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Adsorption Performance and Thermodynamic Analysis of Silica–Bentonite Composite for Methylene Blue Removal

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Abstract The increasing discharge of synthetic dyes into water bodies poses severe environmental risks due to their toxicity, persistence, and resistance to biodegradation. Methylene blue (MB), a widely used cationic dye, is often chosen as a model pollutant for adsorption studies. This work synthesised a bentonite–silica composite via a sol–gel method using tetraethoxysilane (TEOS) as a silica precursor and natural Navbahor bentonite as the clay component. The composite was characterized by Fourier-transform infrared spectroscopy (FTIR) and nitrogen adsorption–desorption analysis (BET, NLDFT). FTIR confirmed the incorporation of an amorphous silica network into the bentonite matrix, while maintaining the layered montmorillonite structure. Textural analysis revealed a surface area of 55.35 m^2/g^{-1}, a pore volume of 0.122 cm^3/g^{-1}, and a dominant pore size of ~1.8–2.0 nm, indicating a hierarchical mesoporous system favourable for adsorption and diffusion. The adsorption of MB was investigated at different temperatures. Langmuir fitting yielded maximum capacities of 30.98, 26.78, and 17.09 mg g^{-1} at 293, 303, and 313 K, respectively, confirming an exothermic process. Freundlich analysis emphasised surface heterogeneity, with $n > 1$ and correlation coefficients up to 0.99. Thermodynamic calculations indicated negative Gibbs free energies (−24 to −26 kJ mol^{-1}), an enthalpy change of −10 kJ mol^{-1}, and positive entropy values (+45–50 J mol^{-1} K^{-1}). These findings demonstrate that MB adsorption is spontaneous, exothermic, and governed by a dual mechanism combining monolayer adsorption on silica-modified sites and heterogeneous sorption in bentonite domains.

Keywords Bentonite–silica composite, Methylene blue adsorption, Sol–gel synthesis, Isotherm models, Thermodynamic analysis

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1. Introduction

Water pollution caused by synthetic dyes is a serious environmental concern due to their extensive use in textile, leather, paper, and other industries. Methylene blue (MB) is often employed as a model organic dye because of its high stability, toxicity, and resistance to biodegradation. Even at low concentrations, MB can reduce light penetration in aquatic environments, inhibit photosynthesis, and pose health risks to living organisms [1–3]. Therefore, developing efficient and cost-effective adsorbents for MB removal from wastewater remains an urgent scientific and technological task.

Natural clay minerals, particularly bentonite, are among the most widely used sorbents owing to their low cost, wide availability, high cation-exchange capacity, and layered structure that enables adsorption of various organic and inorganic pollutants [4,5]. However, pristine bentonite often has limited surface area and pore accessibility, restricting its adsorption capacity toward larger organic molecules such as dyes. To overcome these limitations, bentonite is frequently modified with other materials to create hybrid composites with enhanced textural and surface properties [6,7].

Silica (SiO_2) is an attractive modifier because it provides high surface area, chemical stability, and abundant silanol groups capable of interacting with pollutants. Incorporating silica into bentonite matrices can stabilize the clay structure, prevent layer collapse, and create additional porosity, thus improving adsorption performance [8]. Among various silica precursors, tetraethoxysilane (TEOS) is widely used in sol–gel synthesis because it can undergo controlled hydrolysis and condensation, forming homogeneous silica networks [9].

Recent studies have demonstrated that bentonite–silica composites exhibit improved adsorption capacities for heavy metal ions and dyes compared to raw bentonite. For instance, Zhou et al. [10] showed enhanced uptake of organic pollutants on clay–silica hybrids, while Zhao et al. [11] reported significant improvement in dye removal efficiency

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after silica modification of bentonite. Li et al. [12] developed bentonite–silica composites via sol–gel processing and observed that the introduction of silica increased mesoporosity and sorption efficiency toward methylene blue. These findings confirm that bentonite–silica hybrids can serve as promising adsorbents for wastewater treatment.

