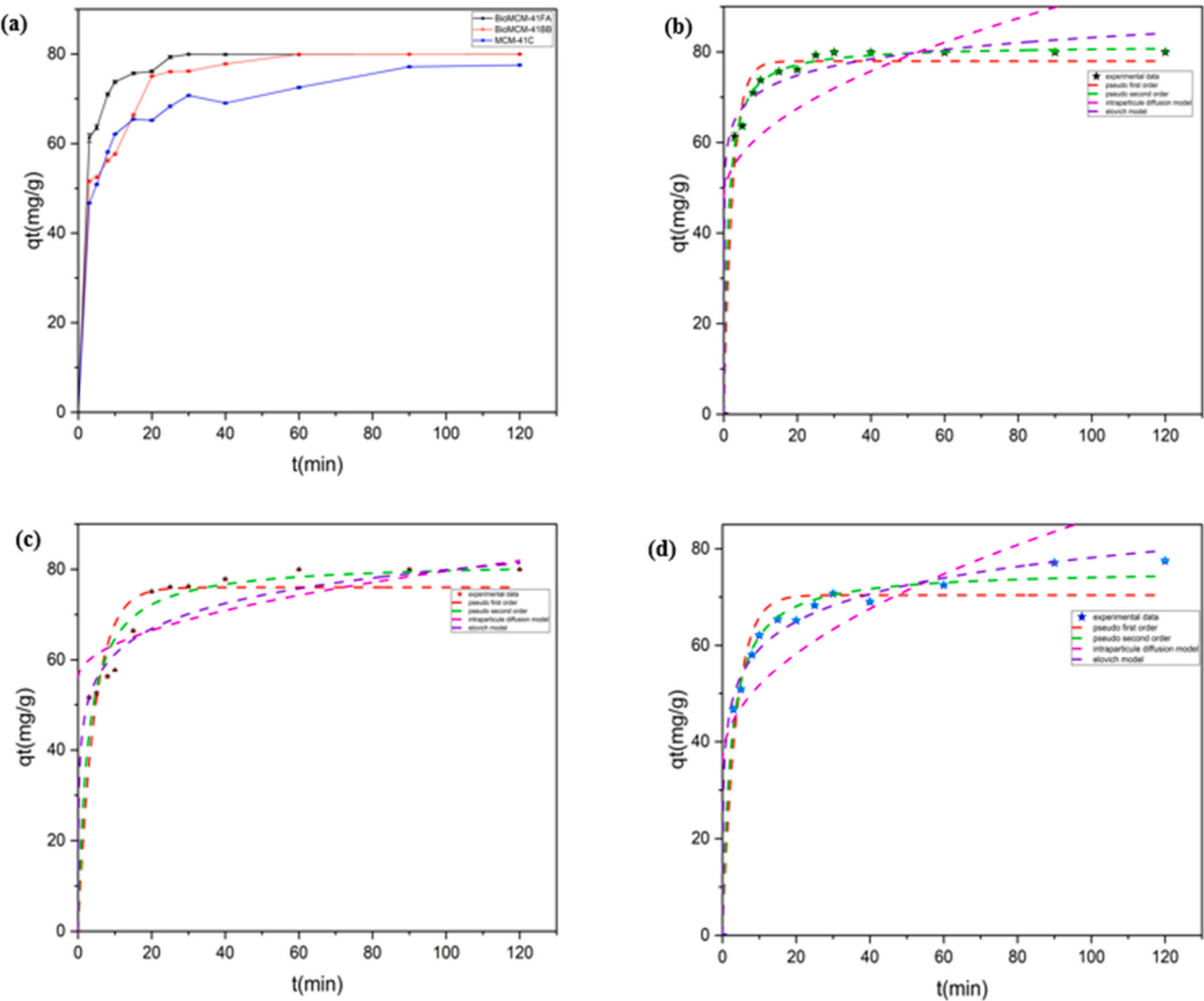


Fig. 15. (a) Effect of contact time and (b–d) nonlinear kinetic model fitting for MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. Conditions: $C_0 = 20 \text{ mg L}^{-1}$, $m = 12.5 \text{ mg}$, $V = 50 \text{ mL}$, $\text{pH} = 6.42$, $v = 210 \text{ rpm}$, and $T = 25^\circ \text{C}$.

internal pores, as reported in previous studies on mesoporous adsorbents [81]. During this stage, external film diffusion plays an important role in the initial uptake of MB molecules [82].

The second phase, from 15 to 30 min, is characterized by a gradual decrease in the adsorption rate, which can be attributed to the progressive occupation of active sites and the reduction of the concentration gradient between the solution and the adsorbent surface. In the third phase, after 30 min, the adsorption rate becomes nearly constant and reaches a plateau, indicating that most available adsorption sites are occupied and that equilibrium is approached. This behavior is consistent with similar adsorption profiles reported in the literature, where adsorption equilibrium is reached after the saturation of active sites on the adsorbent surface [83].

The maximum experimental adsorption capacity was $q_{e,\text{exp}} = 80 \text{ mg g}^{-1}$ for both BioMCM-41 materials, while MCM-41C exhibited a slightly lower value of 77.29 mg g^{-1} . This result indicates that the bio-based MCM-41 adsorbents provide slightly improved adsorption performance, probably due to their favorable surface properties and accessible mesoporous structure.

The kinetic parameters obtained from the different models are presented in Table 8. The pseudo-first-order model showed a relatively good fit for BioMCM-41FA and MCM-41C, with correlation coefficients

Table 8
Kinetic model parameters for MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C ($C_0 = 20 \text{ mg L}^{-1}$, $m = 12.5 \text{ mg}$, $V = 50 \text{ mL}$, $\text{pH} = 6.42$, $v = 210 \text{ rpm}$, and $T = 25^\circ \text{C}$).

Model	Parameter	BioMCM-41FA	BioMCM-41BB	MCM-41C
Pseudo-first-order	$q_{\text{exp}} (\text{mg} \cdot \text{g}^{-1})$	80	80	77.29
	$K_1 (\text{min}^{-1})$	0.43	0.23	0.273
	$q_{e,\text{cal}} (\text{mg} \cdot \text{g}^{-1})$	78.02	75.71	70.55
	R^2	0.97	0.89	0.95
Pseudo-second-order	$K_2 (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.011	0.004	0.005
	$q_{e,\text{cal}} (\text{mg} \cdot \text{g}^{-1})$	81.44	81.39	75.86
	R^2	0.99	0.96	0.98
Intraparticle diffusion	$K_{\text{diff}} (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})$	4.41	5.43	5.03
	$c (\text{mg} \cdot \text{g}^{-1})$	47.97	37.48	35.9
	R^2	0.40	0.59	0.60
Elovich	$\alpha (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	792362	828.1	1145.4
	$\beta (\text{g} \cdot \text{mg}^{-1})$	0.199	0.108	0.12
	R^2	0.98	0.95	0.98

of 0.97 and 0.95, respectively. However, a lower correlation coefficient was obtained for BioMCM-41BB ($R^2 = 0.89$), indicating that this model does not adequately describe the adsorption kinetics for all the studied materials. In addition, the calculated adsorption capacities obtained from the pseudo-first-order model were 78.02, 75.71, and 70.55 mg g^{-1} for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. These values are lower than the experimental capacities of 80, 80, and 77.29 mg g^{-1} , suggesting that the pseudo-first-order model is not the most suitable model for describing MB adsorption onto the synthesized materials.

In contrast, the pseudo-second-order model provided the best agreement with the experimental data for all adsorbents. The correlation coefficients were 0.99, 0.96, and 0.98 for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. Moreover, the calculated adsorption capacities obtained from this model, 81.44, 81.39, and 75.86 mg g^{-1} , were very close to the experimental values. This good agreement indicates that the adsorption rate is strongly related to the availability of active sites and the interactions between MB molecules and the adsorbent surface. However, the good fit of the pseudo-second-order model should not be considered as direct evidence of a purely chemisorption-controlled process, since this model can also describe adsorption systems governed by physical interactions and surface-controlled uptake processes. [84,85].

The intraparticle diffusion model was also applied to evaluate the contribution of diffusion to the adsorption mechanism. The obtained correlation coefficients were relatively low, with R^2 values of 0.40, 0.59, and 0.60 for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. These results indicate that intraparticle diffusion is not the only rate-limiting step in the adsorption process. The non-zero intercept values, 47.97, 37.48, and 35.90 mg g^{-1} , also suggest the contribution of boundary-layer diffusion during MB adsorption. Therefore, the adsorption mechanism likely involves several successive steps, including external film diffusion, diffusion of MB molecules into the mesoporous channels, and final adsorption onto the internal active sites [86,87].

