

Adsorption isotherms and capacity sodium metabisulfite modified duck feather waste as a keratin biosorbent for methylene blue removal

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ABSTRACT

This study aimed to evaluate the effect of duck feather keratin modified with sodium metabisulphite on the physicochemical properties and the adsorption equilibrium of methylene blue (MB). The duck feather powder was modified with a 0.325 M Na₂S₂O₅ solution, and batch adsorption was carried out at pH 8 for 110 minutes using measured initial MB concentrations equivalent to nominal levels of 25 to 300 mg L⁻¹. Each adsorption condition was carried out in three independent batches. SEM-EDX, FTIR and BET analyses showed that the modification resulted in a rougher matrix, changes in morphological composition and a shift in the amide band of the functional groups, as well as an increase in surface area from 0.1437 to 0.2770 m² g⁻¹ and pore volume from 0.0045 to 0.0088 cm³ g⁻¹. Across the entire concentration range, the average equilibrium capacity increased by 9.3–58.9% following modification. Non-linear model calculations showed that the unmodified data could be similarly explained by both the Freundlich and Langmuir equations, with the Freundlich equation yielding a slightly lower RMSE, whilst the modified data were better described by the Langmuir equation. The estimated Langmuir capacity increased from 13.250 ± 0.612 mg g⁻¹ to 20.177 ± 0.751 mg g⁻¹, equivalent to an increase of 52.3%, whilst increased from 0.140 ± 0.032 to 1.656 ± 0.315 L mg⁻¹, with R² = 0.963 and RMSE = 1.333 mg g⁻¹. These results indicate a relationship between sulphitolytic modification, changes in site accessibility and surface chemistry, as well as enhanced MB removal. The characterisation results and equilibrium models remain complementary evidence and do not independently establish the adsorption mechanism.

Keywords: adsorption, duck feathers, methylene blue, Na₂S₂O₅, Langmuir isotherm.

INTRODUCTION

Synthetic dyes released from textile, paper, cosmetic, plastic, and dye-processing industries represent a persistent source of aquatic contamination because many of these compounds are highly water-soluble and resistant to natural degradation (Aragaw and Bogale, 2021; Khan et al., 2022). Their presence in wastewater can reduce light penetration, interfere with photosynthetic activity, and adversely affect aquatic organisms and environmental quality. Among commonly investigated dye pollutants, methylene blue (MB) is a cationic

thiazine dye that has been associated with reduced light transmission, suppression of photosynthetic activity, and adverse effects on aquatic organisms, while exposure to MB may also cause irritation, respiratory complications, and other toxicological effects (Oladoye et al., 2022; Pathania et al., 2017; Rápó and Tonk, 2021). Consequently, the development of effective, affordable, and environmentally sustainable approaches for the removal of synthetic dyes from contaminated water remains an important challenge in environmental engineering.

A range of physicochemical and advanced treatment technologies has been developed for

dye removal. However, the practical implementation of some conventional and advanced processes may be constrained by operational complexity, energy requirements, chemical consumption, or treatment cost. Adsorption has therefore attracted considerable attention as a practical approach for MB removal because of its operational simplicity, process flexibility, relatively low cost, and potential for achieving high removal efficiency. Compared with coagulation, membrane separation, electrochemical treatment, and advanced oxidation processes, adsorption can provide a comparatively straightforward route for the treatment of dye-contaminated water (Al Ashik et al., 2023; Somsesta et al., 2020). Recent environmental engineering studies have likewise demonstrated the potential of adsorption and other environmentally oriented treatment technologies for the remediation of dye-contaminated wastewater, including the use of waste-derived activated carbon for Reactive Black 5 removal and green-synthesized ZnO nanoparticles for photocatalytic degradation of Acid Blue 25 (Belay et al., 2025; Yerima et al., 2024). These studies further highlight the growing importance of combining pollutant removal with sustainable material development and waste valorization in wastewater treatment.

The search for low-cost and environmentally sustainable adsorbents has consequently expanded toward abundant agricultural, biomass, and industrial waste streams. Materials derived from coconut coir, cellulose composites, alkali-treated areca residues, spent tea, citrus biomass, and other renewable resources have been investigated for MB removal, with adsorption equilibrium commonly evaluated using Langmuir and Freundlich models (Lu et al., 2022; Tuli et al., 2020; Zhou et al., 2023). Such approaches are particularly relevant to wastewater treatment because the conversion of waste into functional adsorbents can simultaneously contribute to waste reduction, resource recovery, and pollutant removal. However, adsorption performance depends strongly on the physicochemical characteristics of the precursor material and on the accessibility, abundance, and chemical nature of its surface functional groups.

Duck feather waste represents a potentially valuable but underutilized feedstock for biosorbent production. Its keratin-rich matrix contains amino, carboxyl, hydroxyl, amide, and sulfur-bearing functional groups that may interact with

dissolved pollutants and provide potential adsorption sites (Alvarez et al., 2023; Utami et al., 2020). Duck feathers contain approximately 91% keratin, supporting their conversion from an underutilized organic residue into functional materials with added environmental value (Zubair et al., 2023). Nevertheless, the native keratin structure is stabilized by disulfide cross-links, intermolecular hydrogen bonding, and hydrophobic interactions, resulting in a relatively compact matrix that may limit the accessibility of internal functional groups to adsorbate molecules. Chemical, thermal, and enzymatic pretreatments have therefore been investigated as strategies for modifying keratin structure and potentially increasing the accessibility of adsorption sites (Mattiello et al., 2023).

Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) is of particular interest for keratin modification because sulfite-mediated cleavage of disulfide bonds can alter the structure of the keratin matrix and generate thiol- and cysteine S-sulfonate-containing species, potentially increasing the accessibility of chemically active sites (Marliyana et al., 2024). Wang et al. (2016) reported that $\text{Na}_2\text{S}_2\text{O}_5$ treatment increased the availability of binding sites in feather fibres. Similarly, Utami et al. (2020a) observed an increase in Fe(III) adsorption capacity from 111.11 to 125.00 mg g^{-1} following chemical modification of duck feathers, while other studies have examined the equilibrium behaviour of modified duck-feather materials using Langmuir and Freundlich models (Utami et al., 2020b). These findings suggest that chemical modification can improve the adsorption performance of keratin-based materials, however the extent to which such modification affects the adsorption of organic dyes, particularly cationic dyes such as MB, remains.

The adsorption behaviour of MB is strongly influenced by the surface chemistry, pore structure, and spatial distribution of functional groups in the adsorbent. Studies using modified ZSM-5, natural clays, agar/ κ -carrageenan hydrogels, olive-stone biomass, and other materials have demonstrated that differences in surface heterogeneity and pore architecture can substantially affect equilibrium adsorption behaviour (Al-Ghouti and Al-Absi, 2020; Bentahar et al., 2017; Duman et al., 2020; Hamed et al., 2016). For this reason, understanding whether chemical modification of duck-feather keratin changes its adsorption capacity and equilibrium behaviour requires consideration of both the physicochemical

properties of the material and the mathematical description of the adsorption process. The Langmuir model describes adsorption on a finite population of sites with comparable adsorption energies, whereas the Freundlich model is commonly used to describe heterogeneous surfaces and non-uniform adsorption energies (Ayawei et al., 2017; Danat et al., 2026). Moreover, comparison of linearized and nonlinear isotherm formulations is important because linearization can alter the statistical error structure and may produce different estimates of adsorption parameters, whereas nonlinear regression evaluates the original model formulation directly (Guo and Wang, 2019; Sreńscek-Nazzal et al., 2015).

Despite the growing body of research on waste-derived adsorbents and modified feather-based materials, an important knowledge gap remains concerning the relationship between $\text{Na}_2\text{S}_2\text{O}_5$ -induced modification of duck-feather keratin, changes in its physicochemical characteristics, and the resulting equilibrium adsorption behaviour toward methylene blue. Previous studies have demonstrated the potential of modified duck feathers for the removal of inorganic contaminants such as Fe(III), while other studies have investigated MB adsorption using a wide range of biomass-derived materials. However, the specific effect of $\text{Na}_2\text{S}_2\text{O}_5$ modification on the MB adsorption capacity of duck-feather keratin, together with the associated changes in surface morphology, elemental composition, functional groups, textural properties, and equilibrium model parameters, has not been sufficiently clarified. In particular, it remains unclear whether chemical modification improves MB uptake primarily by increasing the accessibility of adsorption sites, by altering the apparent affinity of the keratin matrix for MB, or by modifying both factors simultaneously.

Therefore, the present study aims to determine how $\text{Na}_2\text{S}_2\text{O}_5$ modification affects the adsorption performance and equilibrium behaviour of duck-feather keratin toward methylene blue. The study specifically seeks to (i) compare the MB adsorption capacity of untreated and $\text{Na}_2\text{S}_2\text{O}_5$ -modified duck-feather materials; (ii) characterize the changes in surface morphology, elemental composition, functional groups, and textural properties associated with chemical modification using SEM-EDX, FTIR, and BET analyses; and (iii) determine whether the modification alters the apparent adsorption capacity and affinity of the material as described by linear and nonlinear

Langmuir and Freundlich models. The central hypothesis is that $\text{Na}_2\text{S}_2\text{O}_5$ treatment disrupts disulfide cross-linking within the keratin matrix and increases the accessibility of functional groups and adsorption sites, thereby enhancing MB uptake and changing the equilibrium adsorption behaviour of the material. By testing this hypothesis through the integrated analysis of material characterization and adsorption isotherms, the study is expected to clarify the extent to which chemical modification improves the functionality of duck-feather waste as a keratin-based biosorbent and to provide new insight into the structure–property relationship governing MB adsorption on modified feather-derived materials.

MATERIAL AND METHODS

Preparation and chemical modification of duck feathers

The preparation stage used 1.0 kg of duck feathers. Water and detergent removed adhering impurities, after which sun drying continued until the material became odourless. The dried feathers were cut, milled, and sieved to obtain a 40-mesh powder. A 24 h petroleum ether treatment removed lipids from the powder. Vacuum filtration through a Buchner funnel separated the solid fraction, which was then dried at 70 °C. The modification step combined 20 g of dried powder with 250 mL of 0.325 M $\text{Na}_2\text{S}_2\text{O}_5$ in a three-necked flask. Continuous magnetic stirring maintained the suspension at 70 °C for 10 h. Filtration recovered the treated solid, repeated washing with distilled water removed residual chemicals, and oven drying at 100 °C produced the final adsorbent.

Determination of adsorption capacity

Equilibrium experiments employed the previously established optimum pH of 8 and a contact period of 110 min, conditions established in preliminary optimisation experiments using the same adsorbent system. Dilution of an MB stock solution produced concentrations of 25, 50, 75, 100, 125, 150, 175, 200, and 300 mg L⁻¹. Each run combined 200 mg of adsorbent with 25 mL of dye solution in an Erlenmeyer flask. An orbital shaker mixed 150 rpm the suspension for 110 min, and filtration then separated the adsorbent from the liquid phase. A GENESYS 10S UV-visible

spectrophotometer (Thermo Scientific) measured the residual MB concentration at the maximum absorption wavelength of 665 nm.