Nevertheless, adsorption mechanisms, isotherm behaviour, and thermodynamic properties strongly depend on the synthesis method, precursor ratio, and properties of the clay source. In particular, the use of local bentonite deposits combined with controlled sol–gel modification offers an opportunity to create low-cost, efficient adsorbents tailored for specific environmental applications.

In this work, a bentonite–silica composite was synthesised via a sol–gel method using natural Navbahor bentonite and TEOS as the silica precursor. The composite was comprehensively characterized by Fourier-transform infrared spectroscopy (FTIR) and low-temperature nitrogen adsorption –desorption analysis (BET, NLDFT). The adsorption performance was evaluated using methylene blue as a model dye pollutant, and the equilibrium data were analysed using Langmuir and the Freundlich isotherm models. Thermodynamic parameters (ΔG°, ΔH°, ΔS°) were also calculated to gain deeper insight into the adsorption mechanism.

This study aims to elucidate the relationship between the structural properties of the TEOS–bentonite composite and its adsorption behaviour toward methylene blue, thereby demonstrating its potential as a low-cost, efficient adsorbent for wastewater treatment.

2. Materials and Methods

Materials. Tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$, analytical grade) was used as a silica precursor without further purification. Ethanol and distilled water were applied as solvents. Natural Navbahor bentonite, preliminarily ground and sieved to <100 μm, served as the aluminosilicate component. All other reagents were of analytical grade.

Synthesis of bentonite–silica composite. The bentonite–silica composite was synthesised via a sol–gel process using TEOS as the silica source. A water–ethanol mixture was adjusted to pH ≈ 10–11 with aqueous ammonia under vigorous stirring. The calculated amount of TEOS was introduced dropwise, and the reaction mixture was heated to 60 ℃. After 15–20 min, when the formation of a white gel-like precipitate was observed, Navbahor bentonite was gradually added in portions at a mass ratio of TEOS/bentonite = 10:1. The reaction was continued for an additional 30–40 min at 60 ℃ under vigorous stirring to ensure homogeneous incorporation of the silica precursor into the clay matrix (Figure 1).

Afterwards, the mixture was cooled to room temperature and aged for 24 h to complete the polycondensation of TEOS and the consolidation of the silica network on the bentonite surface. The final product was collected, dried at ambient conditions, and stored in a desiccator until further physicochemical characterisation.

Characterization techniques

- **FTIR spectroscopy** was used to identify functional groups and confirm the incorporation of silica into the bentonite structure.
- **Low-temperature nitrogen adsorption–desorption (77 K)** was performed to determine specific surface area (BET method), pore volume, and pore size distribution (NLDFT model).
- **Adsorption experiments** were carried out using methylene blue (MB) as a model dye. Initial (C_0) and equilibrium (C_e) concentrations were measured spectrophotometrically. Isotherm data were fitted to the Langmuir and the Freundlich models.
- **Thermodynamic parameters** (ΔG°, ΔH°, ΔS°) were calculated from equilibrium constants at different temperatures.

3. Results and Discussion

FTIR Analysis of the Bentonite–Silica Composite

The FTIR spectrum of the bentonite–silica composite obtained using tetraethoxysilane (TEOS) as a precursor (Figure X) shows the combined features of montmorillonite and amorphous silica. A broad absorption band at 3700–3400 cm^{-1} corresponds to the stretching vibrations of hydroxyl groups, including structural –OH groups of bentonite and silanol groups (Si–OH) of the silica phase. The band near 1630 cm^{-1} is attributed to the bending vibrations of molecular water located in the interlayer space of bentonite (Figure 2).

