Scientific Reports

https://doi.org/10.1038/s41598-026-54665-z

Article in Press

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Received: 29 January 2026

Accepted: 20 May 2026

Published online: 04 June 2026

Cite this article as: Simsek A., Isik B. & Cankurtaran O. Enhanced adsorptive removal of malachite green dye from aqueous solution using raw and acid modified rosemary biomass. *Sci Rep* (2026). https://doi.org/10.1038/s41598-026-54665-z

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Enhanced Adsorptive Removal of Malachite Green Dye from Aqueous Solution Using Raw and Acid Modified Rosemary Biomass

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Abstract

Water contamination resulting from waste systems owing to industrial expansion and escalating human activities has emerged as a significant global environmental issue. Agricultural waste biomass is extensively utilized as a bioadsorbent for the removal of harmful contaminants. This study emphasizes the production of an economical, zero-waste adsorbent derived from rosemary biomass and illustrates how sulfuric acid modification significantly transforms its surface characteristics, resulting in a marked increase in malachite green adsorption capacity. The synthesized bioadsorbent was analyzed utilizing FT-IR, SEM, XRD, zeta potential, and pH_{pzc}. Experimental investigations were performed to examine the effect of process variables, such as contact time (0-180 min), initial dye concentration (100-500 mg/L), pH (2-10), and biomass dosage (0.01-0.20 g/50 mL), on dye removal efficacy. The effect of salt solutions on the adsorption process was examined, revealing that electrostatic interactions significantly contributed to the adsorption mechanism. The modeling investigation demonstrates that the Langmuir and *pseudo-second order* models exhibit strong concordance ($R^2 = 0.9999$) with isotherm and kinetics, respectively. The intraparticle diffusion kinetic model indicated that the adsorption process may transpire through many processes. The monolayer adsorption capacities of raw and sulfuric acid-treated biomass had peak values of 247.5 and 497.4 mg/g at 298 K, respectively. Thermodynamic results have shown that both raw ($\Delta H_A^o =$ 9.930 kJ/mol and $\Delta G_A^o = -22.61$ kJ/mol) and modified rosemary ($\Delta H_A^o = 44.97$ kJ/mol and $\Delta G_A^o = -23.54$ kJ/mol) biomass are endothermic and spontaneous. Consequently, it was determined that sulfuric acid-modified rosemary biosorbent possesses superior efficacy for dye removal in remediation operations.

Keywords: Adsorption, malachite green, modification, rosemary.

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1. Introduction

Environmental water pollution presents significant threats to ecosystems and human health, since freshwater tainted by diverse harmful contaminants disrupts aquatic habitats and diminishes biodiversity[1–4]. Dye chemicals impede light penetration in aquatic environments, hence obstructing photosynthesis in aquatic flora and microorganisms. The textile production process is resource-intensive, necessitating substantial inputs of chemicals, fuel, and water; around 200 liters of water are consumed for each kilogram of fabric produced, resulting in considerable wastewater generation. Reactive dyes, frequently utilized in textile processing, typically traverse standard wastewater treatment systems substantially unaltered, complicating their elimination from aquatic ecosystems[5,6]. It is estimated that around 280,000 tons of textile dyes are released into wastewater streams worldwide each year. A thin layer of dye on the sea surface adversely affects aquatic life by diminishing dissolved oxygen levels. Dye chemicals and their breakdown products can adversely affect human health by harming hemoglobin, skin, lungs, and the hematological system through ingestion or dermal exposure, in addition to their visual effects. Many dyes, owing to their synthetic and aromatic characteristics, are non-biodegradable, carcinogenic, and can induce dermatitis, allergies, and skin irritation. In conclusion, it is imperative that industrial wastewater undergoes effective treatment prior to environmental release[7–9].

Malachite green (MG), a triphenylmethane dye, is extensively utilized in aquaculture and fisheries to avert parasite and fungal illnesses in aquatic species. Nonetheless, owing to its intricate composition, it is challenging to decompose in aquatic ecosystems. MG has garnered considerable interest owing to its toxicological consequences. Even at minimal doses, it can adversely affect animals and people, resulting in elevated heart rate, headaches, and ocular discomfort. Moreover, its bioaccumulation and endurance within the food chain pose a threat

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to human health[10,11]. Due to these detrimental impacts, dyes must be removed from aquatic environments effectively and efficiently with suitable adsorbents.

Conventional wastewater treatment systems exhibit limits due to variables including elevated costs, inadequate pollutant removal, and the necessity for more dependable solutions. Methods such as physical, chemical, and biological treatment may encounter difficulties in eliminating all resultant contaminants and attaining comprehensive treatment. Although methods such as coagulation[12], flocculation[13], and sedimentation[14] are frequently employed, their efficacy is constrained and may not adequately eliminate all contaminants. The elimination of persistent dyes such as MG by conventional procedures might fluctuate based on the treatment type, operational conditions, and the characteristics of the compounds, resulting in incomplete removal. To address these limitations, there is an increasing demand for more efficient and economical wastewater treatment systems capable of effectively managing the varied pollutant composition in wastewater[15–17].

Among several wastewater treatment techniques, adsorption has emerged as an efficacious strategy for eliminating both organic and inorganic contaminants from wastewater. It necessitates minimum energy, features a straightforward design, employs less intricate procedures, incurs cheap operational expenses, and generates no hazardous byproducts[18–21]. The utilization of agricultural waste as renewable, cost-effective, and biodegradable adsorbents for the removal of waterborne pollutants has been documented. Nevertheless, these unaltered agricultural residues exhibit application constraints, including limited adsorption ability for pollutants and potential secondary contamination issues arising from the leaching of some soluble chemicals. Consequently, it is advisable that these materials undergo processing or modification prior to any significant adsorption application. Surface modification, including the incorporation of anionic functional groups to enhance electrostatic interactions with cationic paint types, is seen as useful for augmenting adsorption capacities[22–24]. Deka et al.

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successfully eliminated methylene blue dye utilizing crude *Plumeria alba* biomass and H_2SO_4-modified biomass, determining maximal adsorption capacities of 45.45 mg/g and 250 mg/g, respectively[25]. Uddin et al. quantified the adsorption capacity of MG dye as 567.6 mg/g utilizing sulfuric acid-modified rubber seed pericarp biomass[26]. Ozdeş et al. successfully eliminated methylene blue dye utilizing plane sawdust biomass treated with H_2SO_4, determining its adsorption capacity to be 38.46 mg/g[27].

Rosemary exhibits a moderate tolerance to drought conditions. It serves as a hedge plant in landscaping and is specifically planted in rock gardens throughout the spring. This plant comprises numerous advantageous chemical constituents, such as rosmarinic acid, bornyl acetate, caffeic acid, limonene, rosmaridiphenol, rosmanol, and camphor. The leaves of the rosemary plant possess lignocellulosic compounds, including lignin, cellulose, hemicellulose, and pectin. Consequently, lignocellulosic material is favored as an adsorbent for the adsorption approach, as demonstrated in the current work[28,29].