Adsorbent characterisation

SEM-EDX examination provided information on surface architecture and elemental composition. ATR-FTIR (Bruker) spectroscopy identified the principal functional groups and tracked chemical changes caused by Na₂S₂O₅ treatment and MB adsorption. A surface area analyser quantified the specific surface area, pore volume, and mean pore diameter. The FTIR spectra recorded infrared absorbance as a function of wavenumber, allowing the assignment of characteristic vibrations within the keratin matrix.

Data analysis

The analysis compared MB uptake by untreated and modified duck feather adsorbents. The calculation of equilibrium capacity used the loss of MB from solution, the liquid volume, and the adsorbent mass. For each independent adsorption batch, the study calculated the equilibrium concentration C_e from the UV-Vis calibration equation after applying the corresponding dilution factor. The study then determined the equilibrium adsorption capacity using q_e , where C_0 and C_e represent the measured initial and equilibrium MB concentrations, respectively, in mg L⁻¹, V represents the solution volume in litres, and m represents the adsorbent mass in grams. The study calculated the percentage removal using $100(C_0 - C_e)/C_0$. For each concentration, the study expressed the results as the mean $\pm$ standard deviation from three independent adsorption experiments $n=3$. The study reported the standard errors of the fitted model parameters separately because these values describe parameter-estimation uncertainty and do not replace the experimental standard deviation.

The study fitted the equilibrium results linear rearrangements and the original nonlinear form of the Langmuir equation, as well as the linear and nonlinear Freundlich equations. The mathematical expressions remained unchanged because they constitute standard model formulations.

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

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$q_e = q_m K_L C_e^{1/n} \quad (4)$$

In these expressions, q_e denotes the adsorbed amount at equilibrium (mg g⁻¹), C_e represents the equilibrium concentration in solution (mg L⁻¹), q_m gives the theoretical Langmuir capacity (mg g⁻¹), and K_L describes Langmuir affinity (L mg⁻¹). For the Freundlich model, K_F represents adsorption capacity and n characterises adsorption intensity. The coefficient of determination and the standard errors of fitted parameters served as criteria for comparing model performance.

Study limitation and scope

The present study was designed to evaluate the physicochemical characteristics and equilibrium adsorption performance of untreated and Na₂S₂O₅-modified duck-feather keratin toward methylene blue under controlled laboratory conditions. The scope of the study was therefore limited to material characterization and equilibrium adsorption modelling. Although the combined SEM, EDX, FTIR, and BET results provide evidence of structural, textural, and chemical changes following Na₂S₂O₅ treatment, these analyses do not independently or conclusively establish the molecular mechanism responsible for MB adsorption. Similarly, the equilibrium experiments and isotherm modelling do not assess the regeneration capacity, reusability, long-term stability, or performance of the modified adsorbent in complex or real wastewater matrices. These aspects were beyond the scope of the present investigation and should be addressed in future studies to determine the practical applicability and long-term environmental performance of Na₂S₂O₅-modified duck-feather keratin as a waste-derived biosorbent.

RESULT AND DISCUSSION

Adsorbent characterization

(SEM-EDX) analysis

The archived SEM micrographs were used to compare the surface morphology of untreated duck feathers, Na₂S₂O₅-modified feathers,

and the modified material recovered after MB adsorption. Before imaging, the samples were coated with a thin layer of gold (Au) to improve electrical conductivity and minimise charging under the electron beam. The retained metadata indicated that the micrographs were obtained at 5000x magnification, with an accelerating voltage of 10 kV, a working distance of approximately 7 mm, and a scale bar of 30 μm . Under these imaging conditions, the untreated feathers exhibited a relatively compact and heterogeneous fibrous morphology with limited surface disruption. Following $\text{Na}_2\text{S}_2\text{O}_5$ treatment, the fibres appeared rougher, more fragmented, and less compact, suggesting that the modification altered the organisation of the keratin matrix. After MB adsorption, additional surface coverage and changes in the spaces between fibres were observed. These features are consistent with the presence of adsorbed material on the feather surface, but they do not independently confirm pore filling or a specific binding pathway.

The morphological changes observed after modification may have improved contact between MB molecules and accessible amino, amide, hydroxyl, carboxyl, and sulphur-containing groups within the keratin matrix (Amin et al., 2024). However, SEM provides visual information on surface morphology rather than a direct measurement of adsorption-site density or molecular interactions. Therefore, the micrographs support the hypothesis that $\text{Na}_2\text{S}_2\text{O}_5$ treatment altered the surface structure and potentially affected site accessibility, but they should not be interpreted as definitive evidence of an increased number of active sites adsorption mechanism (Figure 1).

EDX analysis provided complementary semiquantitative information on the surface elemental composition of untreated duck feathers,

$\text{Na}_2\text{S}_2\text{O}_5$ -modified feathers, and the modified material after MB adsorption, as shown in Figure 2. One archived spectrum was available for each sample condition, and the atomic and weight percentages were transcribed directly from the instrument-generated quantification tables. The modified and post-adsorption samples were analysed using an acquisition time of 30 s, whereas the corresponding acquisition time for the untreated sample was not retained in the archived records.