Figure 1. Scheme for Obtaining a Silica-Bentonite Composite

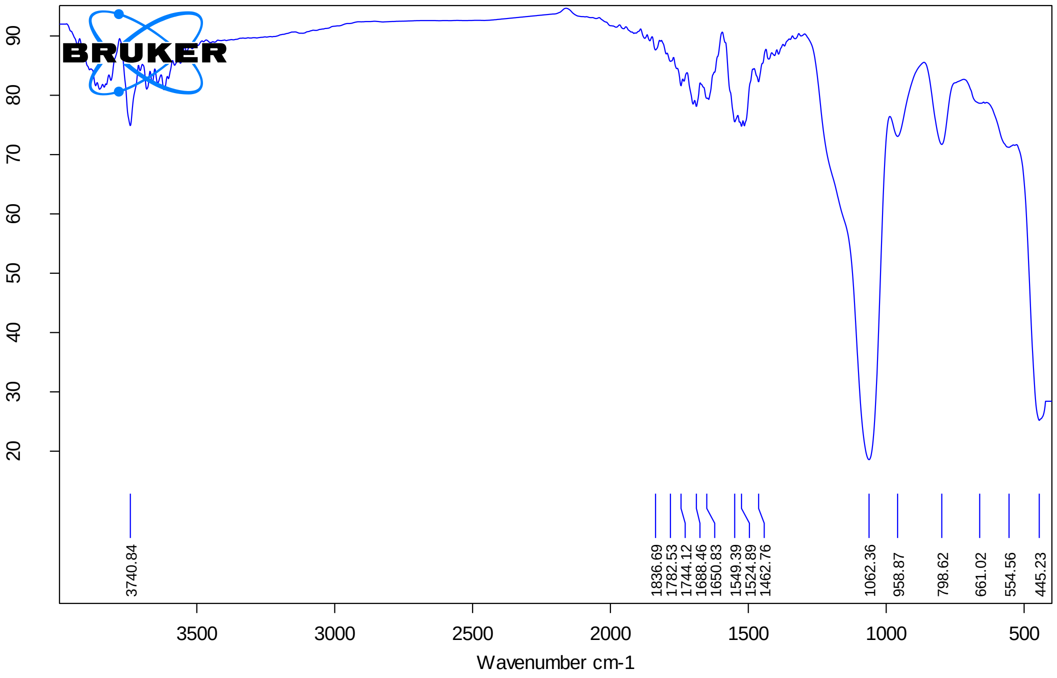

Figure 2. FTIR spectrum of the bentonite–silica composite

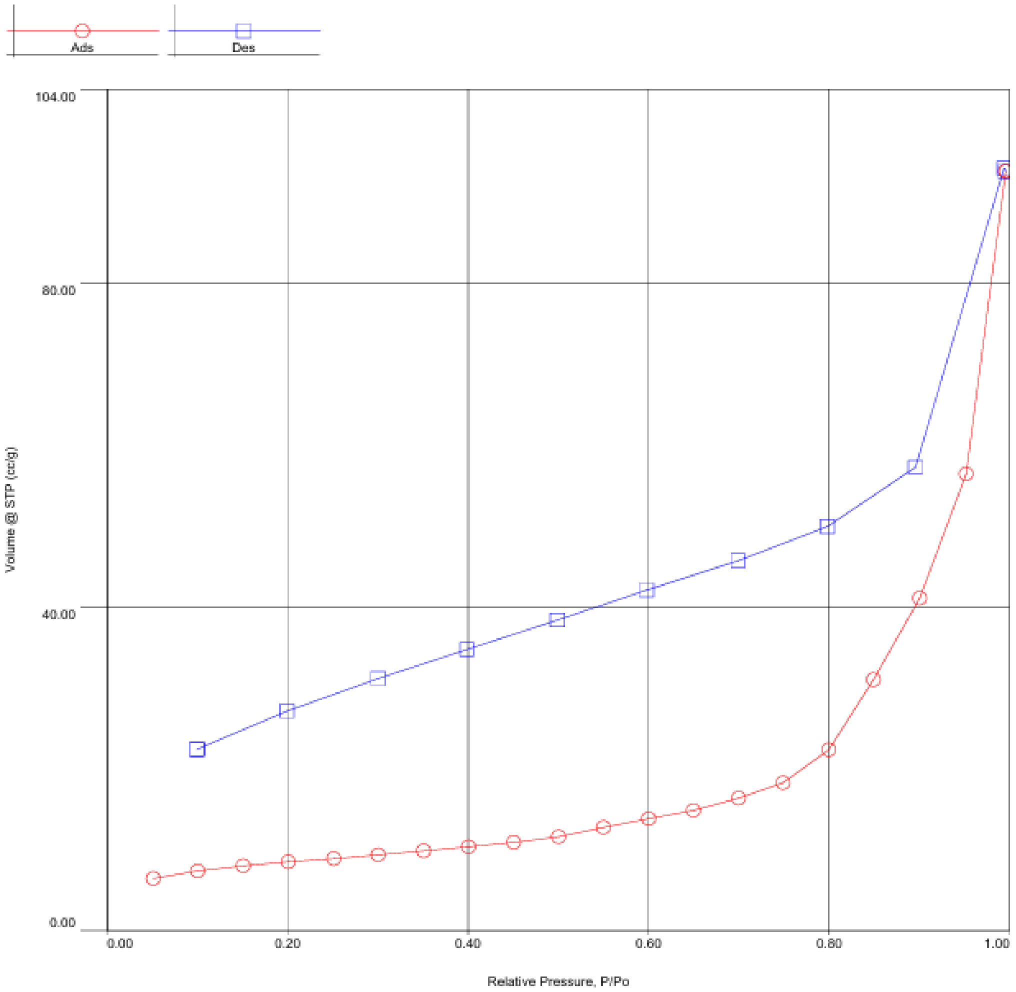

Figure 3. Low-temperature adsorption-desorption of N_2 on bentonite-silica composite

Intense absorptions at 1082 and 1036 cm^{-1} are characteristic of the asymmetric stretching vibrations of Si–O–Si bonds, confirming the formation of an amorphous silica network derived from TEOS hydrolysis and condensation. Additional bands at ~790–800 cm^{-1} and ~460 cm^{-1} correspond to the symmetric stretching and bending vibrations of Si–O–Si, respectively. The band at ~915 cm^{-1} is assigned to Al–Al–OH or Al–Mg–OH vibrations, while the peaks in the range 520–620 cm^{-1} are associated with Al–O–Si bonds typical for montmorillonite.

Compared with raw bentonite, the composite shows a marked increase in the intensity of Si–O–Si vibrations, which indicates the successful formation and deposition of a silica phase on the clay surface. At the same time, the preservation of Al–OH and Al–O–Si bands suggests that the layered structure of bentonite remains intact after modification.

Thus, the FTIR results confirm the synthesis of a bentonite –silica composite, in which TEOS-derived silica is strongly incorporated into the clay matrix while maintaining the fundamental structural characteristics of montmorillonite.

Textural characterization

The porous structure of the TEOS–bentonite composite was evaluated by low-temperature nitrogen adsorption–desorption at 77 K. The isotherm (Figure X) corresponds to type IV according to the IUPAC classification, with a pronounced H3-type hysteresis loop at relative pressures above $P/P_0 \approx 0.8$ (Figure 3). Such behaviour is typical of mesoporous adsorbents with slit-shaped pores formed by the aggregation of layered particles, which is consistent with the plate-like morphology of montmorillonite and the deposition of silica domains derived from TEOS hydrolysis and condensation.