Despite substantial study on adsorption-based dye removal, the advancement of innovative, sustainable, and high-performance adsorbent materials continues to be a pivotal area of investigation. In this context, plant-derived waste biomasses have garnered heightened interest owing to their abundance, renewability, and cost-effectiveness. Nonetheless, numerous described biomaterials exhibit restricted adsorption efficiency or necessitate intricate production methods[30–32]. This study presents rosemary waste biomass as an underutilized lignocellulosic adsorbent and illustrates a straightforward yet very effective H_2SO_4 modification technique to significantly improve its adsorption capacity for MG dye. This work's innovation resides not only in dye elimination but also in the valorization of rosemary plant waste within a zero-waste paradigm, the systematic comparison of raw and acid-modified forms, and the clarification of surface chemistry alterations that enhance adsorption capacity

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significantly. This method elucidates how slight chemical alteration can convert a plentiful agricultural byproduct into a competitive and high-capacity adsorbent for cationic dyes.

Although other agricultural and plant-based biomasses have been extensively employed for dye adsorption, there is a paucity of research examining the application of rosemary plant waste as an adsorbent material, specifically for the removal of MG dye. Furthermore, systematic studies contrasting the adsorption efficacy of unprocessed and chemically altered rosemary biomass, as well as elucidating the impact of surface modification on adsorption effectiveness, are limited. This study fills the existing gap by assessing rosemary plant waste as an economical and sustainable adsorbent, while also illustrating how H_2SO_4 treatment markedly improves its surface characteristics and adsorption capability for MG dye. Analyses such as FT-IR, SEM, XRD, zeta potential, and pH_{pzc} were utilized to characterize the adsorbents that were brought into existence. An analysis was performed to establish the ideal conditions for the adsorption process. Several non-linear isotherm and kinetic models were utilized to assess the effectiveness of the adsorption process. Raw data were utilized in this evaluation. A comparison was made between the adsorption capacities of raw rosemary plants and those of modified rosemary plants, and the potential of each plant as an adsorbent was evaluated.

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2. Results

2.1. Characterization of adsorbents

The FT-IR spectra (Fig. 1a) distinctly illustrate the alterations in functional groups on the raw rosemary surface before and after adsorption. The broad band detected at 3295 cm^{-1} before adsorption is attributed to hydroxyl (–OH) and potential N–H stretching vibrations. Following MG adsorption, this peak changed to 3339 cm^{-1}, signifying a reconfiguration of hydrogen bonds and robust interactions with the dye. The bands at 2918 and 2849 cm^{-1} correspond to aliphatic C–H stretching vibrations, which exhibit minor shifts to 2919 and 2850

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cm^{-1} after adsorption, indicating the involvement of aliphatic structures on the surface in the adsorption process. The carbonyl (C=O) stretching band at 1729 cm^{-1} retained its location, signifying the structural integrity of the carbonyl groups. The transitions from 1688 cm^{-1} to 1687 cm^{-1} and particularly from 1615 cm^{-1} to 1585 cm^{-1} result from aromatic ring vibrations and the interaction of C=C bonds with the dye. The absence of the band at 1557 cm^{-1} indicates substantial alterations in the interactions of amine groups or aromatic structures. The C–H bending vibrations at 1455 and 1375 cm^{-1} moved to 1454 and 1366 cm^{-1}, respectively, following adsorption. The C–O stretching vibrations at 1239, 1158, and 1028 cm^{-1} were recorded as 1238, 1163, and 1027 cm^{-1} following adsorption. These alterations signify the establishment of hydrogen bonds and electrostatic interactions between the hydroxyl and ether groups on the surfaces of MG and raw rosemary biomass. The peak shifts and density alterations in the FT-IR study indicate that the adsorption mechanism transpires via hydrogen bonding, electrostatic interactions, and potential π–π interactions[33,34].

The FT-IR spectra presented in Fig. 1b unequivocally indicate that the modification with H_2SO_4 was effectively executed on rosemary biomass, resulting in a substantial improvement in MG adsorption. The extensive –OH bands between 3492–3281 cm^{-1} in the modified biomass before adsorption signify an enhancement in acidic and reactive properties due to the protonation of hydroxyl groups and the reconfiguration of hydrogen bond networks during acid treatment. Additionally, the pronounced bands near 1742 and 1698 cm^{-1} indicate the formation of new polar C=O centers on the surface during modification, resulting from the protonation of carbonyl groups within the lignocellulosic structure or through partial esterification/oxidation processes. The most compelling evidence of modification is the presence of bands associated with S=O and S–O vibrations in the 1385–1139 cm^{-1} range, which are distinctly observable in the pre-adsorption spectrum; these bands signify the introduction of $–SO_3H$/$–SO_3^-$ functional groups to the biomass surface via H_2SO_4 treatment, thereby

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augmenting the surface's negative charge density. The notable alterations in the position and intensity of these functional group bands subsequent to MG adsorption, coupled with the emergence of aromatic C=C vibrations at 1610 and 1518 cm^{-1} and the distinctive bands associated with $–N^{+}(CH_3)_2$ groups within the 1444–1320 cm^{-1} range, substantiate that MG molecules proficiently attach to the modified biomass surface. The widening and reduction in intensity of the –OH band near 3270 cm^{-1} signifies the establishment of robust hydrogen bonds between the amine groups of MG dye and the surface –OH and $–SO_3H$ groups. Moreover, the electrostatic interaction between cationic MG dye molecules and $–SO_3^-$ groups indicates that this is the primary adsorption mechanism. Considering the comprehensive FT-IR findings, it is concluded that H_2SO_4 modification enhances rosemary biomass, rendering it a more acidic, negatively charged, and functionally enriched adsorbent. The adsorption of MG dye transpires through the synergistic interplay of electrostatic interactions, hydrogen bonds, and π–π interactions among aromatic structures[35–37].

Fig. 2 illustrates that the surface morphology of both raw and H_2SO_4-modified rosemary biomass underwent considerable alterations before and after MG adsorption. Fig. 2a presents the SEM image of raw rosemary biomass before MG dye adsorption, revealing an irregular, compact, and relatively coarse surface morphology; the layered and partially agglomerated particles are indicative of the biomass's inherent lignocellulosic architecture, suggesting a constrained and uneven pore distribution. Fig. 2b illustrates that after MG adsorption, the surface of raw biomass exhibits partially filled holes, resulting in a more compact and closed shape. The persistent heterogeneity of the surface structure and the restricted pore formation indicate that the adsorption effectiveness in raw biomass is constrained to a specific level. Conversely, Fig. 2c presents a SEM image of rosemary biomass modified with H_2SO_4 before MG dye adsorption, indicating that acid modification markedly transforms the surface morphology; the acid treatment produces more prominent fibrous structures, rendering the

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surface rougher and more irregular. Fig. 2d presents a SEM image of the modified biomass after MG adsorption, revealing a substantial coating on the surface, significant pore occlusion by dye molecules, and the formation of a smoother, film-like structure; this morphological alteration unequivocally illustrates the strong adsorption of MG onto the modified biomass surface and the effective role of the newly introduced active sites in the adsorption process.

Fig. 3 illustrates the XRD patterns of both the raw rosemary biomass and the H_2SO_4-modified rosemary biomass. The broad peaks that were observed around ~15° and ~22° (2θ) in the XRD pattern of raw rosemary biomass indicate a semi-crystalline structure that is characteristic of the cellulosic structure. However, the significantly reduced intensity and broadening of these peaks in the H_2SO_4-modified sample demonstrate that the crystalline regions were partially disrupted in the process of acid treatment, resulting in the structure becoming more amorphous. This can be attributed to the reduction in cellulose crystallite size as well as the increase in structural disorder, as well as the removal of hemicellulose and lignin that occurred during the process[38,39].