The untreated feathers were dominated by C, N, O, and S, with atomic percentages of 54.518, 14.071, 28.162, and 3.249%, respectively, which is consistent with the elemental composition of keratin. After $\text{Na}_2\text{S}_2\text{O}_5$ modification, the atomic composition changed to C 48.127%, N 8.094%, O 29.333%, Na 5.410%, and S 9.036%. The appearance of Na and the increase in the relative S content are consistent with the presence of species associated with sodium metabisulphite treatment and suggest that the modification altered the surface elemental environment of the keratin material. However, these changes do not independently establish the chemical form, distribution, or binding state of the incorporated sulphur-containing species.

Following MB adsorption, the measured atomic percentages were C 50.726%, N 15.666%, O 31.129%, Na 0.122%, S 2.237%, and Cl 0.119%. The increase in N and the appearance of a small Cl signal are consistent with the presence of MB-associated species on the adsorbent surface because MB contains nitrogen atoms and chloride as a counter-ion. Similar EDX changes after dye adsorption have been reported for other biosorbent systems and may provide supporting evidence of adsorbate retention on the material surface (Koyuncu and Kul, 2024; Song et al., 2022). Nevertheless, the Cl signal was low, and EDX does

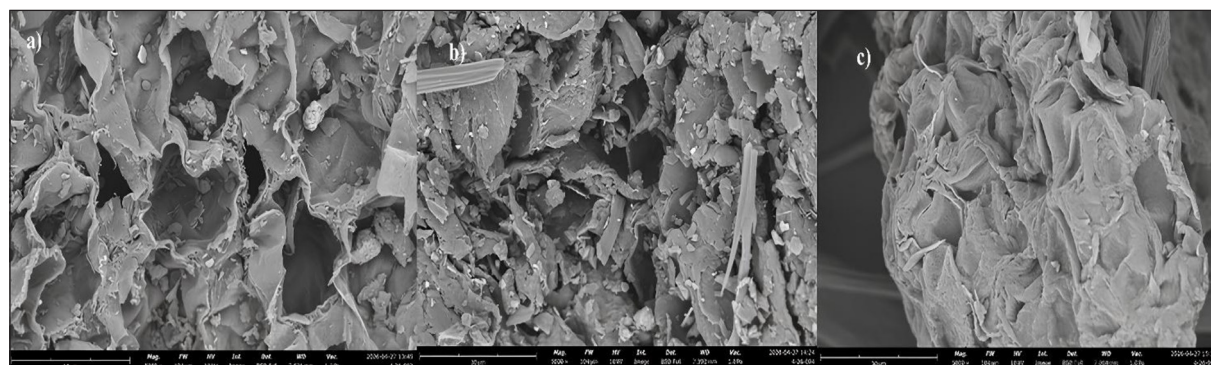


Figure 1. SEM a) Duck feather before modification b) SEM duck feather- $\text{Na}_2\text{S}_2\text{O}_5$ c) SEM duck feather- $\text{Na}_2\text{S}_2\text{O}_5$ -MB

not identify the molecular form or interaction responsible for adsorption. Therefore, these results should be interpreted as complementary evidence consistent with MB uptake rather than as definitive proof of a specific MB-binding mechanism.

FTIR analysis

Untreated duck feathers exhibited characteristic keratin absorption bands at 3269, 2957, 1625, 1517, 1233, and 1069 cm^{-1} . These signals correspond to O-H or N-H stretching, aliphatic C-H stretching, amide I, amide II, amide III, and C-N or C-O vibrations, respectively. This spectral profile is consistent with that reported by Utami et al. (2020b), principal keratin bands for duck feathers at approximately 3266, 1629, 1532, 1236 and 1072 cm^{-1} . Utami et al. (2026a) similarly observed shifts in absorption bands from 1629.27 to 1618.80 cm^{-1} and from 1072.32 to 1023.44 cm^{-1} following $\text{Na}_2\text{S}_2\text{O}_5$ modification of duck feathers. After MB adsorption, the principal bands of the modified keratin remained evident at 1627, 1529 and 1232 cm^{-1} , whereas the band near 1024 cm^{-1} underwent a minor shift to 1022 cm^{-1} . The absence of substantive alterations in the amide I and amide II regions suggests that the primary polypeptide backbone remained intact during adsorption, while the small shift in the lower-wave-number region is indicative of local changes in the chemical environment of C-N, C-O or sulphur containing functional groups.

Therefore, the interaction between MB at pH 8, deprotonated carboxylate sites, and S-sulphate groups may contribute to the cationic affinity of MB, whilst amide, hydroxyl and other polar groups may support hydrogen bonding or dipolar interactions. This explanation remains a mechanistic conclusion, as the current FTIR data indicate band positions rather than specific evidence of direct

bonding. This interpretation is consistent with Utami and Ariyani (2023), who also used shifts in the amide and C-N/C-O bands as supporting evidence for the presence of non-covalent interactions between the adsorbate molecules and the chemically modified duck feather keratin (Figure 3).

Surface area analyzer (SAA)

Nitrogen adsorption at 77.3 K provided the basis for Brunauer-Emmett-Teller analysis of the adsorbents. Measurements used a NOVA 800 surface area analyser. The method generated the specific surface area, pore volume, and mean pore diameter values summarised in Table 1.