The composite exhibited a specific surface area of 55.35 m^2/g^{-1} and a total pore volume of 0.122 cm^3/g^{-1}. Although these values are moderate compared with pristine bentonite, the decrease is attributed to the partial blocking of micropores by the silica network, accompanied by the creation of additional mesoporous channels. This structural reorganisation shifts the material from predominantly microporous to mesoporous character, which is beneficial for the adsorption of larger molecules.

The pore size distribution (PSD), derived from NLDFT analysis, revealed a dominant peak at half-pore width ~9–10 Å (effective pore width ~1.8–2.0 nm). This indicates the prevalence of narrow mesopores at the micro–meso boundary at the clay–silica interface. In addition, the PSD curve shows a long asymmetric tail extending toward larger pore sizes, reflecting the presence of broader slit-like voids and interparticle pores. This hierarchical porosity provides a dual function: narrow mesopores enhance the strength of adsorbate–surface interactions, while wider mesopores facilitate molecular transport and diffusion. The coexistence of these two pore populations explains the observed hysteresis in the isotherm and underlines the heterogeneous nature of the hybrid composite (Figure 4, table 1).

The textural analysis confirms that TEOS modification stabilises the bentonite framework and reorganises its porosity, leading to a hybrid mesoporous structure with balanced adsorption sites and transport pathways. Such properties are expected to improve the material's efficiency in environmental sorption applications significantly.

