Thermodynamic and kinetic analysis of methylene blue adsorption onto chemically modified cotton

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Abstract
This study investigates the adsorption of methylene blue onto chemically modified cotton, focusing on the kinetic and thermodynamic aspects of the process. The primary objective is to assess how chemical modification through carboxylation enhances the interaction between the methylene blue dye and the adsorbent material. The research is grounded in adsorption and thermodynamic theories, addressing the interactions between the dye and the modified substrate. The methodology includes the carboxylation of cotton using monochloroacetic acid and the execution of adsorption experiments at varying dye concentrations, ranging from 1 to 100 mg·L^{-1}, along with kinetic and thermodynamic evaluations. The results demonstrate that cotton carboxylation significantly increases the adsorption capacity for methylene blue, with kinetic data fitting well to the pseudo-second-order model. Thermodynamic analysis indicates that the adsorption process is spontaneous and favorable, characterized by an increase in enthalpy, suggesting that the interactions between the dye and the modified substrate are chemical in nature. Furthermore, adsorption is enhanced at higher temperatures, indicating that temperature positively influences the efficiency of the process. The maximum adsorption capacities obtained were comparable to or exceeded those reported for other low-cost natural adsorbents, highlighting the potential of chemically modified cotton as an effective material for dye removal from effluents. Integrating chemical modification strategies with adsorption dynamics presents promising opportunities for developing innovative purification technologies.
Keywords: adsorption; cotton; carboxylation; methylene blue; thermodynamics.

Análise termodinâmica e cinética da adsorção de azul de metileno em algodão quimicamente modificado

Resumo
Este estudo investiga a adsorção de azul de metileno em algodão quimicamente modificado, com foco nos aspectos cinéticos e termodinâmicos do processo. O objetivo principal é avaliar como a modificação química por meio da carboxilação aumenta a interação entre o corante azul de metileno e o material adsorvente. A pesquisa é fundamentada em teorias de adsorção e termodinâmica, abordando as interações entre o corante e o substrato modificado. A metodologia inclui a carboxilação do algodão usando ácido monocloroacético e a execução de experimentos de adsorção em concentrações variadas do corante, variando de 1 a 100 mg·L^{-1}, juntamente com avaliações cinéticas e termodinâmicas. Os resultados demonstram que a carboxilação do algodão aumenta significativamente a capacidade de adsorção do azul de metileno, com dados cinéticos se ajustando bem ao modelo de pseudo-segunda ordem. A análise termodinâmica indica que o processo de adsorção é espontâneo e favorável, caracterizado por um aumento na entalpia, sugerindo que as interações entre o corante e o substrato modificado são de natureza química. Além disso, a adsorção é aumentada em temperaturas mais altas, indicando que a temperatura influencia positivamente a eficiência do processo. As capacidades máximas de adsorção obtidas foram comparáveis ou superiores às relatadas para outros adsorventes naturais de baixo custo, destacando o potencial do

algodão quimicamente modificado como um material eficaz para a remoção de corantes de efluentes. A integração de estratégias de modificação química com a dinâmica de adsorção apresenta oportunidades promissoras para o desenvolvimento de tecnologias inovadoras de purificação.
Palavras-chave: *adsorção; algodão; carboxilação; azul de metileno; termodinâmica.*

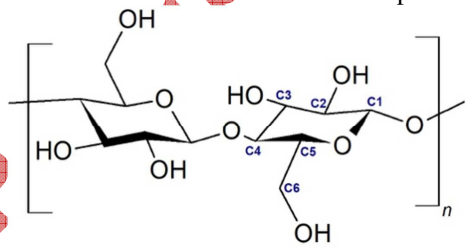
1 Introduction

The significance of textile materials in the manufacturing industry and the development of functional products is well established, as they are essential due to their physical and chemical properties and the functionalities they offer (Ornaghi Júnior *et al*., 2022). These materials can be classified as either natural or synthetic, with the natural types originating from plant, animal, or mineral sources. Among these, cotton has been extensively studied and functionalized, particularly through chemical modification techniques such as carboxylation, which can significantly enhance its interaction with dyes and other target molecules.