The textural properties of untreated and $\text{Na}_2\text{S}_2\text{O}_5$ -modified duck-feather adsorbents were evaluated to identify treatment-associated changes in the keratin matrix, as summarised in Table 1. Modification increased the specific surface area from 0.1437 to 0.2770 $\text{m}^2 \text{g}^{-1}$ and the pore volume from 0.0045 to 0.0088 $\text{cm}^3 \text{g}^{-1}$, corresponding to relative increases of 92.8% and 95.6%, respectively. In contrast, the mean pore diameter increased only slightly, from 52.72 to 55.46 nm, or approximately 5.2%. These results indicate that $\text{Na}_2\text{S}_2\text{O}_5$ treatment altered the texture of the feather material, although the specific surface areas remained very low in absolute terms. Because both adsorbents underwent the same petroleum-ether defatting procedure, differences in their textural properties cannot be attributed primarily to differential removal of waxes or lipids. A more plausible explanation involves structural changes induced by $\text{Na}_2\text{S}_2\text{O}_5$ treatment, which generates bisulphite species in aqueous media and may partially disrupt disulphide cross-links through sulphytolysis, thereby modifying the organisation and accessibility of the cross-linked keratin matrix (Utami et al., 2020a).

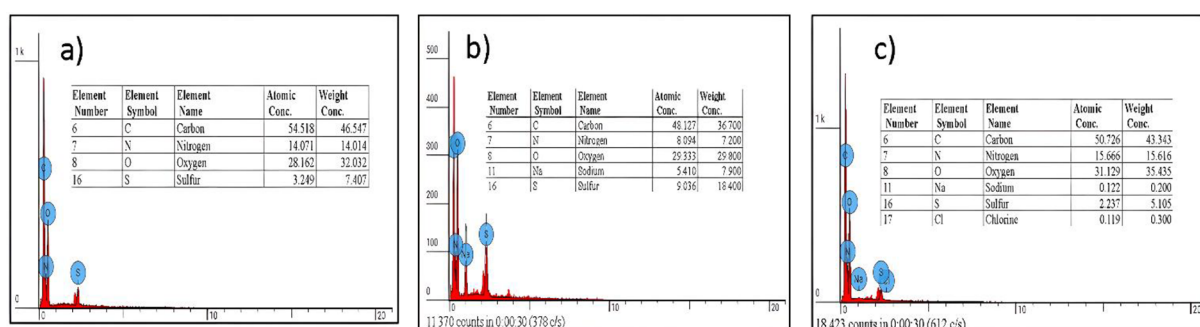


Figure 2. a) EDX duck feather before modification b) EDX duck feather- $\text{Na}_2\text{S}_2\text{O}_5$ c) EDX duck feather- $\text{Na}_2\text{S}_2\text{O}_5$ -MB

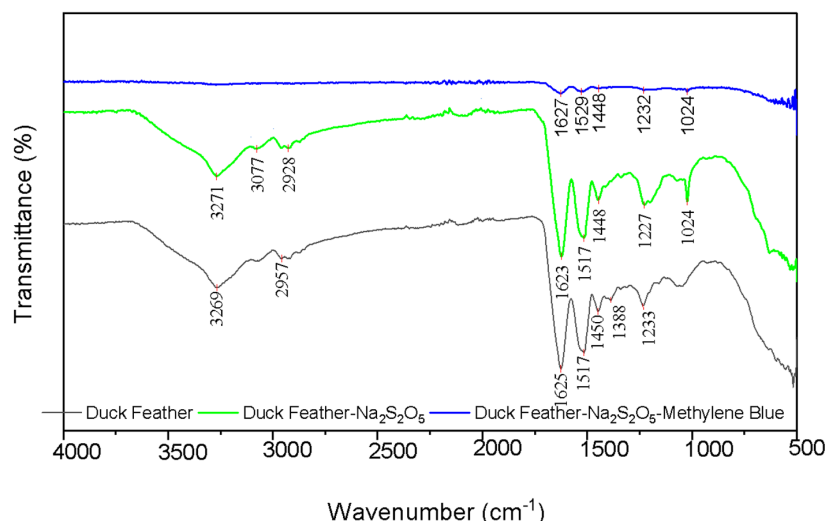


Figure 3. Spekta FTIR duck feather

Table 1. Textural propeties of duck feathers adsorbents

Parameters	Untreated	Na ₂ S ₂ O ₅ -modified	Relative change
Specific surface area (m ² g ⁻¹)	0.1437	0.2770	+92.8%
Pore volume (cm ³ g ⁻¹)	0.0045	0.0088	+95.6%
Mean pore diameter (nm)	52.7233	55.4622	+5.2%

The estimated Langmuir capacity increased by 52.3% following modification. However, this increase cannot be attributed solely to an increase in surface area. Several interrelated factors may have contributed, including changes in external morphology, local pore accessibility, the chemical environment of the keratin functional groups, and the pseudo-affinity of cationic MB towards accessible polar or anionic sites. The calculated average pore diameter lies slightly above the conventional 50 nm threshold used to distinguish mesopores from macropores according to the IUPAC classification (Thommes et al., 2015). However, these values must be interpreted with caution as the original nitrogen adsorption-desorption isotherms are not available for independent re-analysis. Larger pseudo-pores may facilitate the transport of adsorbates to accessible binding sites, but the current BET data do not independently prove the existence of pore-controlled adsorption or a causal relationship between pore dimensions and MB adsorption (Liu et al., 2021). Overall, these results support a relationship between the textural and chemical changes induced by Na₂S₂O₅ and the increased adsorption of MB.

Determination of adsorption capacity

The MB adsorption capacity of the Na₂S₂O₅ treated duck feather biosorbent for was determined under previously optimized conditions (pH 8, contact time 110 min). MB solutions were prepared with starting concentrations of 25 to 300 mg L⁻¹. Independent calculation used measured C₀ values and replicate-specific C_e values. Modification increased mean q_e at every concentration, from a nominal C₀ = 25 mg L⁻¹ at the highest tested concentration, mean q_e increased from 14.393 ± 0.042 to 21.660 ± 0.032 mg g⁻¹ (Table 2).