Adsorption isotherms and thermodynamic analysis

The adsorption equilibrium of methylene blue (MB) on the TEOS–bentonite composite was studied using the Langmuir and the Freundlich models, providing complementary insights into the adsorption mechanism.

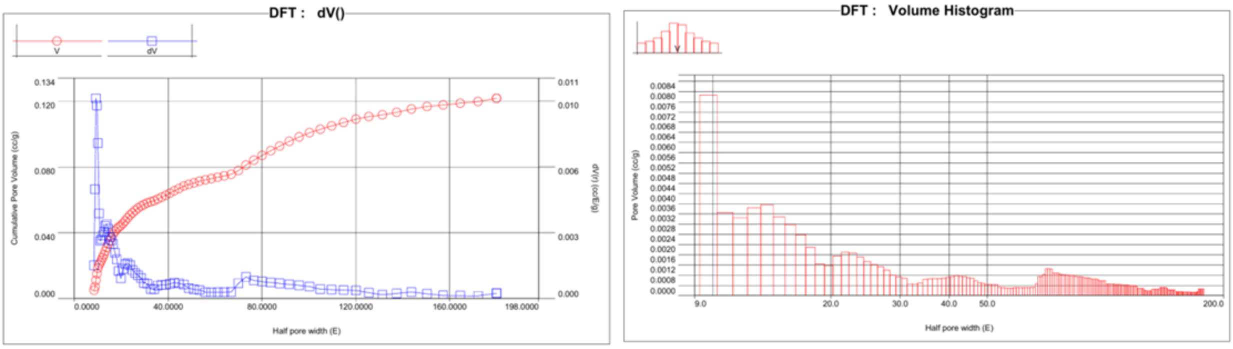

Figure 4. Cumulative pore volume (A) and pore volume (B) distribution

Table 1. Textural parameters of the TEOS–bentonite composite obtained from N_2 adsorption

Parameter	Value	Interpretation
Specific surface area (S_{BET})	55.35 m² g⁻¹	Moderate; indicates partial blocking of bentonite micropores by silica
Total pore volume (V_p)	0.122 cm³ g⁻¹	Typical for non-templated clay–silica hybrids, dominated by mesopores
Modal half-pore width (NLDFT)	9.23 Å	Corresponds to pore width ~1.8–2.0 nm; narrow mesopores at micro–meso boundary.
Pore system	Hierarchical	Narrow mesopores + broad interparticle voids; explains hysteresis loop

According to the Langmuir model, the adsorption capacities (q_{max}) were determined as 30.98, 26.78, and 17.09 mg g^{-1} at 293, 303, and 313 K, respectively. The apparent decrease in capacity with temperature reflects the exothermic nature of the process: at higher temperatures, thermal agitation prevents MB molecules from effectively binding to active sites, thereby reducing adsorption efficiency. Interestingly, the Langmuir affinity constant (K_L) reached its highest value (0.0939 L mg^{-1}) at 303 K, suggesting that at this intermediate temperature, an optimal balance exists between molecular diffusion in solution and sorbent–dye interactions. The correlation coefficients (R^2 = 0.95–0.98) confirm the adequacy of the Langmuir description, particularly at 293 and 313 K, while the slightly lower fit at 303 K hints at the influence of surface heterogeneity (Figure 5).

The Freundlich model, by contrast, emphasises the heterogeneous nature of the adsorption surface. The Freundlich constants (K_F) were 3.11, 4.80, and 1.52 at 293, 303, and 313 K, respectively. The highest value at 303 K reflects a strong affinity at this temperature; however, the drastic drop to 1.52 at 313 K demonstrates the loss of adsorption efficiency with heating. The heterogeneity factors n ranged from 1.79 to 2.34, with all values above unity, which confirms that adsorption is favourable under all tested conditions.