Zeta potential graphs of raw rosemary biomass and H_2SO_4-modified rosemary biomass were displayed in Figs. 4a and b, respectively. Having a zeta potential of –17.2 mV, the raw rosemary biomass shown in Fig. 4a is negatively charged because of the surface functional groups that are present. To produce rosemary biomass that has been modified with H_2SO_4, which possesses a greater negative charge and a zeta potential of –21.9 mV, rosemary biomass was put through the process of being modified with H_2SO_4 (Fig. 4b). A further negative zeta potential is supported by the alteration of the structure with H_2SO_4, which results in the addition of additional sulfate groups to the structure[40].

The pH_{pzc} values of raw rosemary and H_2SO_4-treated rosemary biomass were assessed using the pH draft method to ascertain the total surface charge of the biomass and to anticipate the unique interaction mechanism between MG and biomass during adsorption. Reports

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indicate that when the pH of the adsorbent is below the pH_{pzc}, the adsorbent's overall surface charge is positive due to the predominance of H^+ ions; conversely, when the pH exceeds the pH_{pzc}, the surface charge becomes negative due to the predominance of OH^- ions. The pH_{pzc} value of H_2SO_4-modified rosemary biomass was determined to be greater than that of raw rosemary biomass (pH_{pzc} = 6.91 for raw rosemary biomass, pH_{pzc} = 7.11 for H_2SO_4-modified rosemary biomass). Consequently, the pH_{pzc} results indicate that the surface of H_2SO_4-modified rosemary biomass possesses a higher negative charge, making it conducive to the electrostatic attraction of cationic species. Consequently, an enhancement in the elimination of MG, a cationic dye, is anticipated[41].

2.2. Selectivity experiments

Raw rosemary and H_2SO_4-modified rosemary biomass were utilized to eliminate MB, MO, SO, MG, RhB, CR, CV, and AO dyes. 50 mg of the material was combined with 50 mL of dye adsorbate for a contact time of 90 min. Upon achieving adsorption equilibrium, the solution was examined using a UV-Vis spectrophotometer at wavelengths of 663, 469, 519, 554, 498, 591, and 435 nm, respectively. The adsorption efficacy of the biomass was demonstrated through a comparison experiment involving the adsorption of eight dyes (MB, MO, SO, MG, RhB, CR, CV, and AO). Fig. 6 illustrates the removal percentages of raw rosemary biomass for MB, MO, SO, MG, RhB, CR, CV, and AO, which were 64.6%, 8.4%, 63.2%, 68.4%, 21.2%, 25.1%, 65.6%, and 52.5%, respectively. The H_2SO_4-modified rosemary biomass exhibited removal efficiency of 85.2% for MB, 1.2% for MO, 77.7% for SO, 90.2% for MG, 24.6% for RhB, 37.4% for CR, 89.8% for CV, and 73.5% for AO, respectively. The results indicate that the incorporation of additional anionic groups through H_2SO_4 alteration enhanced the quantity of active moieties, resulting in a marked improvement in adsorption performance[42]. Fig. 6 illustrates that biomass had superior efficacy with cationic dyes, however its performance with anionic dyes was suboptimal. Due to its superior clearance % compared

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to other cationic dyes, cationic MG dye was selected as the model dye. The anionic functional groups of both raw rosemary biomass and rosemary biomass treated with H_2SO_4 interact effectively with the cationic components of MG dye, markedly enhancing its adsorption capacity.

2.3. Effect of optimum conditions

Fig. 7a illustrates the effect of adsorbent dose on both removal efficiency (R%) and adsorption capacity (q_e) for both crude and H_2SO_4-modified rosemary biomass. Increasing the adsorbent dose resulted in a sustained increase in removal efficiency; this can be attributed to the increased availability of active adsorption sites and larger surface area at higher doses[43]. Conversely, adsorption capacity (q_e) showed a decreasing trend with increasing dose; this is generally associated with unsaturated adsorption sites and partial aggregation of adsorbent particles at higher solid concentrations, leading to a decrease in effective surface area per unit mass. The optimum adsorbent dose is usually determined at the point where a balance is reached between removal efficiency and adsorption capacity[44]. In this study, this was observed at an adsorbent dose of 0.05 g/50 mL for both raw and modified rosemary biomass. Therefore, 0.05 g/50 mL was selected as the optimum dose for subsequent experiments. Similar dose-dependent trends and optimization criteria were commonly reported in dye removal studies using lignocellulosic and chemically modified biomaterials, supporting the validity of the optimum dose selected in this study. Largo et al. investigated the effect of adsorbent dose range of 0.2 to 1.5 g/L in the adsorption study of MG dye on carbon@Sep and similarly reported that they selected the optimum adsorbent dose as the equilibrium value of 0.8 g/L[45]. Similarly, Saravanan et al. investigated the adsorption of MG dye using *Ipomoea pes caprae* biomass modified with sulfuric acid and determined the optimum adsorbent amount as 3.5 and 1.75 g for raw and modified biomass, respectively, based on equilibrium conditions[46].

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Fig. 7b illustrates the impact of pH fluctuations on the adsorption efficacy of both raw and H_2SO_4-modified rosemary biomass. The adsorption performance of raw rosemary biomass grew steadily until around pH 7, while that of H_2SO_4-modified rosemary biomass peaked at roughly pH 8, beyond which no significant changes were observed at elevated pH levels. Fig. 5 illustrates that the pH_{pzc} values of raw and H_2SO_4-modified rosemary biomass are 6.91 and 7.11, respectively, signifying that the biomass surface charges are electronegative when the solution pH exceeds the pH_{pzc} value. The adsorbent generated additional adsorption sites because of electrostatic attraction with rising pH levels. This phenomenon can be elucidated by the competition between H^+ ions in the acidic solution and the MG molecule. MG is a cationic dye, and the electrostatic interaction can enhance the adsorption process. The adsorption and removal of MG dye with raw and H_2SO_4-modified rosemary biomass achieved peak values of 68.43% and 91.11%, respectively, at solution pH levels of roughly 7 and 8. Comparable findings were reported in prior research[47]. Das et al. investigated the MG adsorption process using *Aegle marmelos*-derived activated biochar in the pH range of 3-11 and similarly determined the optimum pH value to be approximately 7[48]. Considering this, the study results are consistent with the literature data.

Adsorption isotherms delineate the process by which a substance adheres to or is liberated from the aqueous phase to the solid phase at a constant temperature. They are crucial for comprehending the adsorption mechanism, adsorption capacity, surface characteristics, and the interaction between adsorbate and adsorbent[49,50]. Fig. 7c illustrates the isotherm curves of both raw and H_2SO_4-modified rosemary biomass. The isotherm curves of raw rosemary biomass adhere to type L2 as per Giles' isotherm categorization. A plateau is attained with rising concentration. Conversely, an analysis of the isotherm curves for H_2SO_4-modified rosemary biomass reveals a closer alignment with type L1-type rather than L2-type, signifying a substantial enhancement in adsorption performance and capacity.