Linear isotherm analysis

Figure 4 presents the linearised Langmuir and Freundlich plots, while Table 3 summarises the fitted parameters and the corresponding error statistics evaluated on the original q_e scale. The Langmuir linearisation produced high coefficients of determination for both materials, with R² values of 0.988 for the untreated feathers and 0.998 for the modified feathers. The fitted q_m increased from 14.716 ± 0.612 to 21.566 ± 0.385 mg g⁻¹ after Na₂S₂O₅ treatment, corresponding to an increase of approximately 46.5%. The apparent Langmuir affinity constant, K_L also increased

Table 2. Measured initial concentrations for untreated and modified adsorbents (mean $\pm$ SD, $n = 3$)

Nominal C_0 (mg L ⁻¹)	Measured C_0 (mg L ⁻¹)	Untreated C_e mean $\pm$ SD	Untreated q_e mean $\pm$ SD	Modified C_e mean $\pm$ SD	Modified q_e mean $\pm$ SD
25	24.805	2.173 $\pm$ 0.180	2.829 $\pm$ 0.023	0.062 $\pm$ 0.022	3.093 $\pm$ 0.003
50	50.274	4.539 $\pm$ 0.217	5.717 $\pm$ 0.027	0.145 $\pm$ 0.022	6.266 $\pm$ 0.003
75	71.554	8.111 $\pm$ 0.088	7.930 $\pm$ 0.011	0.557 $\pm$ 0.005	8.875 $\pm$ 0.001
100	97.323	25.137 $\pm$ 0.000	9.023 $\pm$ 0.000	1.148 $\pm$ 0.013	12.022 $\pm$ 0.002
125	124.589	40.349 $\pm$ 0.220	10.530 $\pm$ 0.027	1.871 $\pm$ 0.013	15.340 $\pm$ 0.002
150	147.032	57.423 $\pm$ 0.725	11.201 $\pm$ 0.091	4.614 $\pm$ 0.013	17.802 $\pm$ 0.002
175	171.405	74.270 $\pm$ 0.418	12.142 $\pm$ 0.052	17.390 $\pm$ 0.083	19.252 $\pm$ 0.010
200	194.264	97.046 $\pm$ 0.254	12.152 $\pm$ 0.032	41.430 $\pm$ 0.166	19.104 $\pm$ 0.021
300	280.299	165.157 $\pm$ 0.523	14.393 $\pm$ 0.065	107.021 $\pm$ 0.254	21.660 $\pm$ 0.032

from 0.080 ± 0.022 to 0.809 ± 0.459 L mg⁻¹. These changes are consistent with higher apparent MB uptake and affinity after modification within the concentration range investigated. However, the relatively large standard error associated with K_L for the modified material indicates considerable uncertainty in the magnitude of this parameter and therefore warrants cautious interpretation.

The Freundlich parameters also changed after modification. The K_F value increased from 3.077 ± 0.467 to 9.536 ± 0.959 , while n increased from 3.131 ± 0.420 to 4.266 ± 0.718 . The n values above unity are consistent with favourable adsorption under the experimental conditions. Nevertheless, the Freundlich linearisation yielded lower R^2 values of 0.888 and 0.834 for the untreated and modified adsorbents, respectively. These transformed-scale results indicate that the Freundlich linear plots followed the experimental trend less closely than the corresponding Langmuir plots, particularly for the modified material. Interpretation based solely on the transformed R^2 values would, however, be incomplete because linearisation changes the weighting and residual

structure of the original equilibrium data. The RMSE values calculated on the original q_e scale provide a complementary assessment. For the modified adsorbent, Langmuir produced a lower RMSE than Freundlich, namely 2.337 compared with 3.883 mg g⁻¹, indicating that the Langmuir parameters gave a more adequate empirical description of the modified-feather data. In contrast, for the untreated adsorbent, Freundlich produced a slightly lower RMSE than Langmuir, with values of 1.127 and 1.293 mg g⁻¹, respectively. Thus, although the Langmuir linearisation displayed a higher transformed R^2 , the original-scale error statistics do not show a clear superiority of Langmuir for the untreated material.

Nonlinear isotherm analysis

Figure 5 presents the nonlinear Langmuir and Freundlich fits, while Table 4 summarises the estimated parameters and the corresponding error statistics calculated on the original q_e scale. The results show that the relative performance of the two models differed between the untreated and modified duck-feather adsorbents.

Table 3. Linearised-model parameters and original q_e scale error statistics

Models	Parameter	Untreated	Modified
Langmuir	q_m (mg g ⁻¹)	14.716 $\pm$ 0.612	21.566 $\pm$ 0.385
	K_L (L mg ⁻¹)	0.080 $\pm$ 0.022	0.809 $\pm$ 0.459
	R^2	0.988	0.998
	RMSE (mg g ⁻¹)	1.293	2.337
Freundlich	K_F	3.077 $\pm$ 0.467	9.536 $\pm$ 0.426
	n	3.131 $\pm$ 0.420	4.266 $\pm$ 0.718
	R^2	0.888	0.834
	RMSE (mg g ⁻¹)	1.127	3.883