Table 2. Langmuir isotherm parameters for MB adsorption on TEOS–bentonite composite *(q_{max}, K_L, R^2at 293–313 K)*

T (K)	q_{max} (mg/g)	KL (L/mg)	R^2
293	30.98	0.0605	0.95
303	26.78	0.0939	0.94
313	17.09	0.046	0.98

The best statistical fits were obtained at 293 and 313 K (R^2 ≈ 0.96–0.99), showing that the Freundlich model is especially suitable when adsorption occurs on diverse binding sites and mesoporous structures. At 303 K, however, the correlation coefficient decreased to 0.85, indicating that adsorption behaviour at this temperature is closer to the idealised monolayer mechanism described by Langmuir.

Table 3. Freundlich isotherm parameters for MB adsorption on TEOS–bentonite composite *(K_F, n, R^2at 293–313 K)*

T (K)	K_F	n	R^2
293	3.11	1.79	0.96
303	4.8	2.34	0.85
313	1.52	1.82	0.99

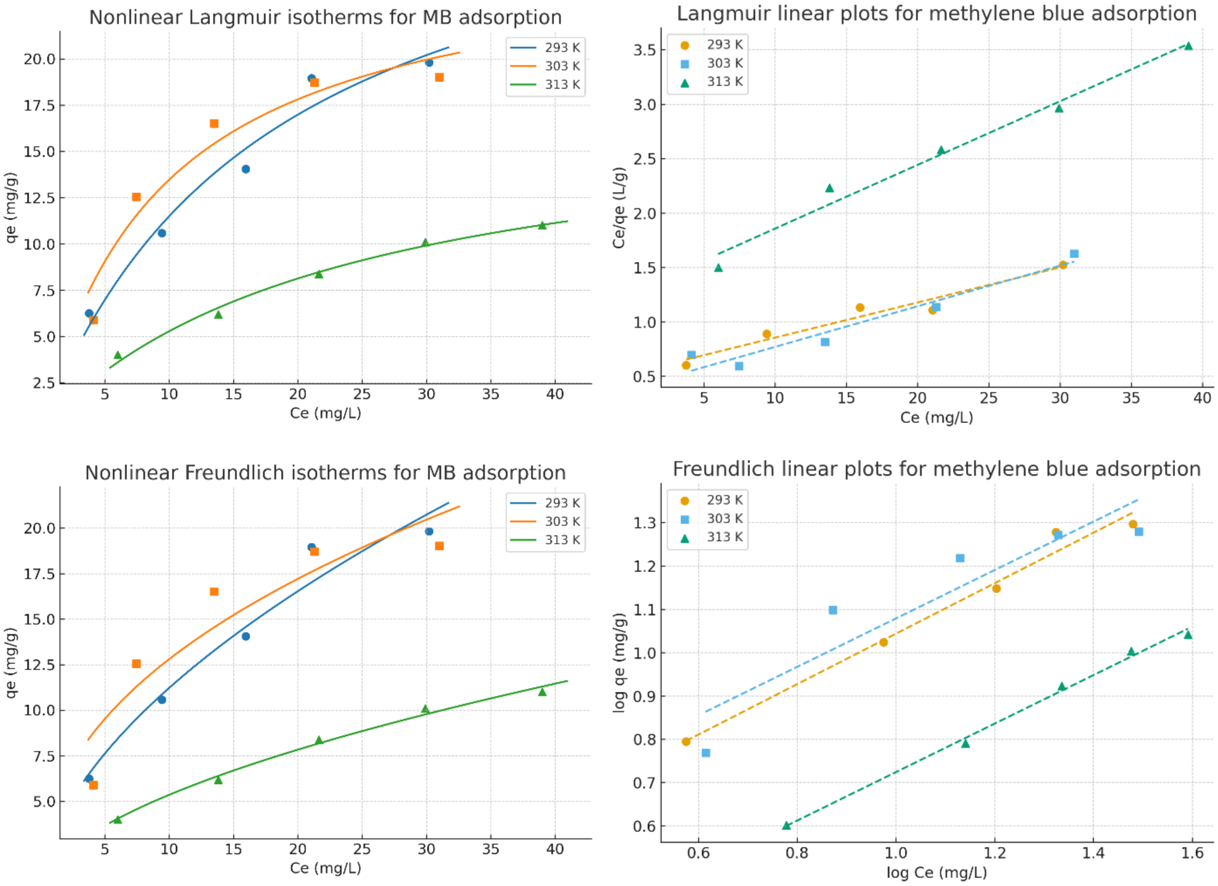

Figure 5. Adsorption isotherms of MB on TEOS-bentonite composite and Langmuir/Freundlich linear plots for methylene blue adsorption