The Elovich model also showed good fitting for BioMCM-41FA and MCM-41C, with R^2 values of 0.98, and an acceptable fit for BioMCM-41BB, with $R^2 = 0.95$. This indicates that heterogeneous surface interactions may contribute to MB adsorption. The high α values suggest a rapid initial adsorption rate, especially for BioMCM-41FA, whereas the β values reflect the progressive decrease in adsorption rate as the available active sites become occupied. Nevertheless, the pseudo-second-order model remains the most appropriate model for describing the overall adsorption kinetics of MB onto BioMCM-41FA, BioMCM-41BB, and MCM-41C.

This result is consistent with previous studies on MB adsorption onto MCM-41-based materials, in which the pseudo-second-order model was also found to best describe the adsorption kinetics, particularly for NiO/MCM-41 and Al-MCM-41 adsorbents [88] [89]. Similar behavior has also been reported for other porous adsorbents, where intraparticle diffusion was involved in the adsorption process but was not the only rate-limiting step [90].

3.6. Adsorption isotherm

According to the classification of Giles et al. [91], the isotherms obtained by plotting (q_e) as a function of (C_e) exhibit an (L) type profile, indicating a high affinity between MB molecules and the adsorbent surface, especially at low equilibrium concentrations. This behavior suggests that MB adsorption is favorable and that the available active sites are progressively occupied as the dye concentration increases.

The experimental equilibrium data were fitted using four commonly applied isotherm models, namely Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R). These models have been widely used to describe MB adsorption onto mesoporous silica-based adsorbents, including MCM-41 and related materials, in order to evaluate monolayer adsorption capacity, surface heterogeneity, adsorption energy, and the

nature of adsorbate–adsorbent interactions [92]. The adsorption parameters were calculated using a nonlinear optimization method, and the obtained results are summarized in Table 9 and illustrated in Fig. 16.

The Langmuir model showed satisfactory fitting for BioMCM-41FA and MCM-41C, with ($R^2 = 0.95$), while BioMCM-41BB showed a slightly lower correlation coefficient of ($R^2 = 0.92$). Based on this model, the maximum monolayer adsorption capacities (q_m) were 186.23, 104.83, and 179.71 mg.g^{-1} for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. These values confirm the high adsorption potential of the synthesized mesoporous materials toward MB, particularly BioMCM-41FA and MCM-41C. Comparable adsorption behavior has been reported for MB removal using Al-MCM-41 and MCM-41-based adsorbents, confirming the strong potential of ordered mesoporous silica materials for the removal of cationic dyes [88,93].

However, the Freundlich model provided a better description of the adsorption equilibrium, especially for BioMCM-41FA and BioMCM-41BB, with (R^2) values of 0.98 and 0.99, respectively. For MCM-41C, the Freundlich model also showed an acceptable fit, with ($R^2 = 0.94$). This indicates that MB adsorption does not occur exclusively as a homogeneous monolayer process, but rather involves heterogeneous adsorption sites with different adsorption energies. The values of ($1/n$), namely 0.93, 0.11, and 0.437 for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively, are lower than 1, confirming the favorable nature of MB adsorption onto the studied materials. The particularly low ($1/n$) value obtained for BioMCM-41BB suggests a more favorable adsorption behavior at low MB concentrations and reflects the heterogeneous nature of the adsorption surface [94].

The Temkin model also showed very good fitting, with (R^2) values of 0.99, 0.98, and 0.95 for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. This model assumes that the heat of adsorption decreases progressively with increasing surface coverage due to adsorbate–adsorbent interactions. The good agreement obtained with the Temkin model suggests that MB molecules interact with energetically heterogeneous surface sites and that the adsorption energy decreases as the most active sites become progressively occupied. Such behavior is consistent with adsorption onto mesoporous silica materials, where surface silanol groups, silanolate sites, and accessible pores contribute to dye retention through electrostatic attraction, hydrogen bonding, and pore filling.

The D–R model was further applied to evaluate the nature of the adsorption process. The calculated mean adsorption energies were 0.258, 1.042, and 0.433 kJ mol^{-1} for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively. Since all these values are lower than 8 kJ mol^{-1} , the adsorption process can be mainly associated with physisorption [95]. This result agrees with previous studies on MB adsorption onto mesoporous silica-based adsorbents, where low D–R

Table 9

Parameters of the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models for MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C ($V = 50 \text{ mL}$, $\text{pH} = 6.42$, $v = 210 \text{ rpm}$, and $T = 25 \text{ }^\circ\text{C}$).

Isotherm	Parameters	BioMCM-41FA	BioMCM-41BB	MCM-41C
Langmuir	$q_m (\text{mg. g}^{-1})$	186.23	104.83	179.71
	$K_l (\text{l. mg}^{-1})$	0.3	3.39	0.45
	R^2	0.95	0.92	0.95
Freundlich	$K_f (\text{mg. g}^{-1})$	31.74	83.42	63.63
	$1/n$	0.93	0.11	0.437
	R^2	0.98	0.99	0.94
Temkin	B	91.56	10.24	44.31
	$K_t (\text{l. mg}^{-1})$	0.00088	3.33	0.00345
	R^2	0.99	0.98	0.95
Dubinin-Radushkevich	$\beta \cdot 106 / \text{mol}^2$	7.49	0.46	2.66
	J^{-2}	167.35	99.84	113.17
	$q_{D-R} / \text{mg g}^{-1}$	0.258	1.042	0.433
	$E / \text{kJ mol}^{-1}$	0.99	0.85	0.96
	R^2			

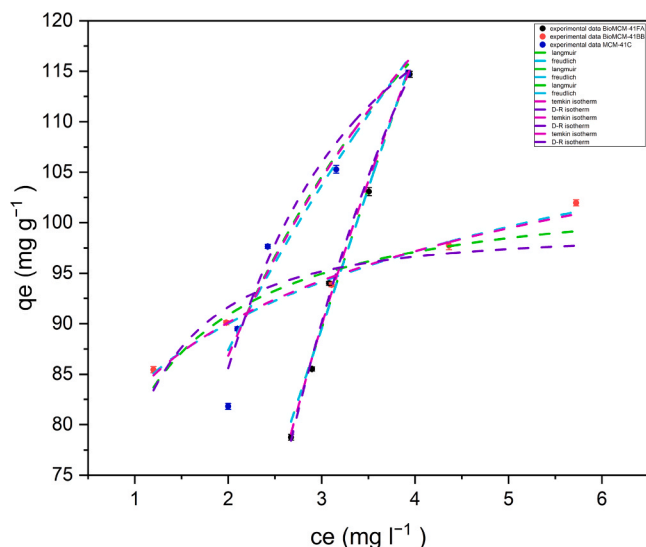


Fig. 16. Experimental adsorption data and nonlinear fitting to the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models for MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C. Conditions: $V = 50$ mL, $pH = 6.42$, $v = 210$ rpm, and $T = 25$ °C.

adsorption energy values were used to support a physical adsorption mechanism [92]. However, this does not exclude the contribution of electrostatic interactions and hydrogen bonding, which are expected due to the presence of surface silanol and silanolate groups on the MCM-41-based materials.

Overall, the isotherm analysis confirms that MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C is favorable and occurs on energetically heterogeneous surfaces. The good fitting of the Freundlich and Temkin models, together with the low adsorption energy obtained from the D–R model, suggests that the adsorption mechanism involves heterogeneous surface interactions, progressive occupation of active sites, and physical adsorption within the ordered mesoporous structure. These findings support the proposed adsorption mechanism, in which mesoporous accessibility, surface silanol/silanolate groups, electrostatic attraction, hydrogen bonding, and pore filling act together to enhance MB adsorption.

3.7. Adsorption mechanism

Multiple adsorption mechanisms, including electrostatic attraction, hydrogen bonding, pore filling, and surface interactions, may contribute to the removal of dye molecules by solid adsorbents in aqueous solutions. In the present study, the adsorption of the cationic dye methylene blue (MB) onto BioMCM-41FA, BioMCM-41BB, and MCM-41C is mainly attributed to the combined effects of surface chemistry and mesoporous accessibility. The ordered mesoporous structure of MCM-41-based materials provides accessible channels and a high number of available adsorption sites, facilitating the diffusion and retention of MB molecules inside the pore network.