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This work examined the impact of contact time on removal efficiency for dye concentrations between 100 and 500 mg/L, with the resulting trends for both raw rosemary and H_2SO_4-modified rosemary biomass illustrated in Fig. 7d. The elevated dye removal efficiency in the initial phases is attributed to the abundance of vacancies and the swift penetration of the solvent into these vacancies; thereafter, once equilibrium is attained, the removal efficiency diminishes due to the scarcity of vacancies for additional solvent molecule absorption. Equilibrium was attained in 90 min for both raw rosemary and H_2SO_4-modified rosemary biomass. The most notable discovery is that equilibrium was attained in a remarkably brief contact duration for both adsorbents[51]. Algethami et al. investigated the effect of contact time (3-510 min) on the adsorption of MG dye onto magnetic hydrochar-grafted chitosan adsorbent and determined the optimum condition as 420 min, the point at which saturation is reached[52]. In this case, it was observed that the study yielded results consistent with the literature.

2.4. Effect of salinity

The adsorption of dye is influenced by the ionic strength of the solution, and textile effluent frequently contains salt. The impact of varying ionic strengths on the adsorption of MG dye was examined utilizing NaCl or $CaCl_2$. The effects of ionic strength were examined within the range of 0.1–1.0 M, maintaining a constant dye concentration of 200 mg/L, an adsorbent dosage of 0.05 g/50 mL, and optimal pH values. Two tests were executed concurrently to elucidate the impact of ionic strength. One experiment was a control trial comprising solely the dye solution and salt. The subsequent experiment included the dye solution, salt, and adsorbent. Fig. 8 illustrates that the ionic strength of $CaCl_2$ or NaCl, ranging from 0.1 to 1.0 M, did not produce any discernible alteration in MG concentration during the control experiment. Elevating the ionic strength of both $CaCl_2$ and NaCl markedly diminished the adsorption of MG dye by crude and H_2SO_4-modified rosemary biomass. This may result from competition between Ca^{2+} or Na^{+} ions and cationic dye molecules for binding sites,

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resulting in the creation of a monolayer of ions, or from shielding effects between Ca^{2+} or Na^{+} ions and positively charged MG molecules. $CaCl_2$ exhibited a more significant impact in diminishing the absorption of MG dye than NaCl. The elevated ionic strength of the $CaCl_2$ salt may occupy additional active sites, hence impeding the absorption of dye molecules more efficiently[53].

2.5. Adsorption isotherms

Adsorption isotherms are a crucial feature that contribute to a more in-depth comprehension of the interactions that take place between dye molecules and adsorbents. To acquire a comprehensive understanding of the adsorption mechanism, the raw data were analyzed using four distinct isotherm models: the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin isotherm models. On the surface of the adsorbent, the Langmuir model presupposes that homogenous and monolayer adsorption of the adsorbate takes place in a restricted number of comparable regions. The following provides an expression of its non-linear form[54]:

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

In this equation, q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant (L/mg).

The non-linear Langmuir isotherm curves, derived from Eq. (1), for both raw and H_2SO_4-modified rosemary biomass, were illustrated in Fig. 9a. The isotherm parameters were derived using non-linear graphs generated using the Microsoft Excel Solver application, with all results presented in Table 1. Table 1 indicates that the q_m values of raw and H_2SO_4-modified rosemary biomass at 298 K were measured at 247.5 mg/g and 497.4 mg/g, respectively. Upon examination of these results, it is evident that the adsorption capacity of H_2SO_4-modified rosemary biomass is nearly twice that of raw rosemary biomass. The scenario arises from the substantial enhancement of the active components in rosemary biomass after H_2SO_4 alteration,

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which consequently amplifies its adsorption ability. Conversely, it was noted that the adsorption capacity augmented with rising temperature for both biomass types, signifying that the process transpires endothermically. The Langmuir isotherm constant (K_L) varied from 0.0199 L/mg to 0.0975 L/mg for both biomass types, indicating the beneficial nature of the process[55].

The maximum MG adsorption capacities (q_m) of raw rosemary and modified biomass treated with H_2SO_4, as determined by the Langmuir isotherm model, were 247.5 mg/g and 497.4 mg/g, respectively. Table 2 presents the highest adsorption capabilities of various natural or modified materials for comparative analysis. Rosemary biomass treated with H_2SO_4 shown markedly superior adsorption efficacy in MG retention relative to numerous other modified substances and functioned as an economical and accessible resource.

The Freundlich isotherm is predicated on multilayer adsorption and adsorption on heterogeneous surfaces exhibiting varying adsorption capacities and energy. The non-linear form of Freundlich isotherm model was given as follows[56]:

$$q_e = K_F \times C_e^{(1/n)} \quad (2)$$

In this equation, K_F is the Freundlich isotherm constant (mg/g)(L/g)$^{1/n}$ and n is the Freundlich exponential factor. The Freundlich isotherm curves were generated using Eq. (2) and were depicted in Fig. 9b. All isotherm parameters were enumerated in Table 1. Table 1 illustrates that the "n" values range from 2.139 to 3.094 for both raw and H_2SO_4-modified rosemary biomass, signifying that the adsorption procedure is advantageous for both types of biomasses. Conversely, an examination of the correlation coefficients reveals that the Langmuir isotherm model is more appropriate to the adsorption process than the Freundlich isotherm model, as its values are far closer to one. Correlation coefficients are inadequate for assessing the applicability of isotherm models. Consequently, diverse error functions were calculated utilizing theoretical and experimental data, allowing for a more accurate assessment of the

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applicability of isotherm models. Considering this, the error function values calculated in accordance with Eq. (16), (17), (18), and (19) were presented in Table 3. Table 3 demonstrates that the error function values of the Langmuir isotherm model are significantly lower than those of the Freundlich isotherm model. This corroborates the notion that the Langmuir model is a more appropriate isotherm model for the adsorption process.

To provide a description of the adsorption of adsorbate molecules within the micropores of the adsorbent, the Dubinin-Radushkevich (D-R) model was utilized. Instead of surface adsorption, this concept proposes that molecule adsorption takes place in micropores, which ultimately results in the creation of a single or several layers. This model is frequently utilized for the adsorption of supercritical vapor through the pores of the adsorbent, and it is represented by the equation that is shown below[57]:

$$q_e = q_{D-R} \times e^{-\beta \times \left(R \times T \times ln\left(1+\frac{1}{C_e}\right)\right)^2} \quad (3)$$

In this equation, q_{D-R} is the theoretical adsorption capacity (mg/g), β is the activity coefficient (mol^2/J^2), which indicates the adsorption energy. The average free adsorption energy (E_{D-R}) was calculated according to following equation:

$$E_{D-R} = (2\beta)^{-0.5} \quad (4)$$

For determining whether chemisorption or physisorption took place, the D-R isothermal model is typically applied. A representation of the D-R isotherm curves can be found in Fig. 9c. Table 1 contains the results of the calculation of the isotherm parameters based on these graphs. As can be observed from the data shown in Table 1, the E_{D-R} value for both adsorbents ranges from 64.27 J/mol to 412.2 J/mol. The fact that this value is lower than 8000 J/mol supports the hypothesis that the adsorption process takes place in a physical manner[58].