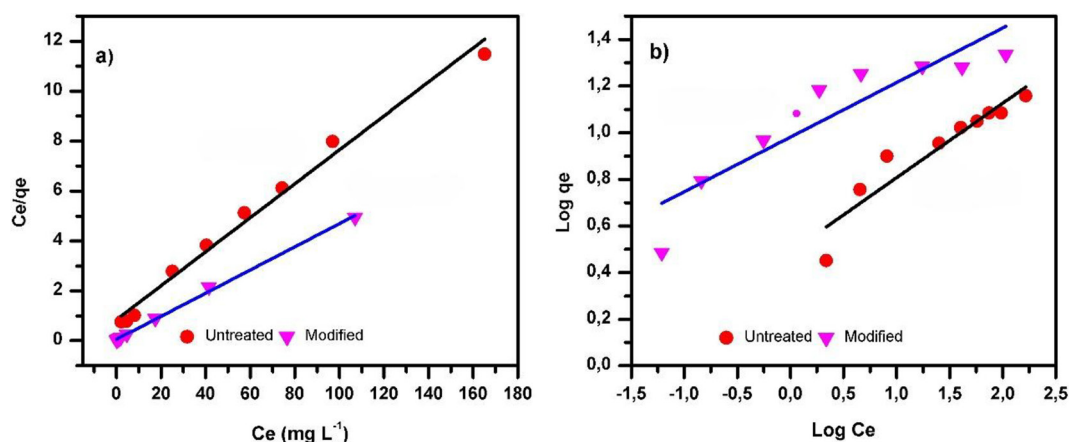


Figure 4. Linear regression of (a) Langmuir and (b) Freundlich isotherm plots

Therefore, model suitability should be evaluated separately for each material rather than inferred from a single R^2 value.

For the untreated feathers, the nonlinear Freundlich model produced a slightly higher R^2 and a lower RMSE than the nonlinear Langmuir model. The Freundlich values were $R^2 = 0.944$ and $RMSE = 0.912 \text{ mg g}^{-1}$, whereas the Langmuir model gave $R^2 = 0.936$ and $RMSE = 0.973 \text{ mg g}^{-1}$. Although the differences were relatively small, these statistics indicate that the Freundlich equation provided a marginally better empirical description of MB adsorption by the untreated material within the investigated concentration range. This result may be consistent with variation in adsorption energies or accessibility among sites on the untreated keratin surface. However, the model fit alone does not establish the physical heterogeneity of the adsorbent or confirm multilayer adsorption.

The nonlinear Langmuir formulation was selected as the preferred model because it fits the original equation without mathematically transforming the response variable. This approach avoids the

unequal alteration of residual errors that can occur during linearisation (Vitek and Masini., 2023). Different linear forms of the Langmuir equation may produce inconsistent values of q_m and K_L , whereas direct nonlinear optimisation estimates the parameters by minimising the discrepancy between observed and predicted q_e values (Danat et al., 2026; Sreńscek-Nazzal et al., 2015).

Taken together, the results demonstrate that $\text{Na}_2\text{S}_2\text{O}_5$ modification substantially improved the adsorption performance of duck-feather keratin toward methylene blue, while also altering the physicochemical characteristics of the precursor material. The estimated maximum Langmuir adsorption capacity increased from 13.250 ± 0.612 to $20.177 \pm 0.751 \text{ mg g}^{-1}$ after modification, corresponding to an improvement of approximately 52.3%. At the same time, the Langmuir affinity constant increased from 0.140 ± 0.032 to $1.656 \pm 0.315 \text{ L mg}^{-1}$, indicating a marked increase in the apparent affinity of the modified material toward MB. These changes are consistent with the SEM observations, which showed that $\text{Na}_2\text{S}_2\text{O}_5$ treatment transformed the relatively compact and

Table 4. Nonlinear-model parameters and original q_e scale error statistics

Models	Parameter	Untreated	Modified
Langmuir	$q_m \text{ (mg g}^{-1}\text{)}$	13.250 ± 0.612	20.177 ± 0.751
	$K_L \text{ (L mg}^{-1}\text{)}$	0.140 ± 0.032	1.656 ± 0.315
	R^2	0.936	0.963
	$RMSE \text{ (mg g}^{-1}\text{)}$	0.973	1.333
Freundlich	K_f	3.785 ± 0.466	11.108 ± 1.085
	n	3.773 ± 0.422	6.200 ± 1.144
	R^2	0.944	0.848
	$RMSE \text{ (mg g}^{-1}\text{)}$	0.912	2.709

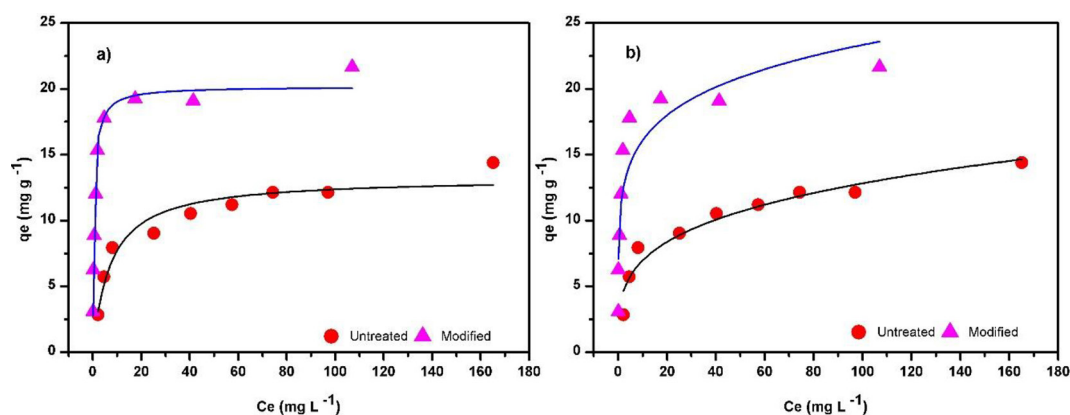


Figure 5. Nonlinear (a) Langmuir and (b) The Freundlich isotherm models

heterogeneous feather structure into a rougher, more fragmented, and apparently more accessible matrix. The increase in specific surface area from 0.1437 to $0.2770 \text{ m}^2 \text{ g}^{-1}$ and pore volume from 0.0045 to $0.0088 \text{ cm}^3 \text{ g}^{-1}$ further supports the possibility that chemical treatment increased the accessibility of adsorption sites. The EDX and FTIR results provide additional evidence that chemical modification altered the surface chemistry of the keratin matrix and that the modified material subsequently interacted with MB. However, these characterization results should be interpreted as complementary evidence rather than direct proof of a single adsorption mechanism.