The pH-dependent adsorption behavior indicates that electrostatic attraction plays a major role in MB uptake. At higher pH values, surface silanol groups (Si–OH) are progressively deprotonated into negatively charged silanolate groups (Si–O[−]), which strongly interact with the cationic MB⁺ molecules [96]. This interpretation is consistent with previous studies on MB adsorption onto mesoporous silica-based materials, where the increase in adsorption capacity at higher pH was attributed to the formation of negatively charged Si–O[−] sites on the silica surface. In addition, hydrogen bonding may occur between surface silanol groups and the nitrogen-containing groups of MB, further contributing to dye retention [97].

The kinetic, isotherm, and thermodynamic results support this

proposed mechanism. The good fitting of the pseudo-second-order model suggests that the adsorption rate is strongly related to the availability of active sites and surface interactions, while the intraparticle diffusion analysis indicates that MB adsorption is not controlled by a single diffusion step, but involves external diffusion, diffusion inside the mesoporous channels, and final adsorption on internal active sites. Moreover, the good agreement with the Freundlich and Temkin models confirms the heterogeneous nature of the adsorption surface. In contrast, the low adsorption energies obtained from the Dubinin–Radushkevich model and the negative enthalpy values indicate that physical interactions contribute significantly to the adsorption process. Therefore, the overall adsorption mechanism can be described as a synergistic process involving external diffusion, intraparticle diffusion, electrostatic attraction, hydrogen bonding, and pore filling within the ordered mesoporous structure.

To further clarify the proposed adsorption mechanism, a schematic illustration was added, showing the main steps involved in MB adsorption, including diffusion, electrostatic attraction, hydrogen bonding, and pore filling (Fig. 17).

3.8. Thermodynamic analysis

The effect of temperature on methylene blue adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C is shown in Fig. 18(a). The adsorption capacity decreased as the temperature increased from 30 to 70 °C, indicating that the adsorption process is unfavorable at higher temperatures. This behavior suggests an exothermic adsorption process, where increasing temperature provides additional kinetic energy to MB molecules, facilitating their desorption from the adsorbent surface and promoting their transfer from the solid phase back to the liquid phase [98]. Similar behavior has been reported for MB adsorption on mesoporous and bio-based adsorbents, in which adsorption efficiency decreases with increasing temperature due to weakened adsorbate–adsorbent interactions.

The thermodynamic parameters, namely the standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°), were calculated using Eqs. 15–17 from the slope and intercept of the plot of $\ln(K_d)$ versus $1/T$, as shown in Fig. 18(b). The calculated values are presented in Table 10. The negative ΔG° values obtained for all adsorbents and temperatures confirm that MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C is thermodynamically favorable and spontaneous. However, the absolute values of ΔG° gradually decreased with increasing temperature, indicating that the spontaneity of the adsorption process becomes weaker at higher temperatures. This result confirms that low temperature is more favorable for MB adsorption onto the synthesized MCM-41-based materials.

The negative ΔH° values obtained for BioMCM-41FA, BioMCM-41BB, and MCM-41C, namely -21.425 , -16.105 , and -15.244 KJ. mol^{−1}, respectively, further confirm the exothermic nature of the adsorption process. These relatively low enthalpy values are within the range generally associated with physical adsorption, suggesting that MB retention is mainly governed by weak interactions such as electrostatic attraction, hydrogen bonding, van der Waals forces, and pore filling rather than strong chemical bonding. This interpretation is consistent with the low adsorption energy values obtained from the Dubinin–Radushkevich model, which also suggested a physisorption-dominated mechanism.

The negative ΔS° values, -47.55 , -29.53 , and -26.97 J. mol^{−1}. K^{−1} for BioMCM-41FA, BioMCM-41BB, and MCM-41C, respectively, indicate a decrease in randomness at the solid–liquid interface during MB adsorption. This reduction in disorder can be attributed to the fixation of MB molecules onto the adsorbent surface and inside the mesoporous channels. Therefore, the adsorption process is accompanied by a more ordered arrangement of dye molecules on the surface of the MCM-41-based materials.

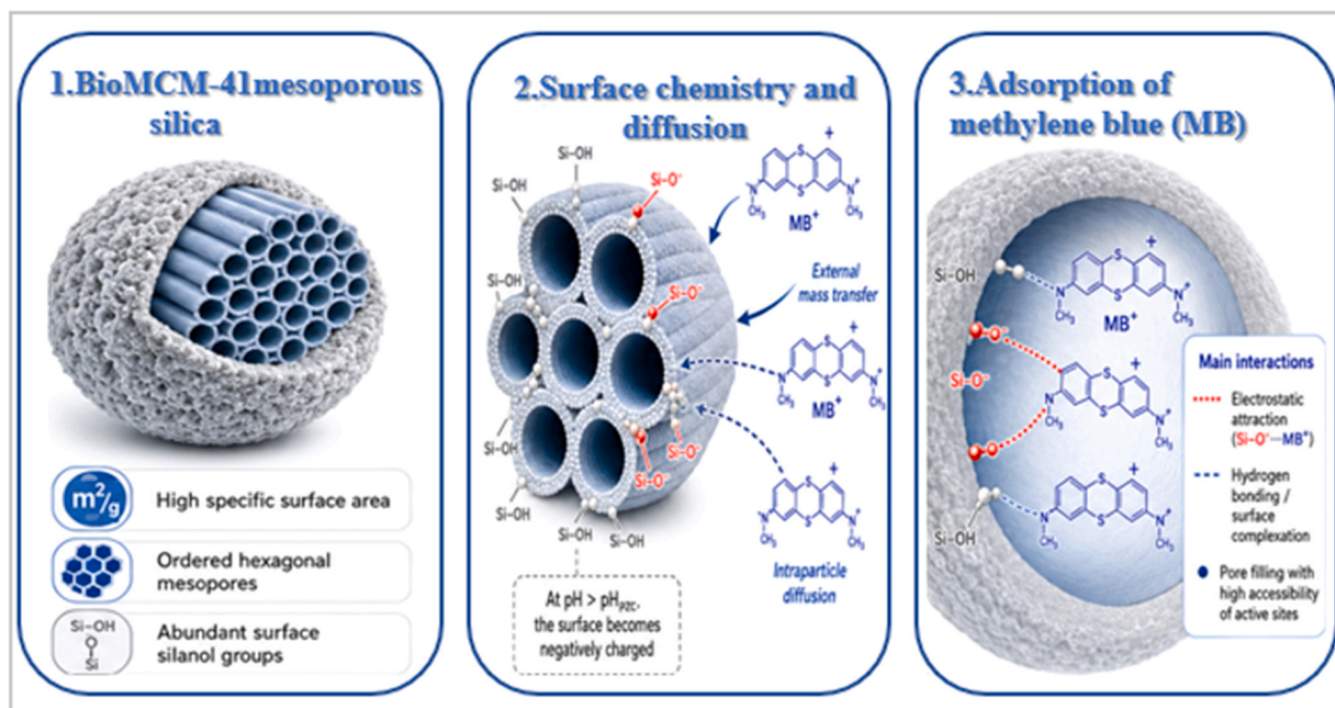


Fig. 17. The adsorption mechanisms of MB onto MCM-41.