The Temkin isotherm model is used to represent the interaction that occurs between the adsorbent and the adsorbate, as well as the heat that is produced because of the adsorption process. The Temkin isotherm is calculated as follows[59]:

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$$q_e = \frac{R \times T}{b_T} \times ln(K_T \times C_e) \quad (5)$$

In this equation, b_T is the fluctuation of adsorption energy (J/mol) and K_T is the binging equilibrium value (L/mg). The isotherm curves that were plotted in accordance with Eq. (5) were displayed in Fig. 9d. Calculations of isotherm parameters were performed using these curves, and the results were presented in Table 1. The Temkin model has a higher r^2 value, which implies that the adsorption process involves chemical adsorption, as can be shown in Table 1. The results of the model being adapted to the Temkin model demonstrate that the binding force reduces linearly with increasing MG molecular coating layer. These results were acquired by obtaining good fit results. Therefore, the primary characteristic of adsorption is a binding force that is spread uniformly across the material[60]. Considering the error functions given in Table 3, the order of applicability of the isotherms is as follows: Langmuir > Temkin > D-R > Freundlich.

2.6. Adsorption kinetics

To ensure that the rate-limiting stage in the MG adsorption process was accurately predicted, adsorption kinetics models were utilized. The *pseudo-first-order*[61], *pseudo-second-order*[62], intraparticle diffusion[63], and Elovich[64] kinetic models were all trained on the raw data. The following equations contain the kinetic models that are being discussed[65].

$$q_t = q_e \times (1 - e^{-k_1 \times t}) \quad (6)$$

$$q_t = \frac{q_e^2 \times k_2 \times t}{1 + q_e \times k_2 \times t} \quad (7)$$

$$q_t = k_d \times t^{0.5} + C \quad (8)$$

$$q_t = \frac{1}{\beta} \times \ln(1 + \alpha \times \beta \times t) \quad (9)$$

In these equations, k_1 is the *pseudo-first-order* kinetic constant (min^{-1}), k_2 is the *pseudo-second-order* kinetic constant (g/mg.min), k_d is the intraparticle diffusion constant ($min^{0.5}$), C

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is the constant associated with the thickness of the boundary layer (mg/g), α is the the initial adsorption rate (mg/g.min^{-1}), and β is the desorption constant during any one experiment (mg/g).

Fig. 10 displays the graphs of various kinetic models. The kinetic parameters derived from the graphs were listed in Table 4. Table 4 demonstrates that the *pseudo-second-order* kinetic model is the most suitable model for the adsorption process conducted with both adsorbents, as indicated by the high correlation coefficient of 0.9999. The proximity of the estimated and experimental q_e values is crucial for the accuracy of the adsorption kinetic model fit. Table 4 illustrates that the computed and experimental results for the *pseudo-second-order* kinetic model are well aligned, indicating that the process adheres to this kinetic model. This indicates that chemical adsorption significantly influences the adsorption processes of MG dye onto both raw and H_2SO_4-modified rosemary biomass.

The intraparticle diffusion model indicates that the plots of q_t versus $t^{0.5}$ in all instances (Fig. 10c) were segmented into three linear regions, signifying that the MG removal processes were governed by a multi-step mechanism. The rate constants for the initial step (k_{d1}) exceeded those of the subsequent step (k_{d2}), indicating that the adsorption processes are influenced by rapid liquid layer diffusion and sluggish pore diffusion, respectively. The minimal values of k_{d3} suggested that adsorption equilibria were attained in the third step[66,67].

The Elovich equation is depicted at different temperatures, as illustrated in Fig. 10d. The correlation coefficients (r^2) of the Elovich kinetic model are significantly elevated at all temperatures, suggesting that the diffusion-limiting impact is markedly more pronounced in MG adsorption. Observations indicate that elevating the adsorption temperature can enhance the adsorption rate[68].

To assess the relevance of kinetic models to the adsorption of MG dye on both raw and H_2SO_4-modified rosemary biomass, error functions were calculated based on Eqs. (16), (17),

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(18), and (19), with the findings presented in Table 5. When the error functions in Table 5 were examined, the order of applicability of kinetic models to the adsorption process is determined as follows: Elovich > *pseudo-second order* > intraparticle diffusion > *pseudo-first order*.

2.7. Possible adsorption mechanism

The adsorption mechanism of MG dye onto both raw and H_2SO_4-modified rosemary biomass is a complicated process characterized by many interactions, as evidenced by the combined analysis of FT-IR, zeta potential, pH_{pzc}, kinetic, and isotherm data. When the pH exceeds the pH_{pzc} values, both the raw biomass and the modified adsorbent exhibit a negative surface charge. Particularly following H_2SO_4 alteration, the incorporation of $–SO_3H$/$–SO_3^-$ groups onto the surface reduced the zeta potential to more negative values, hence enhancing the adhesion of cationic MG molecules to the surface by robust electrostatic attraction. The alterations noted in the –OH, C–O, and aromatic C=C bands in the FT-IR spectra signify the presence of hydrogen bonds and π–π interactions between the amino and aromatic structures of MG and the hydroxyl, carbonyl, and sulfone groups on the surface. The validity of the Langmuir isotherm suggests that adsorption occurs via a monolayer mechanism dominated by chemical interactions on a uniform surface, whereas the *pseudo-second order* and Elovich models imply that chemical interactions involving electron or ion exchange are predominant. The three-stage lines based on the intraparticle diffusion model demonstrate that adsorption begins with film diffusion, advances to intraparticle diffusion, and concludes with equilibrium in the final stage. The reduced adsorption by Na^+ and especially Ca^{2+} ions further confirms that the predominant mechanism is the electrostatic interaction between negative surface sites and MG. The comprehensive analysis of these results reveals that the adsorption of MG onto rosemary biomass occurs via a multi-stage mechanism including electrostatic attraction, hydrogen bonding, π–π interactions, and intrapore diffusion[69,70]. Overall, the adsorption of MG onto both raw and H_2SO_4-modified rosemary biomass is predominantly chemisorptive in

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nature, governed mainly by electrostatic interactions and surface chemical bonding, while physical diffusion processes contribute as auxiliary rate-controlling steps[9].

2.8. Adsorption thermodynamics

To investigate the thermodynamic nature of the adsorption process, thermodynamic parameters were calculated using the following equations[71]:

$$K_e^o = \frac{1000 \times K_L \times M_{MG} \times [Adsorbate]^o}{\gamma} \quad (10)$$

$$\ln K_e^o = -\frac{\Delta G^o}{R \times T} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \times \frac{1}{T} \quad (11)$$

$$\Delta G^o = \Delta H^o - T \times \Delta S^o \quad (12)$$

In these equations, K_e^o is the thermodynamic equilibrium constant, M_{MG} is the molecular mass of MG dye (g/mol), $[Adsorbate]^o$ is the standard adsorbate concentration, and γ is the dimensionless separation factor. Adsorption enthalpy (ΔH^o) and entropy (ΔS^o) values were calculated from the linear graphs plotted between $1/T$ and $\ln K_e^o$ using Eq. (18) (Fig. 11). Gibbs free energy (ΔG^o) values at different temperatures were calculated by substituting these values into Eq. (12). All results were listed in Table 6.

The thermodynamic parameters of the adsorption process of MG dye on raw rosemary biomass and rosemary biomass that was treated with H_2SO_4 were presented in Table 6. Upon examination of this table, it can be observed that the values obtained for ΔS° and ΔH° are positive, whilst the values obtained for ΔG° are negative. There is a tabular representation of the three adsorption thermodynamic parameters of MG dye for both types of biomasses available. It has been shown that the ΔH° values are positive for both types of biomasses. The ΔH° value for MG dye in raw rosemary biomass is 9.930 kJ/mol, but in H_2SO_4-modified rosemary biomass, it is 44.97 kJ/mol. The presence of a positive ΔH° value is indicative of the endothermic nature of the adsorption process, which implies the potential for a robust bond to be formed between the dye molecules and the biomass used. Additionally, the values of ΔG°

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are negative for each of the three temperatures in both biomasses. The spontaneous nature of the adsorption process is indicated by the fact that the changes in ΔG° have a negative sign as they occur[72].