The observed improvement should also be considered in relation to previous studies of chemically modified feather-based adsorbents. Earlier work has shown that $\text{Na}_2\text{S}_2\text{O}_5$ treatment can increase the availability of binding sites in feather fibres (Wang et al., 2016), while chemical modification of duck feathers was reported to increase Fe (III) adsorption capacity from 111.11 to 125.00 mg g^{-1} (Utami et al., 2020a). Other studies have also examined modified duck-feather materials using Langmuir and Freundlich equilibrium models (Utami et al., 2020b). The present results extend these observations by demonstrating that $\text{Na}_2\text{S}_2\text{O}_5$ modification is also associated with improved equilibrium uptake of the cationic organic dye MB and by integrating adsorption performance with SEM-EDX, FTIR, and BET characterization. In this context, the main contribution of the present study is not simply the preparation of another modified feather-based adsorbent, but the identification of a consistent relationship between $\text{Na}_2\text{S}_2\text{O}_5$ treatment changes in the physicochemical properties of duck-feather keratin, and the resulting equilibrium adsorption behaviour toward MB.

The stronger performance of the nonlinear Langmuir model after modification, together with the increase in the estimated q_m and K_L values, suggests that the treatment may have increased the accessibility and apparent affinity of effective adsorption sites. Nevertheless, the superior fit of the Langmuir model should not be interpreted as definitive proof of a strictly monolayer adsorption mechanism or a completely homogeneous adsorbent surface, because empirical isotherm models describe the equilibrium behaviour of the system and do not, by themselves, establish the molecular mechanism of adsorption. The present data are more appropriately interpreted as indicating that MB uptake by the modified feather material is better described by the Langmuir model within the investigated concentration range and is consistent with predominant occupation of accessible adsorption sites. The FTIR shifts and changes in elemental composition further suggest that surface functional groups and chemical interactions may contribute to MB binding, while the observed morphological and textural changes may facilitate improved contact between MB molecules and the keratin matrix. The relative contribution of these mechanisms, however, cannot be distinguished conclusively from the present dataset alone.

Overall, the findings address an important gap concerning the relationship between sulphitolytic modification of duck-feather keratin and its adsorption behaviour toward methylene blue. The results indicate that $\text{Na}_2\text{S}_2\text{O}_5$ treatment can substantially enhance the apparent adsorption capacity and affinity of duck-feather keratin while modifying its surface morphology, textural properties, and chemical environment. Thus, the study provides evidence that an abundant keratin-rich waste material can be converted into a more

functional biosorbent through chemical modification. At the same time, the findings should be viewed as a mechanistic and equilibrium-level assessment rather than as definitive evidence of a single molecular adsorption pathway or of full-scale treatment applicability. The demonstrated increase in adsorption capacity, together with the observed changes in material characteristics, provides a basis for further investigation of modified feather-derived keratin as a low-cost adsorbent for dye-contaminated water.

CONCLUSIONS

The experimental results demonstrate that $\text{Na}_2\text{S}_2\text{O}_5$ treatment substantially altered the physicochemical characteristics of duck-feather keratin and improved its performance for MB adsorption. SEM, EDX, FTIR, and BET characterization consistently indicated that chemical modification transformed the compact feather matrix into a rougher and more accessible structure, accompanied by increases in specific surface area and pore volume and changes in the surface chemical environment. These findings support the hypothesis that sulphitolytic modification can improve the accessibility of effective adsorption sites and enhance the interaction of the keratin-based material with MB.

The equilibrium modelling further showed that the estimated Langmuir maximum adsorption capacity increased from 13.250 ± 0.612 to $20.177 \pm 0.751 \text{ mg g}^{-1}$, while the apparent Langmuir affinity constant (K_L) increased from 0.140 ± 0.032 to $1.656 \pm 0.315 \text{ L mg}^{-1}$ after modification. The nonlinear Langmuir model provided the best description of the experimental equilibrium data among the models evaluated, indicating that MB adsorption by the modified material was better represented by Langmuir-type behaviour within the investigated concentration range. However, this result should be interpreted as evidence of the best empirical model fit rather than definitive proof of a strictly monolayer molecular mechanism.

At the same time, the present findings provide a basis rather than definitive evidence for the underlying molecular adsorption mechanism. The specific contributions of surface functional groups, structural accessibility, pore characteristics, and possible chemical interactions with MB require further experimental verification. Future studies should therefore focus on establishing the

detailed adsorption mechanism, evaluating regeneration and reusability, and assessing the performance of the modified biosorbent in complex and real wastewater matrices. Such work will determine the extent to which $\text{Na}_2\text{S}_2\text{O}_5$ -modified duck-feather keratin can be developed from a laboratory-scale waste-derived material into a practical and sustainable adsorbent for dye-contaminated water treatment.

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