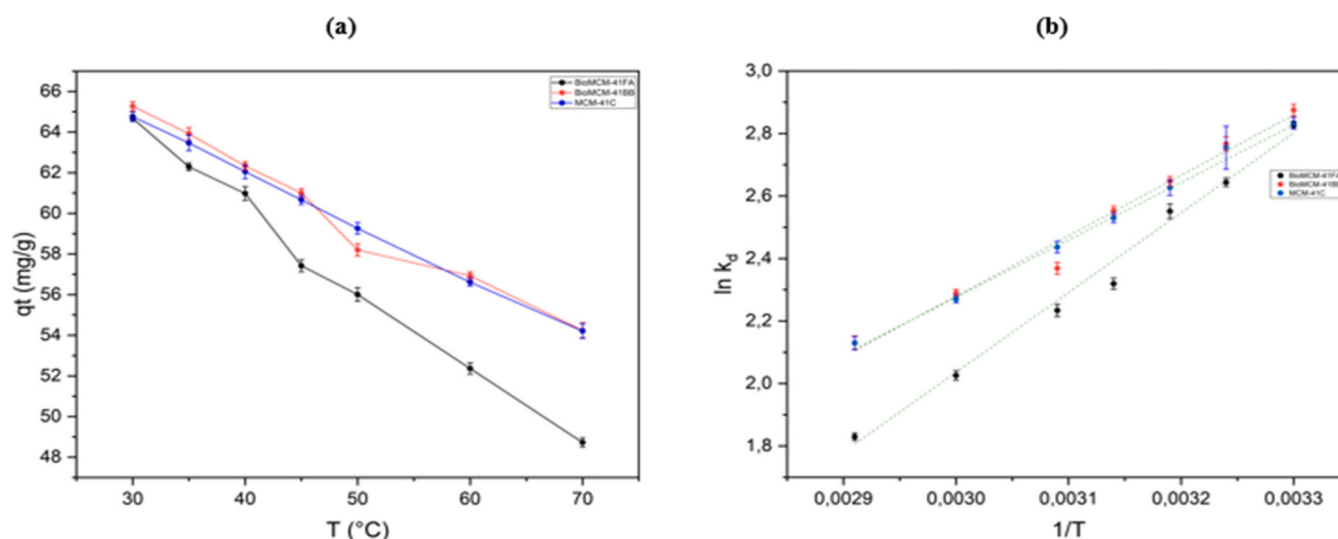


Fig. 18. (a) Effect of temperature and (b) thermodynamic analysis of MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C. Conditions: $T = 30\text{--}70\text{ }^{\circ}\text{C}$, $C_0 = 20\text{ mg L}^{-1}$, $m = 12.5\text{ mg}$, $V = 50\text{ mL}$, $\text{pH} = 6.42$, and $v = 210\text{ rpm}$.

Overall, the thermodynamic analysis demonstrates that MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C is spontaneous, exothermic, and mainly governed by physical interactions. These findings are consistent with previous studies reporting that negative ΔG° values indicate spontaneous adsorption, while negative ΔH° values indicate an exothermic process for MB removal using mesoporous silica, MCM-41-based materials, and bio-based adsorbents [99,100].

3.9. Comparison with other adsorbents

Table 11 presents the maximum adsorption capacities for methylene blue, as determined using the Langmuir model, for the materials synthesized in this research and for various MCM-41 materials reported in the literature. The data indicate that the adsorption capacity of MCM-41

adsorbents varies considerably with silica supply and experimental parameters, especially temperature and pH. In this study, BioMCM-41FA had the greatest adsorption capacity (186.23 mg/g), succeeded by MCM-41C (179.71 mg/g) and BioMCM-41BB (104.83 mg/g). The results demonstrate that the synthesized materials exhibit competitive adsorption performance compared with other MCM-41 materials reported in the literature. Specifically, BioMCM-41FA exhibited an adsorption capacity comparable to that of RH-MCM-41 (196.1 mg/g) and superior to numerous other MCM-41 samples enumerated in Table 9. These findings affirm the significant promise of the synthesized MCM-41 materials, particularly BioMCM-41FA, for methylene blue removal.

Table 10

Thermodynamic parameters for MB adsorption onto BioMCM-41FA, BioMCM-41BB, and MCM-41C ($T = 30\text{--}70\text{ }^{\circ}\text{C}$, $C_0 = 20\text{ mg L}^{-1}$, $m = 12.5\text{ mg}$, $V = 50\text{ mL}$, $\text{pH} = 6.42$, and $v = 210\text{ rpm}$).

Adsorbent	Temperature ($^{\circ}\text{C}$)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1}\text{K}^{-1}$)
BioMCM-41FA	30	-7.103	-21.425	-47.55
	35	-6.760		
	40	-6.609		
	45	-6.160		
	50	-5.988		
	60	-5.592		
	70	-5.190		
BioMCM-41BB	30	-7.179	-16.105	-29.53
	35	-7.016		
	40	-6.844		
	45	-6.715		
	50	-6.310		
	60	-6.284		
	70	-6.017		
MCM-41C	30	-7.787	-15.244	-26.97
	35	-6.913		
	40	-6.765		
	45	-6.636		
	50	-6.471		
	60	-6.229		
	70	-5.988		

Table 11

Maximum adsorption capacities of methylene blue on MCM-41 materials: literature vs. this study.

The source of MCM-41	T ($^{\circ}\text{C}$)	pH	Adsorption capacity (mg/g)	S_{BET}	Ref
MCM-41	30	5.86	1.5×10^{-4}	1059	[101]
RH-MCM-41	-	7	196.1	1051	[102]
MCM-41	-	-	17.67	1207	[103]
MCM-41	25	7	302.317	630	[93]
MCM-41	25	-	28.89	1378	[104]
BioMCM-41FA	22	6.42	186.23	1090	This study
BioMCM-41BB	22	6.42	104.83	1081	This study
MCM41-C	22	6.42	179.71	1042	This study

3.10. ANN results

Artificial Neural Networks (ANNs) were selected in this study because adsorption processes involve complex nonlinear interactions among several operating variables, including pH, initial dye concentration, contact time, and adsorbent dosage. Unlike conventional statistical approaches, which generally rely on predefined mathematical relationships, ANNs can efficiently learn nonlinear patterns directly from experimental data without assuming a specific functional form. Therefore, ANN modeling was adopted as a complementary predictive tool to accurately describe the adsorption behaviour of the synthesized

materials.

3.10.1. Data Analysis

Prior to ANN modeling, a preliminary data analysis was conducted to assess the statistical characteristics, variable distributions, and relationships in the experimental dataset. The dataset consisted of 165 observations, including eight input variables such as pH, adsorbent mass, initial BM concentration, silica percentage, temperature, agitation speed, NaCl concentration, and contact time and one output variable, yield. The descriptive statistics are presented in Table 12.

The yield values ranged from 0.409 to 1.000, with a mean value of 0.815 and a standard deviation of 0.156, indicating generally high adsorption performance with moderate variability. Among the input variables, pH varied from 2 to 11, initial BM concentration ranged from 5 to 40 mg L^{-1} , and contact time ranged from 180 to 7200 s, showing that these factors covered relatively wide experimental domains. In contrast, some variables, such as silica percentage, adsorbent mass, temperature, agitation speed, and NaCl concentration, exhibited concentrated or skewed distributions, as confirmed by the violin plot in Fig. 19.

The Pearson correlation heatmap shown in Fig. 20 revealed that pH had the strongest positive correlation with yield ($r = 0.460$), followed by adsorbent mass ($r = 0.385$). This suggests that increasing pH and adsorbent dosage may contribute positively to adsorption yield. Conversely, the initial BM concentration showed a moderate negative correlation with yield ($r = -0.403$), indicating that higher initial concentrations may reduce removal efficiency, probably due to saturation of available adsorption sites. Temperature also showed a weak negative correlation with yield ($r = -0.218$), while agitation speed, contact time, NaCl concentration, and silica percentage exhibited weaker correlations.

Most correlations among the input variables were low, indicating limited multicollinearity and suggesting that the predictors provide relatively independent information for the ANN model. The only noticeable inter-variable relationship was observed between silica percentage and contact time ($r = -0.432$), but this correlation remained moderate.

3.10.2. ANN modeling results

The ANN model was developed using 165 experimental data points, divided into a training set of 132 samples and an independent external test set of 33 samples. Hyperparameter optimization was performed using Optuna on the training set only to avoid data leakage. The best ANN architecture consisted of two hidden layers with 35 and 20 neurons, respectively, using the ReLU activation function, Adam optimizer, a learning rate of 0.00257, batch size of 16, dropout rate of 0.075, and L2 regularization of (5.99–6) (Table 13).

The predictive performance of the optimized ANN model is summarized in Table 14. The model showed excellent fitting ability on the training set, with ($R^2 = 0.941$), RMSE = 0.0369, MAE = 0.0257, and MAPE = 3.53%. More importantly, the external test set also showed strong predictive performance, with ($R^2 = 0.900$), RMSE = 0.0526, MAE = 0.0354, MAPE = 4.79%, and ($Q_{\text{ext}}^2 = 0.900$). The close agreement

Table 12

Descriptive statistics of the experimental variables and yield.