2.9. Real wastewater experiments

Fig. 13 illustrates the results of this study, which examined the adsorption of MG dye onto both raw and H_2SO_4-modified rosemary biomass utilizing several water samples in a laboratory setting. To eliminate the MG dye, a biomass dosage of roughly 0.05 g for each adsorbent was agitated at 120 rpm for 90 min. The adsorption procedure was conducted under optimal conditions. Fig. 13 illustrates that distilled water exhibited the highest adsorption efficiency. The adsorption process was influenced by the presence of diverse ions in tap and drinking water, leading to a decrease in MG dye concentration. The adsorption percentage for raw rosemary biomass diminished to 65.7% in drinking water and 62.3% in tap water. Conversely, the adsorption percentage for H_2SO_4-modified rosemary biomass diminished to 88.4% in drinking water and 82.5% in tap water. This substantiates the notion that the electrostatic interaction between the MG dye molecules and the biomass components is highly effective. The findings indicate that both biomass materials have significant efficacy across diverse water samples.

2.10. Reusability

The reusability of adsorbents is essential for their effective use in wastewater treatment[73]. A 200 mg/L MG solution was chosen for the adsorption cycle experiment, and the reusability of both raw and H_2SO_4-modified rosemary biomass was examined. Following each adsorption cycle, desorption was conducted using a 0.1 M HCl solution, and the outcomes were recorded after five iterations of adsorption-desorption testing. Fig. 14 illustrates that the initial removal rates of MG by raw and H_2SO_4-modified rosemary biomass were 68.4% and 90.2%, respectively. Following five experimental cycles, the removal efficiency of MG by raw and

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H_2SO_4-modified rosemary biomass diminished marginally to 45.5% and 59.4%, respectively. The findings indicate that both raw and H_2SO_4-modified rosemary biomass may consistently be employed for the elimination of MG and analogous dyes from wastewater.

3. Discussion

This research indicated that rosemary biomass, particularly treated with sulfuric acid, serves as an efficient and sustainable bioadsorbent for the extraction of MG dye from aqueous solutions. Thorough characterization analyses (FT-IR, SEM, XRD, zeta potential, and pH_{pzc}) validated that H_2SO_4 treatment markedly improved the surface functionality and adsorption capacity of the biomass. Adsorption investigations demonstrated that contact time, pH, initial dye concentration, and adsorbent dosage influenced removal effectiveness, with the process predominantly regulated by electrostatic interactions. The adsorption data demonstrated strong concordance with the Langmuir isotherm and the *pseudo-second order* kinetic model, with error function studies reinforcing the credibility of these models. Thermodynamic analyses indicated that the adsorption process was endothermic and spontaneous for both raw and modified biomass, as evidenced by positive $\Delta H°$ and $\Delta S°$ values and negative $\Delta G°$ values. Moreover, salt tolerance assessments validated the enhanced efficacy of the modified biomass, underscoring the process's susceptibility to competing ions and indicating a reduction in adsorption effectiveness in tap and potable water. Reusability evaluations indicated that both adsorbents maintained considerable adsorption capability after five cycles, with the H_2SO_4-modified biomass demonstrating superior stability and efficacy. The findings indicate that rosemary biomass treated with sulfuric acid is a highly promising, economical, and eco-friendly bioadsorbent for the remediation of dye-contaminated wastewater, presenting substantial potential for practical applications.

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4. Materials and methods

4.1. Chemicals and instrumentations

During experimental research, the textile dye that was utilized was MG, which was bought from Sigma Aldrich and possessed a molecular formula of $C_{23}H_{25}N_2 \cdot C_2HO_4 \cdot 0.5C_2H_2O_4$. The dye content of MG was at least 90%. For adsorption research, rosemary biomass was procured from local market in Istanbul, Türkiye and utilized as an adsorbent. Sigma Aldrich was the supplier of the textile dyes that were utilized in the dye selectivity study. These dyes included Congo red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$), Safranin O (SO, $C_{20}H_{19}N_4Cl$), Auramine O (AO, $C_{17}H_{21}N_3 \cdot HCl$), methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$), crystal violet (CV, $C_{25}H_{30}N_3Cl$), and Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$). The pH of the solution was adjusted at various points throughout the adsorption investigations by using solutions of 0.1 M NaOH and 0.1 M HCl, both of which were supplied by Sigma Aldrich. In addition, Sigma Aldrich was the supplier of sodium nitrate ($NaNO_3$), which was needed for pH_{pzc} research. To investigate the impact that various salt solutions have on the adsorption process, sodium chloride (NaCl) and calcium chloride ($CaCl_2$) (both of which were bought from Sigma Aldrich) were required. For modification process, the sulfuric acid (H_2SO_4) and sodium bicarbonate ($NaHCO_3$) were purchased from Sigma Aldrich.

During the process of adsorbent characterization, FT-IR spectra before and after adsorption were collected with a Nicolet IS10 Thermo FT-IR instrument. The purpose of these spectra was to identify the functional groups that were present in the structure. An investigation using scanning electron microscopy (SEM) was carried out to investigate the surface morphology that occurred throughout the adsorption process. To investigate the crystallinity of the adsorbent both before and after the modification, an X-ray diffraction (XRD, PANalytical) examination was carried out. Using zeta potential (Malvern instruments) and pH_{pzc} studies, the surface charge of the adsorbents was successfully identified. Following the completion of the

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adsorption experiments, a Peak Analysis C-7200 UV-vis spectrophotometer was utilized to conduct an analysis on the standard dye solutions as well as the portion of the supernatant.

4.2. Preparation of raw and H_2SO_4 modified rosemary

This study utilized rosemary biomass, regarded in the context of zero waste, sourced from local market in Istanbul, Türkiye, as an adsorbent. The biomass was meticulously rinsed with distilled water to eliminate soil, dust, and assorted contaminants. Subsequently, it was subjected to many washes with boiling water to eliminate constituents such as oils and fatty acids. The meticulously cleaned plants were desiccated in a vacuum oven at 90 °C for 24 h. After drying, it was pulverized with a grinder and sifted to achieve a particle size within the 80-100 mesh range. After sieving, it was desiccated at 60 °C for 2 h and preserved in a sample container for utilization in adsorption investigations. During the biomass modification procedure, roughly 5 g of biomass was combined with 100 mL of 2N sulfuric acid solution (1:20 w/v) and subjected to mixing in a reflux system at ambient temperature for 8 h. After this procedure, the resultant sludge was thoroughly rinsed with ample distilled water until it neared a neutral pH. Subsequently, to equilibrate the biomass pH, it is combined with 1.0% sodium bicarbonate for 2 h at 25 °C, filtered to eliminate unreacted bicarbonate and sodium ions, and dehydrated at 110 °C for roughly 12-16 h[74]. The altered rosemary biomass is preserved for application in adsorption research. The preparation mechanism of adsorbents was illustrated in Fig. 15.