Thermodynamic analysis derived from both models yields highly consistent results. Gibbs free energy values (ΔG°) were negative at all temperatures, approximately −24 to −26 kJ mol−1, confirming the spontaneous nature of the adsorption process. The enthalpy change was around −10 kJ mol^{-1}, typical of physisorption, dominated by weak van der Waals forces, electrostatic interactions, and possible *π–π* stacking between the dye's aromatic rings and the surface. The positive entropy change (ΔS° ≈ +45–50 J mol−1 K−1) indicates an increase in disorder at the solid–liquid interface, consistent with the release of hydration water molecules and counterions from bentonite interlayers and silica pores upon dye adsorption.

Table 4. Thermodynamic parameters of MB adsorption derived from Langmuir and Freundlich models (ΔG°, ΔH°, ΔS° at different T)

T (K)	ΔG° Langmuir (kJ/mol)	ΔG° Freundlich (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	-24.05	-23.4	-10.0	+49
303	-25.97	-25.5	-10.0	+49
313	-24.97	-24.2	-10.0	+49

Taken together, the two models highlight different aspects of the adsorption mechanism. The Langmuir model provides precise estimates of maximum adsorption capacity and confirms the exothermic monolayer character of MB uptake, with the best applicability at 303 K. The Freundlich model, in turn, better describes the adsorption behaviour at 293 and 313 K, where the heterogeneity of active sites is dominant. Despite these differences, both models converge thermodynamically, demonstrating that MB adsorption is favourable, spontaneous, and exothermic under all studied conditions.

Thus, MB adsorption on the TEOS–bentonite composite proceeds through a dual mechanism: homogeneous monolayer adsorption on silica-modified sites (Langmuir-type) coexists with heterogeneous and multilayer interactions within bentonite interlayers and mesoporous domains (Freundlich-type). This synergy ensures high capacity and adaptability to a wide range of dye concentrations, confirming the composite's strong potential as an effective adsorbent for water purification applications.

4. Conclusions

A bentonite–silica composite was successfully synthesised via a sol–gel process using tetraethoxysilane (TEOS) and natural Navbahor bentonite. Characterization confirmed the formation of an amorphous silica network within the clay matrix while preserving the structural features of montmorillonite. FTIR analysis revealed the coexistence of Si–O–Si vibrations typical of silica and Al–O–Si bands characteristic of bentonite. Nitrogen adsorption–desorption analysis demonstrated that TEOS modification transformed the material from predominantly microporous to mesoporous, with a surface area of 55.35 m^{2}g^{-1}, a pore volume of 0.122 cm^{3}g^{-1}, and a hierarchical pore system that improves adsorption and diffusion.

Adsorption studies using methylene blue (MB) as a model dye pollutant showed maximum adsorption capacities of 30.98, 26.78, and 17.09 mg g^{-1} at 293, 303, and 313 K, respectively. Langmuir fitting indicated monolayer adsorption with high correlation coefficients, particularly at 303 K, while the Freundlich analysis confirmed surface heterogeneity with n > 1, indicating favourable sorption. Thermodynamic parameters (ΔG° = −24 to −26 kJ mol^{-1}, ΔH° ≈ −10 kJ mol^{-1}, ΔS° ≈ +45–50 J mol^{-1} K^{-1}) verified that adsorption is spontaneous, exothermic, and dominated by physisorption.

Overall, MB uptake on the TEOS–bentonite composite proceeds via a dual mechanism: monolayer adsorption on silica-modified sites and heterogeneous sorption in bentonite domains. This synergy enhances adsorption efficiency and stability, demonstrating that TEOS–bentonite composites are promising, low-cost, and eco-friendly adsorbents for wastewater treatment. Such materials, derived from abundant natural resources and prepared via a simple sol–gel method, can contribute significantly to sustainable environmental remediation technologies.

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