Variable	Mean	Std	Min	25%	50%	75%	Max
pH	6.4345	1.2289	2	6.42	6.42	6.42	11
mass adsorbent	11.5909	2.3291	2.5	12.5	12.5	12.5	12.5
$C_0\text{ BM mg L}^{-1}$	20.3636	4.4709	5	20	20	20	40
% of silice	0.9890	0.0038	0.985	0.985	0.988	0.994	0.994
Temperature	25.2000	9.6159	22	22	22	22	70
Agitation speed	210.0000	23.8900	100	210	210	210	300
$c_0\text{ NaCl}$	9.0909	35.8999	0	0	0	0	200
time	3279.2727	1747.2095	180	1800	3600	5400	7200
yield	0.8145	0.1556	0.4093	0.7102	0.8348	0.9532	1

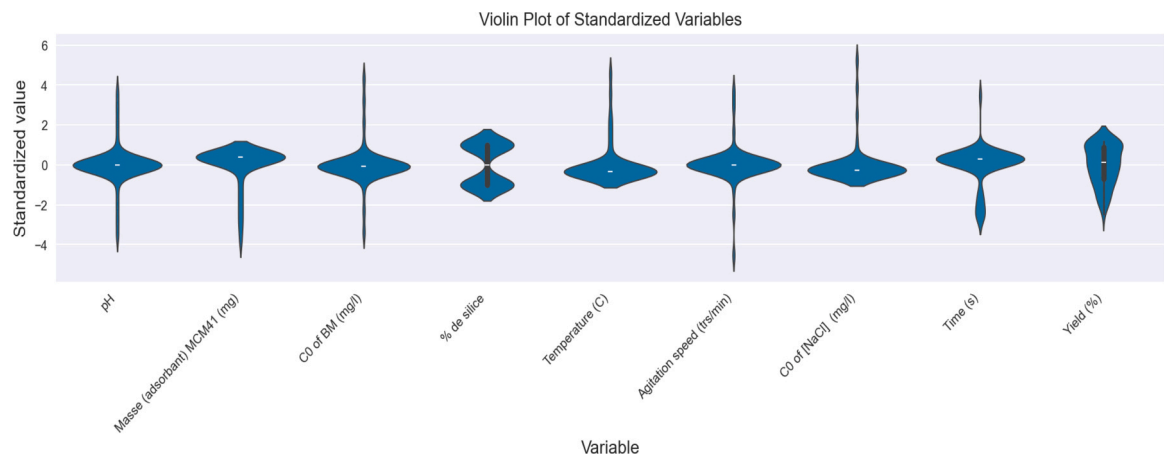


Fig. 19. Violin plot of standardized input variables and yield.



Fig. 20. Pairwise correlation heatmap of input variables and yield.

Table 13
Optimized ANN hyperparameters obtained by Optuna.

Parameter	Best Value
Number of hidden layers	2
Activation function	ReLU
Optimizer	Adam
Learning rate	0.002573
Batch size	16
Dropout rate	0.0753
L2 regularization	5.99×10^{-6}
Neurons in layer 1	35
Neurons in layer 2	20

between (R^2) and (Q^2_{ext}) confirms the good external predictability of the model. The 5-fold cross-validation performed on the training set gave ($R^2_{CV} = Q^2_{CV} = 0.735$), indicating acceptable internal robustness.

The predicted-versus-experimental plot (Fig. 21) shows that most training and external test points were closely clustered around the ideal 45° line, confirming strong agreement between predicted and measured yield values. The residual plot (Fig. 22) further supports this observation, as most residuals were randomly distributed around zero without a clear systematic trend. Only a few larger deviations were observed, particularly in the intermediate yield region, which may be related to nonlinear interactions between adsorption variables. The training and validation loss curves (Fig. 23) decreased rapidly during the first epochs

Table 14
Performance metrics and overfitting diagnosis of the optimized ANN model.

Dataset	R	R ²	MAE	RMSE	MSE	MAPE (%)	Q ²	R ² gap	RMSE ratio	Diagnosis
Training	0.973	0.941	0.0257	0.0369	0.00136	3.53	—	—	—	—
External test	0.951	0.900	0.0354	0.0526	0.00277	4.79	0.900	0.041	1.425	No strong overfitting signal
5-fold CV	0.857	0.735	0.0563	0.0784	0.00615	7.95	0.735	—	—	—

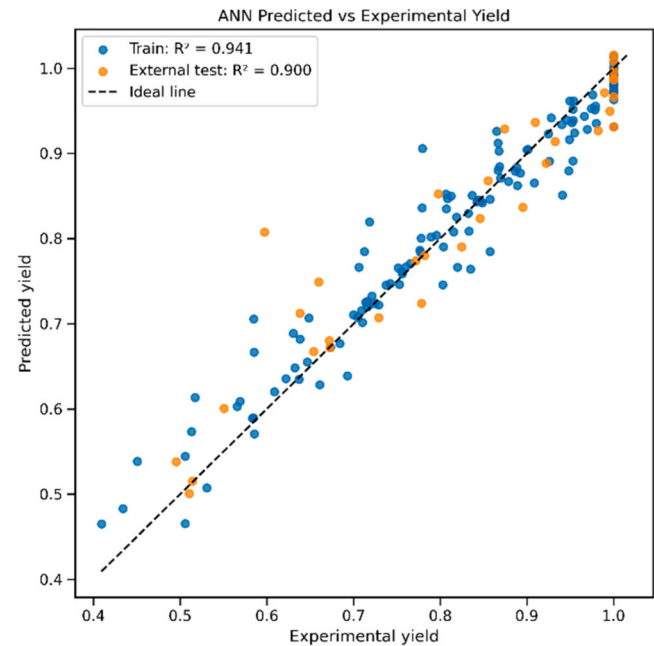


Fig. 21. ANN predicted versus experimental yield for training and external test sets.

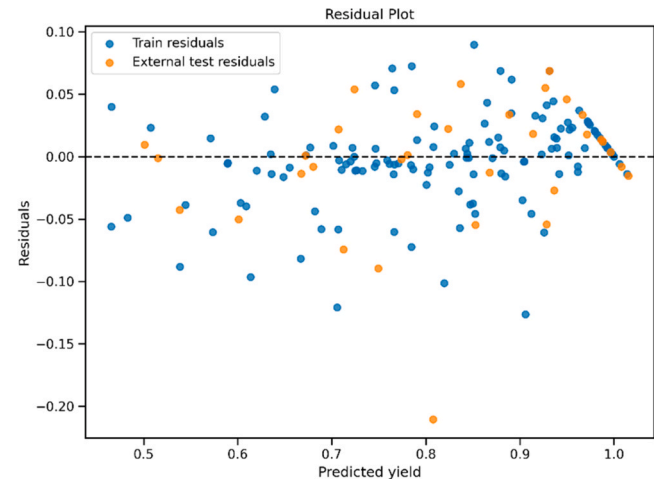


Fig. 22. Residual distribution of the ANN model.

and then stabilized, indicating efficient model convergence. The Optuna optimization history (Fig. 24) showed a progressive reduction in the objective value, confirming the effectiveness of the hyperparameter optimization procedure.

To assess the risk of overfitting, the difference between training and external test performance was examined (Table 14). The (R^2) gap between training and test sets was only 0.041, while the RMSE ratio was 1.43. These values indicate that the model maintained good generalization ability and showed no strong overfitting signal. This result confirms the effectiveness of the applied regularization strategies,

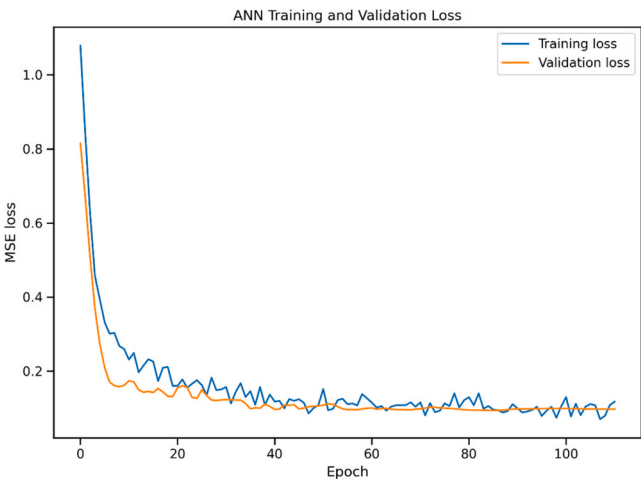


Fig. 23. Training and validation loss curves of the ANN model.

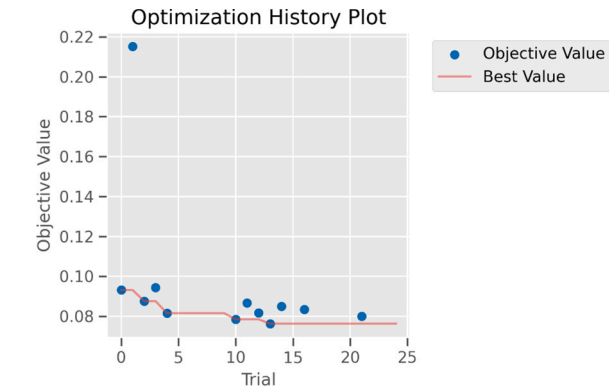


Fig. 24. Optuna optimization history plot.

including early stopping, dropout, L2 regularization, learning-rate reduction, and the use of an independent external test set.