4.3. Batch adsorption experiments

For conducting equilibrium, kinetic, and thermodynamic studies, batch adsorption experiments were carried out in 100 mL Erlenmeyer flasks containing 50 mL of dye solution. These experiments were carried out in a water bath that was heated and equipped with a shaker. The purpose of these experiments was to investigate the effect of various physicochemical parameters on the adsorption process. It was decided to make a stock solution of MG dye (1000

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mg/L). A total of one gram of powdered dye was dissolved in 1000 mL of distilled water to produce the stock solution. MG dye solutions with starting concentrations of 100, 200, 300, 400, and 500 mg/L were prepared by dilution with distilled water and used in adsorption tests. These solutions were derived from the stock solution being used. Until the system reached equilibrium, adsorption kinetic experiments were carried out with the adsorbent concentration, starting concentration, and pH values remaining unchanged. This was done until the system reached equilibrium. Following that, the optimal kinetic study range for adsorption experiments was found to be between 5- and 180-min. Adsorption equilibrium investigations were performed at starting concentrations in the range of 100-500 mg/L, at temperatures of 298, 308, and 318 K, at constant pH, constant contact time, and constant adsorbent quantity. The adsorption trials were finished, and then the solutions were centrifuged for five min at a speed of roughly 9000 rpm. A UV-vis spectrophotometer with a wavelength of 610 nm was utilized to do an analysis on the standard dye solutions as well as the supernatant solution that was collected via centrifugation. By utilizing Eqs. (13), (14), and (15), respectively, we were able to determine the adsorption percentage (R%), the equilibrium adsorption capacity (q_e, mg/g), and the adsorption capacity after time "t" (q_t, mg/g)[75].

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$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (13)$$

$$q_e = (C_o - C_e) \times (V/m) \quad (14)$$

$$q_t = (C_o - C_t) \times (V/m) \quad (15)$$

In these equations, C_o and C_e are the concentrations at initial and equilibrium (mg/L), V is the volume of MG dye solution (L), and m is the dosage of the adsorbent (g).

The pH values of the produced biomass samples were determined using a digital pH meter, specifically the Ohaus Starter 3100. To ascertain this, 0.02 g of each biomass sample was combined with 50 mL of 0.1 M $NaNO_3$ solution for a duration of 24 h, after which the pH of the solution was assessed. The zero charge point (pH_{pzc}) values of the biomass surfaces were

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determined using the method given by Milonjic et al.[76]. The pH_{pzc} values of the chosen biomass samples (0.02 g) were ascertained in a 0.01 M $NaNO_3$ solution at pH levels ranging from 2.0 to 12.0 (pH_i) using this approach. The initial pH values were modified using 0.1 M HCl and 0.1 M NaOH solutions. Following a 24-h reaction period, the final pH (pH_f) of the solutions was assessed, and a pH_f-pH_i diagram was generated to ascertain the pH_{pzc}[77].

4.4. Error functions

The outcomes of the nonlinear fit will be assessed utilizing statistical metrics such as sum of squares errors (SSE), absolute relative errors (ARE), standard deviation (SD), and chi-square error ($\chi 2$). A nonlinear least squares method utilizing the SOLVER tool, based on the Generalized Reduced Gradient (GRG) iterative technique from Microsoft Excel, was applied to align experimental data with chosen models. All statistical parameters are optimized and assessed utilizing the Microsoft Excel Solver Add-in. The most suitable model will be chosen according to the ideal values of the established statistical and error criteria[78].

$$SSE = \sum_{i=1}^{n} \left(q_{e,exp} - q_{e,cal}\right)^2 \tag{16}$$

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right| \tag{17}$$

$$SD = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(q_{e,cal} - q_{e,exp}\right)^2} \tag{18}$$

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,cal}} \tag{19}$$

In these equations, the estimated and experimental adsorption capacities in mg/g were denoted by the variables $q_{e,cal}$ and $q_{e,exp}$, respectively.

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Acknowledgments

Not applicable

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by [Arif Simsek], [Birol Isik], and [Ozlem Cankurtaran]. The first draft of the manuscript was written by [Arif Simsek], [Birol Isik], and [Ozlem Cankurtaran] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Additional Information

The authors have no relevant financial or non-financial interests to disclose.

Funding

This work was supported by Yildiz Technical University Scientific Research Projects Coordination Department (Grant number [FLO-2025-7151]) and the Scientific and Technological Research Council of Turkey (TUBITAK). Project number: TUBITAK 2209–A–2024/1–1919B012405179.

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Figure legends

Figure 1. The FT-IR spectra of biomasses: (a) raw rosemary before and after MG dye adsorption and (b) H_2SO_4–modified rosemary before and after MG dye adsorption.

Figure 2. The SEM images of biomasses: (a) raw rosemary before MG dye adsorption, (b) raw rosemary after MG dye adsorption, (c) H_2SO_4–modified rosemary before MG dye adsorption, and (d) H_2SO_4–modified rosemary after MG dye adsorption.

Figure 3. The XRD patterns of raw rosemary and H_2SO_4–modified rosemary biomass.

Figure 4. The zeta potential curves of biomasses: (a) raw rosemary and (b) H_2SO_4–modified rosemary.

Figure 5. The pH_{pzc} curves of raw rosemary and H_2SO_4–modified rosemary biomass.

Figure 6. The column graphs of selectivity of synthetic dye adsorption onto raw rosemary and H_2SO_4–modified rosemary biomass.

Figure 7. The influence of operational parameters on MG dye adsorption onto rosemary and H_2SO_4–modified rosemary biomass: (a) adsorbent dosage, (b) initial pH, (c) equilibrium concentration, and (d) contact time.

Figure 8. The effect of salinity on synthetic dye adsorption onto raw rosemary and H_2SO_4–modified rosemary biomass.

Figure 9. The non-linear isotherm curves on MG dye adsorption onto raw rosemary and H_2SO_4–modified rosemary biomass: (a) Langmuir, (b) Freundlich, (c) D-R, and (d) Temkin.

Figure 10. The non-linear kinetic curves on MG dye adsorption onto raw rosemary and H_2SO_4–modified rosemary biomass (a) *pseudo-first order*, (b) *pseudo-second order*, (c) intraparticle diffusion, and (d) Elovich.

Figure 11. Proposed MG dye adsorption mechanism onto raw and H_2SO_4 – modified rosemary biomass.

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Figure 12. The linear Van't Hoff graphs of MG dye adsorption onto raw and H_2SO_4 – modified rosemary biomass.

Figure 13. The adsorption performance of raw rosemary and H_2SO_4 – modified rosemary biomasses in several water samples.

Figure 14. The reusability of raw and H_2SO_4 – modified rosemary biomass for MG dye adsorption.

Figure 15. The schematic representation of fabrication process of raw and modified rosemary.

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Table 1. Non-linear isotherm models for the adsorption of MG dye on raw rosemary and H_2SO_4–modified rosemary biomass.