The individual sensitivity curves (Fig. 25) show that increasing pH and adsorbent mass improved the predicted yield, with a tendency toward stabilization at higher values. In contrast, increasing the initial BM concentration strongly reduced the predicted yield, which is consistent with possible saturation of adsorption sites. Temperature also showed a decreasing trend, suggesting that high temperature conditions were less favorable in the studied experimental domain. Contact time increased the predicted yield, especially at shorter times, followed by a slower improvement at longer durations. NaCl concentration showed a slight negative effect, while silica percentage presented a weak nonlinear response.

3.10.3. Deployment of the optimized ANN model

To facilitate practical use of the optimized ANN model, a web-based deployment interface was developed using Streamlit (Fig. 26). The deployment system was designed to predict adsorption yield for new experimental conditions without requiring the user to interact directly with the Python training code. After model training, all necessary

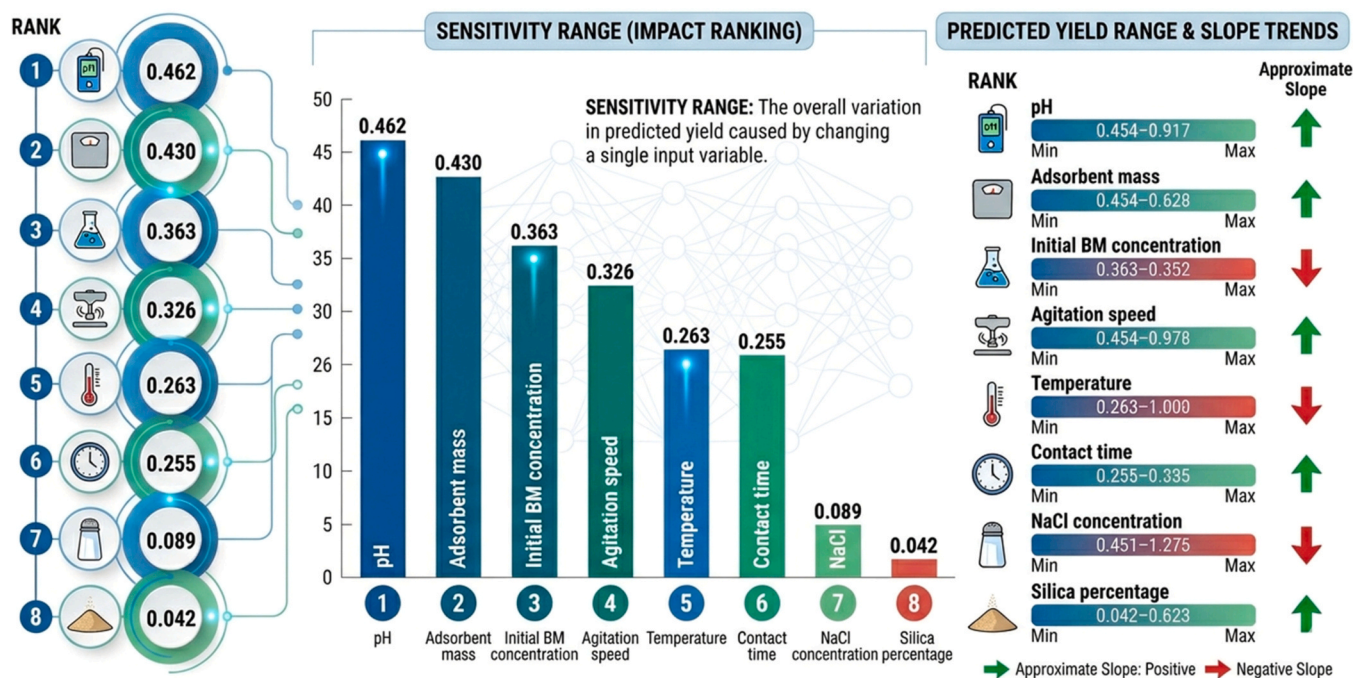


Fig. 25. One-at-a-time sensitivity curves of the ANN model for pH, adsorbent mass, initial BM concentration, temperature, agitation speed, NaCl concentration, silica percentage, and contact time.

objects were saved, including the optimized ANN model, input scaler, output scaler, selected feature names, training reference data, and applicability-domain threshold. These files were then loaded automatically by the web application.

The deployed application allows two prediction modes. In the first mode, the user can manually enter the values of the eight input variables: pH, adsorbent mass, initial BM concentration, silica percentage, temperature, agitation speed, NaCl concentration, and contact time. In the second mode, the user can upload an Excel or CSV file containing multiple experimental conditions for batch prediction. For each new sample, the application returns the predicted yield and evaluates whether the sample is located inside or outside the applicability domain of the model.

The applicability domain was assessed using a distance-based approach calculated from the standardized training data. Samples located inside the applicability domain were considered reliable predictions, whereas samples outside the domain were flagged for cautious interpretation. The web application also provides downloadable prediction results in Excel or CSV format, making it suitable for laboratory use, process optimization, and rapid screening of new adsorption conditions.

In conclusion, the optimized ANN model demonstrated high predictive performance for adsorption yield, with strong agreement between experimental and predicted values and no significant overfitting tendency. The feature-importance and sensitivity analyses confirmed that adsorbent mass, initial BM concentration, pH, temperature, and contact time were the main factors controlling the process. The deployment of the model through a web application provides a practical and user-friendly tool for rapid yield prediction and decision support under new experimental conditions.

Taken together, the adsorption and ANN results can be directly related to the structural and physicochemical properties of the synthesized BioMCM-41 materials.

The excellent adsorption performance of the BioMCM-41 materials can be attributed to the synergistic effect of their high silica purity, ordered mesoporosity, large surface area, and accessible pore channels. The high SiO₂ content suggests that the biomass-derived silica precursor

was sufficiently purified to form an ordered MCM-41 framework with limited interference from mineral impurities. This is important because residual inorganic species may interfere with the condensation of silica species and negatively affect pore ordering and surface accessibility.

The ordered hexagonal mesostructure of MCM-41 provides open, uniform mesoporous channels that facilitate the diffusion of methylene blue molecules to internal adsorption sites. Besides, the high surface area and pore volume provide a large number of available adsorption sites, and the surface silanol groups can promote electrostatic attraction and hydrogen-bonding interactions with the cationic dye. It is therefore not a single factor that controls adsorption efficiency, but rather the interplay of structural order, textural properties, surface chemistry, and pore accessibility.

That the BioMCM-41 materials remove methylene blue completely compared to 95% removal by conventional MCM-41 indicates that silica derived from agricultural waste can be used to prepare adsorbents that are as good as or better than those prepared from conventional silicates. This result is important because it indicates that the adsorption capacity of MCM-41 is unaffected by using biomass-derived silica rather than conventional silica precursors. In contrast, the bio-derived materials maintained the critical structural features necessary for efficient adsorption, providing a more sustainable mode of synthesis.

The ANN interpretation further confirms the experimental results. The adsorbent mass and the initial MB concentration were found to be the most effective variables, confirming that adsorption performance is primarily governed by the availability of active sites and the dye loading in solution. The positive influence of pH is consistent with the gradual deprotonation of surface silanol groups, thereby increasing electrostatic attraction to cationic methylene blue molecules. Similarly, the positive effect of contact time is because of the gradual diffusion of dye molecules into the available mesopore channels. The adverse effect of high initial dye concentration and temperature, on the other hand, may be due to the saturation of available adsorption sites and the exothermic nature of the adsorption process.

Structural characterization, adsorption experiments, and ANN-based interpretation are integrated to understand the adsorption mechanism better. The results indicate that the performance of BioMCM-41 is

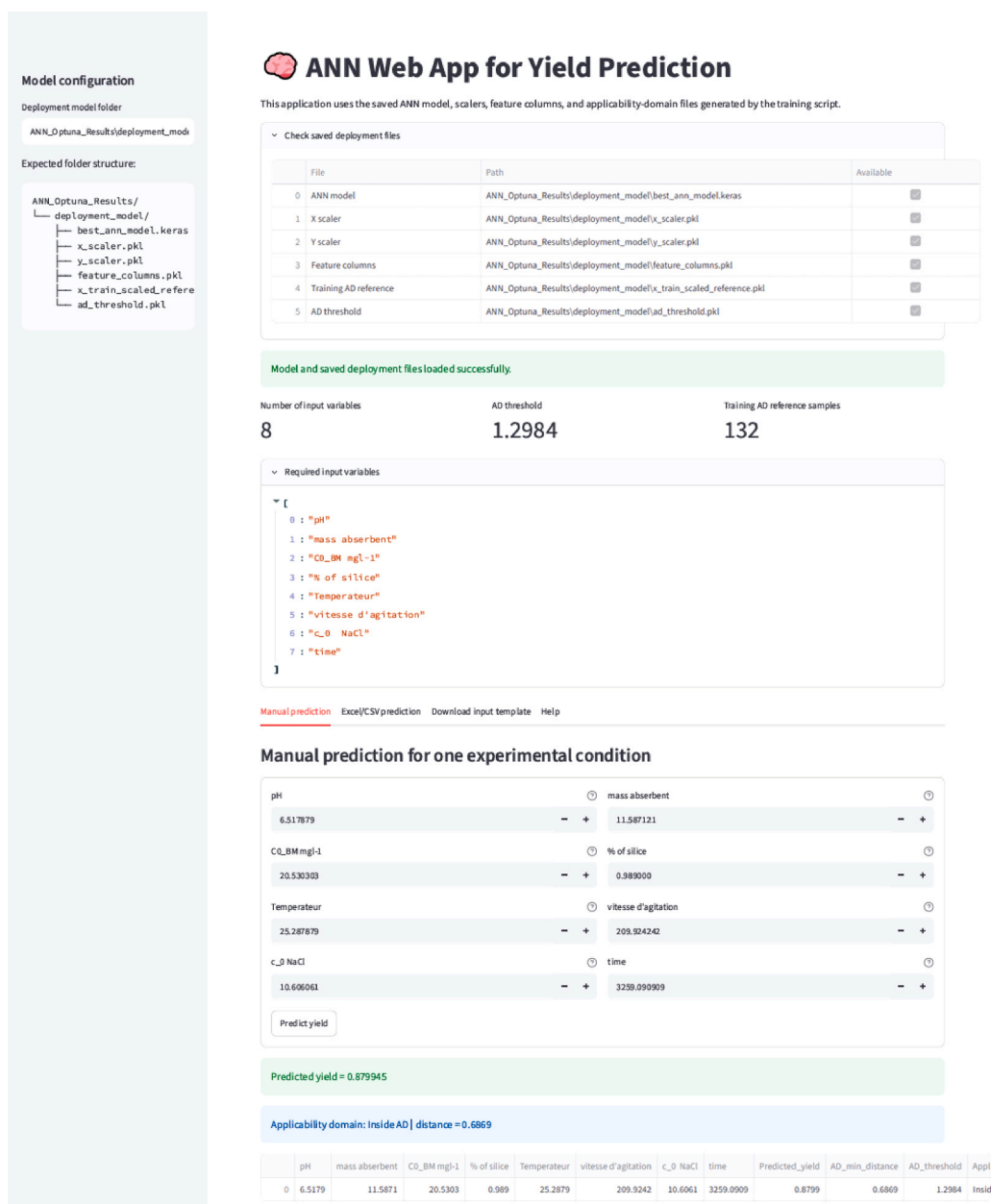


Fig. 26. Web application interface for deployment of the optimized ANN model.

directly related to its ordered mesoporosity, high surface area, silica purity and surface functionality. BioMCM-41 showed high adsorption efficiency and a sustainable synthesis strategy based on the valorization of agricultural biomass, compared with many reported adsorbents. This indicates its potential as an effective, eco-friendly adsorbent for treating dye-contaminated aqueous solutions.

3.11. Comparison with previous adsorption and modeling studies

Table 15 provides a comparative overview of recent sustainable adsorbent systems, including biomass-derived silica, mesoporous silica, MCM-41-based materials, low-cost bio adsorbents, and AI-assisted adsorption studies. This comparison highlights the position of the present work within the recent literature by considering the silica source, synthesis route, surface area, target pollutant, adsorption capacity, modeling approach, and environmental benefit. Unlike many previous studies that focused mainly on either material synthesis, dye adsorption, or predictive modeling separately, this work successfully unifies these

complementary dimensions within a single, streamlined workflow for the very first time. It involves the extraction of bio-silica from two underexplored biomasses, *Festuca arundinacea* and barley bran, the synthesis of BioMCM-41 materials under comparable conditions, direct comparison with commercial MCM-41C, detailed physicochemical characterization, systematic methylene blue adsorption modeling, thermodynamic evaluation, adsorption mechanism discussion, and ANN-based prediction. By simultaneously establishing real-time correlations among all operating, structural, and predictive parameters, this comparative table emphasizes the integrated character of the present study and supports the potential of these biomasses as sustainable precursors for the development of efficient mesoporous adsorbents.

4. Practical limitations and future research perspectives

The present study successfully demonstrated the feasibility of recovering silica from *Festuca arundinacea* and barley bran and using it as an alternative precursor for the synthesis of bio-based MCM-41

Table 15

Comparative overview of recent biomass-derived silica/MCM-41 adsorbents and AI-assisted adsorption studies, emphasizing the unique contributions and benefits demonstrated in this study.

Authors	Silica source / precursor	Materials	Synthesis strategy of materials	the specific surface area	Dye / pollutant	Adsorption performance $q_{\max}$	Modeling / prediction	Main advantage / novelty
Azoug et al. (2025) [105]	Algerian kaolin	MCM-41	ultrasonic method	1311 m ² /g	no dye adsorption tested.	Not applied to dye adsorption.	No	Valorization of GOO sand, a siliceous by-product of Algerian kaolin, as a sustainable silica source for ultrasonic MCM-41 synthesis, reducing the use of costly precursors and promoting circular economy.
Han et al. (2021)[78]	iron ore tailings	Mesoporous silica	alkaline fusion followed by acid leaching	525 m ² /g	methylene blue	192.00 mg/g	No	Valorization of iron ore tailings into low-cost mesoporous silica adsorbent, reducing mining waste accumulation and enabling efficient methylene blue removal from wastewater
Liu et al. (2020) [3]	Peanut Shell Ash	MCM-41	Hydrothermal synthesis	-	Crystal violet	1428.57 mg/g	No	Valorization of low-silicon peanut shell ash into PS-MCM-41 adsorbent, reducing biomass ash waste and replacing costly toxic silica precursors while enabling efficient crystal violet dye removal from wastewater
Naseem et al. (2021) [76]	bagasse ash	mesoporous silica	Alkali fusion-assisted CTAB-templated wet chemical synthesis	210 m ² /g	crystal violet	24.75 mg/g a 293 K	No	Use of sugarcane bagasse ash, an agro-industrial waste, as a low-cost silica source for mesoporous SiO ₂ synthesis, reducing ash disposal problems and replacing conventional commercial silica precursors for crystal violet removal from wastewater
Boudinar et al. (2024) [106]	Saidite clay	Al-MCM-41	hydrothermal synthesis.	633 m ² /g	Malachite green	58.72 mg/g	No	Use of local Saidite clay as a low-cost natural source of Si, Al, and Fe to synthesize Al-MCM-41, reducing reliance on expensive commercial precursors and enabling fast removal of malachite green dye from wastewater
de Jesus et al. (2024) [107]	sugarcane bagasse ash	Bio-silica	Alkaline dissolution	306 m ² /g	methylene blue	27.91 mg/g	ANN modeling R ² = 0.99 RMSE = 0.0387	Sustainable valorization of sugarcane bagasse ash into low-cost bio-silica adsorbent, reducing agro-industrial waste and enabling efficient methylene blue removal from wastewater.
Kumari et al. [32]	-	<i>Oryza sativa</i> straw	-	-	methylene blue	1.35 mg/g	R ² /RMSE = 0.9216/1.1013 for RSM, 0.8864/1.3062 for ANN, and 0.9589/0.7864 for ANFIS	Valorization of <i>Oryza sativa</i> straw biomass, an abundant agricultural waste, as a low-cost and eco-friendly adsorbent for methylene blue removal, reducing biomass disposal/burning and supporting circular wastewater treatment
Çimen Mesutoğlu [31]	-	activated olive stone	-	-	Methylene Blue	128.70 mg/g	ANN modeling R ² = 91%	Valorization of olive stone, an agro-industrial waste from olive oil production, into activated olive stone adsorbent for high-efficiency methylene blue removal, reducing organic waste disposal and supporting low-cost sustainable wastewater treatment.
Ertuş (2026) [108]	Wheat husk ash	Mesoporous silica	CTAB-assisted precipitation synthesis	880 m ² /g	Methylene blue	103.20 mg/g	No	Valorization of wheat husk ash, an abundant agricultural waste, into CTAB-templated mesoporous silica for methylene blue removal, reducing biomass waste while producing a low-cost reusable adsorbent for wastewater treatment.
Juárez et al. (2025) [109]	rice husk	MCM-41	hydrothermal synthesis	644 m ² /g	hydrogen	-	No	valorization of rice husk, an abundant agricultural by-product rich in silica, into mesoporous silica templates and ordered carbon replicas for hydrogen storage, reducing agricultural waste while supporting clean-energy material development.