	Raw Rosemary			***H_2SO_4–modified rosemary***		
Temperature (K)	**298**	**308**	**318**	**298**	**308**	**318**
Langmuir isotherm						
$q_m\ (mg/g)$	247.5	280.3	309.8	497.4	552.9	621.7
$K_L\ (L/mg)$	0.0199	0.0228	0.0256	0.0310	0.0453	0.0975
r^2	0.9998	0.9998	0.9997	0.9999	0.9941	0.9991
Freundlich isotherm						
$K_F\ (mg/g).(L/g)^{1/n}$	33.70	40.85	45.98	48.74	61.82	96.74
n	3.039	3.094	3.063	2.333	2.176	2.139
r^2	0.9992	0.9991	0.9992	0.9990	0.9986	0.9987
Dubinin-Radushkevich isotherm						
$q_{D-R}\ (mg/g)$	195.1	221.6	241.9	368.3	392.5	425.8
$E_{D-R}\ (J/mol)$	64.27	75.37	92.67	101.5	172.2	412.2
r^2	0.9997	0.9995	0.9994	0.9686	0.9742	0.9841
Temkin isotherm						
$K_T\ (L/mg)$	0.1866	0.2124	0.2415	0.3077	0.4982	0.9714
$b_T\ (J/mol)$	45.64	41.64	39.08	22.68	21.87	19.39
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999

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Table 2. Various adsorbents prepared from natural and modified biomass materials MG dye adsorption from wastewater

Adsorbent	q_m (mg/g)		Ref.
Raw rosemary	247.5	MG	This study
H_2SO_4–modified rosemary	497.4	MG	This study
SRSPC	567.6	MG	26
Sulphuric acid–modified *Ipomoea pes caprae* biomass	302.1	MG	46
Base-modified *Artocarpus odoratissimus* leaves	425.6	MG	79
Pinus roxburghii cone–activated char	250.0	MG	80
Organic acid-modified sawdust	280.3	MG	81
MHRS-HNO_3	21.10	MG	82

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Table 3. Error functions for the non-linear isotherm models of adsorption of MG dye on raw rosemary and H_2SO_4–modified rosemary biomass.

	Raw rosemary			*H_2SO_4–modified rosemary*		
Temperature (K)	**298**	**308**	**318**	**298**	**308**	**318**
Langmuir isotherm						
SSE	415.88	913.41	1063.4	182.68	200.78	159.81
ARE	5.6268	7.8256	7.1594	2.5042	3.0854	1.7524
SD	9.1201	13.516	14.583	6.0446	6.3369	5.6535
χ^2	2.6399	5.2139	5.1480	0.79963	1.3718	0.50497
Freundlich isotherm						
SSE	1691.5	3058.9	3783.9	1732.1	1317.4	3354.7
ARE	12.828	15.378	15.518	9.2481	7.4932	11.569
SD	18.393	24.734	27.509	18.613	16.232	25.902
χ^2	11.778	18.856	20.914	9.4858	6.5804	15.205
Dubinin-Radushkevich isotherm						
SSE	966.73	1437.8	2431.5	9731.1	13240	12464
ARE	8.4233	9.5277	12.379	24.021	26.927	23.543
SD	13.905	16.958	22.052	44.116	51.459	49.928
χ^2	6.6785	9.5086	15.119	3644.1	4256.1	514.75
Temkin isotherm						
SSE	845.96	1667.4	1968.7	359.03	575.69	504.39
ARE	7.7790	9.6683	9.0464	3.8848	5.5237	4.3235
SD	13.007	18.261	19.843	8.4739	10.731	10.044
χ^2	5.0531	8.8408	9.0085	2.0249	3.3765	2.2469

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Table 4. Kinetic parameters for the adsorption of MG dye on raw rosemary and H_2SO_4–modified rosemary biomass.

	Raw rosemary			*H_2SO_4–modified rosemary*		
Temperature (K)	**298**	**308**	**318**	**298**	**308**	**318**
Pseudo-first order						
k_1 (min^{-1})	0.1053	0.1533	0.1586	0.1250	0.1571	0.2135
q_e (cal) (mg/g)	136.9	148.6	157.8	180.4	188.8	195.4
q_e (exp) (mg/g)	129.0	143.3	149.4	173.7	182.9	188.3
r^2	0.9993	0.9997	0.9997	0.9995	0.9997	0.9999
Pseudo-second order						
k_2 (g/mg.min)	0.0011	0.0017	0.0016	0.0011	0.0014	0.0020
q_e (cal) (mg/g)	136.9	148.6	157.8	180.4	188.8	195.4
q_e (exp) (mg/g)	140.1	152.3	159.2	186.1	193.7	197.4
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
Intraparticle diffusion						
k_{d1} ($min^{0.5}$)	11.58	16.01	11.50	14.79	18.52	14.94
C_1 (mg/g)	47.33	55.62	74.99	72.57	77.81	105.7
r^2	0.9994	0.9999	0.9981	0.9835	0.9819	0.9794
k_{d2} ($min^{0.5}$)	9.052	5.903	8.041	8.941	6.117	4.562
C_2 (mg/g)	55.51	97.07	88.73	104.5	135.6	152.5
r^2	0.9942	0.9935	0.9996	0.9994	0.9868	0.9809
k_{d3} ($min^{0.5}$)	-0.0123	0.6281	0.4516	0.4838	0.6901	0.7445
C_3 (mg/g)	137.2	142.6	153.4	175.9	182.2	188.3
r^2	0.0028	0.9876	0.9876	0.9780	0.9902	0.9860
Elovich						
α (mg/g.min)	145.13	1006.2	1001.8	462.79	1779.5	16579
β (g/mg)	0.05008	0.05915	0.05604	0.04281	0.04839	0.05936
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999

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Table 5. Error functions for the non-linear kinetic models of adsorption of MG dye on raw rosemary and H_2SO_4–modified rosemary biomass.

	Raw rosemary			*H_2SO_4–modified rosemary*		
Temperature (K)	**298**	**308**	**318**	**298**	**308**	**318**
Pseudo-first order						
SSE	1262.6	749.65	1393.5	1541.2	1164.4	1191.9
ARE	11354	13192	13810	15631	16885	17880
SD	11.236	8.6583	11.804	12.415	10.791	10.917
χ^2	14.744	6.7094	11.633	13.648	8.6333	7.3006
Pseudo-second order						
SSE	389.92	111.84	395.93	374.51	186.62	226.89
ARE	11417	13226	13849	15700	16932	17906
SD	6.2444	3.3443	6.2923	6.1197	4.3199	4.7633
χ^2	4.4536	1.0097	3.3448	3.3103	1.4328	1.4403
Intraparticle diffusion						
SSE	578.17	640.79	457.95	1191.8	1124.5	558.33
ARE	6419.7	13234	13864	7987.7	16942	17912
SD	7.6037	8.0049	6.7672	10.917	10.604	7.6702
χ^2	4.9980	5.1577	3.3122	7.8472	7.0222	3.4228
Elovich						
SSE	139.03	132.03	88.633	295.33	288.64	119.27
ARE	10054	11914	12978	12768	14055	16719
SD	3.7287	3.6335	2.9771	5.4344	5.3725	3.4535
χ^2	1.0850	1.0149	0.58749	1.8043	1.7222	0.67264

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Table 6. Thermodynamic parameters for the adsorption of MG dyes on raw rosemary and H_2SO_4–modified rosemary biomass.

Thermodynamic parameters	ΔH_A^o (kJ/mol)	ΔS_A^o $(J/mol.K)$	ΔG_A^o (kJ/mol)		
			298 K	**308 K**	**318 K**
Raw rosemary	9.930	109.2	-22.61	-23.70	-24.80
H_2SO_4–modified rosemary	44.97	229.9	-23.54	-25.84	-28.14

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