(continued on next page)

Table 15 (continued)

Authors	Silica source / precursor	Materials	Synthesis strategy of materials	the specific surface area	Dye / pollutant	Adsorption performance q_{max}	Modeling / prediction	Main advantage / novelty
Barna et al. (2024) [110]	-	banana leaf powder	NaOH-assisted chemical modification of banana leaf powder.	-	methyl blue	118.24 mg/g	$R^2/KNN = 0.8155$ $SVM = 0.2644$ $ANN = 0.4610$ and $LSTM = 0.5995$	Valorization of banana leaf waste into chemically modified banana leaf powder as a biodegradable, low-cost adsorbent for methyl blue removal, reducing agricultural waste and offering an eco-friendly alternative to conventional adsorbents.
Celoria et al. (2025)[28]	rice husk	Nanosized MCM-41	Double-surfactant-assisted synthesis	1050 m ² /g	rhodamine B	-	No	Valorization of rice husk waste into nanosized MCM-41 mesoporous silica for dye removal, replacing costly alkoxysilane precursors and providing a greener adsorbent for water treatment
Present work	Festuca arundinacea and barley bran	BioMCM-41FA and BioMCM-41BB compared with commercial MCM-41C	Biomass pretreatment, biosilica extraction, sodium silicate preparation and CTAB-assisted BioMCM-41 synthesis.	1090 m ² /g 1081 m ² /g 1042 m ² /g	Methylene blue	186.23 mg/g 104.83 mg/g 179.71 mg/g	ANN prediction. $R^2 = 0.941$ RMSE= 0.0526	New biomass sources, high silica purity, efficient dye removal, comparison with MCM-41C, and ANN prediction.

materials. The synthesized BioMCM-41 adsorbents were comprehensively characterized, and their methylene blue adsorption performance was evaluated and compared with that of MCM-41C under identical experimental conditions. The effects of the main operating parameters were systematically investigated, and the adsorption behavior was examined through kinetic, equilibrium, thermodynamic, and artificial neural network analyses. These results fulfilled the main objectives of the present work and provided a controlled assessment of the adsorption potential of the synthesized materials. Nevertheless, some limitations should be considered before their practical application in wastewater treatment.

The adsorption experiments were conducted using synthetic methylene blue solutions under controlled laboratory conditions. Although this approach enabled the individual effects of the operating parameters to be assessed and ensured a reliable comparison among BioMCM-41FA, BioMCM-41BB, and MCM-41C, it does not fully reproduce the complexity of industrial effluents. Real wastewater matrices may contain competing contaminants, dissolved salts, suspended solids, and natural organic matter, which can affect adsorption-site accessibility, selectivity, and overall removal performance. Future investigations will therefore focus on simulated and real industrial wastewater systems to evaluate the robustness and practical applicability of the synthesized BioMCM-41 materials under more realistic operating conditions.

In addition, regeneration and reuse experiments were beyond the scope of the present study. Consequently, the retention of adsorption capacity, structural stability, regeneration efficiency, and long-term economic feasibility of the adsorbents over successive operating cycles could not be assessed. Future work will therefore investigate multiple adsorption-desorption cycles, together with post-regeneration characterization using XRD, BET, and FTIR analyses, to evaluate possible changes in the structural order, textural properties, surface chemistry, and long-term adsorption performance of the BioMCM-41 adsorbents.

5. Conclusion

The main findings and perspectives of this study can be summarized as follows:

- High-quality BioMCM-41 mesoporous silica was successfully prepared using *Festuca arundinacea* grass and barley bran as sustainable and low-cost sources of silica. The extracted silica from both biomasses exhibited an amorphous structure and high purity of about 98%, indicating that agricultural biomass can serve as an alternative silica source.
- BioMCM-41FA BioMCM-41BB and the commercial reference MCM-41 exhibited well-ordered hexagonal mesostructures. Nitrogen adsorption and desorption analysis showed high specific surface areas of 1090, 1080, and 1030 m² g⁻¹, pore volumes of 0.92, 0.32, and 0.23 cm³ g⁻¹, and average pore diameters of 3.9, 3.2, and 2.9 nm for BioMCM-41FA, BioMCM-41BB, and MCM-41, respectively. These properties, together with high thermal stability, confirm that the materials are highly porous and structurally robust.
- The adsorption performance of methylene blue was assessed for BioMCM-41FA, BioMCM-41BB, and MCM-41C. BioMCM-41 and BioMCM-41BB showed the highest adsorption capacities, while MCM-41C exhibited slightly lower performance. These differences were attributed to minor variations in structural and textural properties, particularly in pore diameter, pore volume, and surface accessibility.
- The adsorption kinetics of MB onto all MCM-41 materials were best described by the pseudo-second-order and Elovich models, while intraparticle diffusion was not the sole rate-controlling step.
- The Freundlich and Temkin models best described MB adsorption onto both BioMCM-41 materials, indicating heterogeneous adsorption surfaces, whereas MCM-41C showed satisfactory agreement

with the different tested models. The low Dubinin–Radushkevich adsorption energies indicated predominantly physical adsorption.

- Thermodynamic analysis indicated that adsorption on the three mesoporous materials was spontaneous and exothermic. The decrease in entropy with ΔS° values ranging from $-26,97$ to $-47,302 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ suggests that dye molecules became more ordered after being trapped within the pores at the solid-liquid interface.
- The adsorption mechanism was mainly driven by hydrogen bonding and electrostatic interactions, with solution pH significantly influencing the effectiveness of dye removal.
- Both BioMCM-41 materials showed slightly higher adsorption capacities than commercial MCM41. The large specific surface area, ordered mesoporous structure and environmentally friendly preparation route make these materials promising adsorbents for contaminant removal from wastewater and other environmental sources. Their use also supports circular-economy principles by sustainably valorizing agricultural biomass.
- An ANN model was developed to predict the adsorption yield using eight input variables. The optimized model showed good prediction performance, with $R^2 = 0.941$ for training, $R^2 = 0.900$ for the external test set, $Q^2 = 0.900$, $\text{RMSE} = 0.0526$, $\text{MAE} = 0.0354$, and $\text{MAPE} = 4.79\%$. These results confirm that ANN modeling is a useful tool for predicting methylene blue adsorption by agricultural-waste-derived BioMCM-41 materials.
- The combination of biosilica extraction from agricultural biomass, BioMCM-41 synthesis, dye adsorption evaluation, and ANN-based prediction represents a distinctive and novel aspect of this work, distinct from previous studies that generally address these aspects separately.
- Future work will focus on regeneration and cyclic reuse studies over multiple adsorption–desorption cycles, together with post-regeneration characterization using XRD, BET, and FTIR analyses. These investigations will be necessary to evaluate the structural stability, surface properties and long-term adsorption performance of the BioMCM-41 adsorbents.
- Future studies will extend the evaluation of the synthesized BioMCM-41 materials to simulated and real industrial effluents. Testing under these more complex conditions, which may involve competing pollutants, dissolved salts, suspended matter, and natural organic compounds, will be essential to determine the adsorbents' selectivity, operational robustness, and suitability for practical wastewater-treatment applications.

CRediT authorship contribution statement

Gaigneaux Eric: Writing – review & editing, Validation, Supervision. **Naima Bouchenafa-Saib:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Meriem Khelif:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Selmane Boumessaidia:** Data curation. **Chennouf-Abdellatif Zohra:** Supervision. **Abdellah Ibrir:** Writing – review & editing, Visualization, Methodology.

Declaration of Generative AI and AI-assisted technologies in the writing process

The authors used AI-assisted language editing tools to improve clarity and grammar.

All scientific content, analysis, and conclusions were developed entirely by the authors.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Naima Bouchenafa-Saib reports financial support and travel were provided by Ministry of Higher Education of Algeria. Eric M. Gaigneaux reports financial support and travel were provided by Wallonie-Bruxelles International. If there are other authors, they 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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