Cotton stands out as one of the most widely utilized natural resources in this context, not only for its intrinsic qualities but also due to its broad availability and versatility. Composites based on renewable materials, including those derived from cotton, have gained increasing attention in recent years due to their biodegradability, low cost, and potential for chemical functionalization (Thapliyal *et al*., 2023). This cellulosic material, primarily composed of glucose units linked by β-1,4-glycosidic bonds, is recognized for its strength and durability (Sarkar *et al*., 2023).

The fibrillar structure of cellulose provides cotton with mechanical strength and durability, while the hydroxyl groups at the C2, C3, and C6 positions of the glucose units enable strong interactions with polar molecules (Figure 1). These characteristics make cotton a highly absorbent, breathable, and functional material, qualities that are particularly valued in textile applications (Henriksson; Lennholm, 2009; Kwon *et al*., 2018; Medronho *et al*., 2012). Moreover, the biodegradability of natural fibers such as cotton has attracted increasing interest for applications in environmental engineering and water purification systems (Daria; Krzysztof; Jakub, 2020).

Figure 1 – Chemical structure of cellulose and carbon position in glucose units



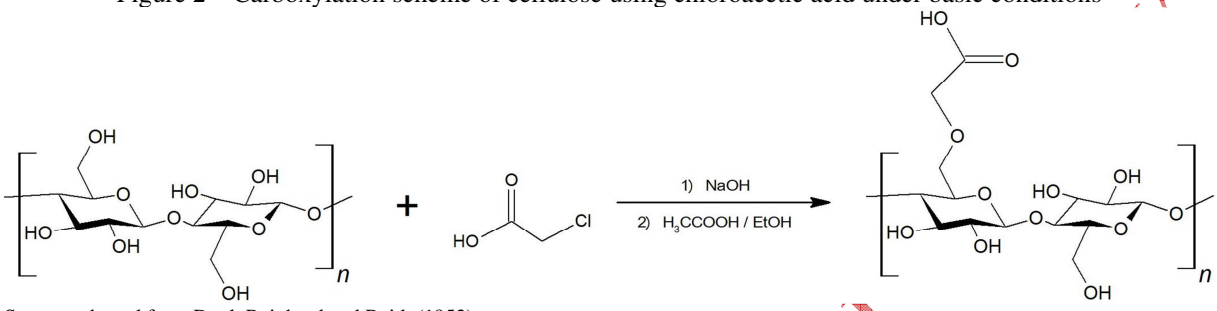
Source: adapted from Henriksson and Lennholm (2009)

The chemical modification of textile fibers, such as cotton, is a common industrial practice aimed at enhancing or introducing new functionalities to the material (Cortese *et al*., 2013; Joseph; Tretsiakova-McNally, 2013; Perepelkin, 2005). Textile finishing treatments may include processes that improve water resistance, increase dye adsorption capacity, or confer antimicrobial properties, among others. In the case of cotton, surface modification can be achieved by introducing new functional groups that alter its interaction with external molecules. One prevalent modification technique is oxidation, which results in the insertion of carboxyl groups (–COOH) into the cellulose chains (Bashar; Khan, 2013). This process, known as carboxylation, is particularly significant in adsorption studies, as carboxyl groups enhance the material's ability to interact with various molecules, including dyes and heavy metals. Carboxylation involves the selective oxidation of specific hydroxyl groups within cellulose, leading to the formation of carboxylic acid groups (Toshikj *et al*., 2019). This alteration improves the surface hydrophilicity of cotton and increases its ability to form hydrogen bonds and electrostatic interactions with charged molecules.

Daul, Reinhart, and Reid (1952) conducted pioneering studies on the carboxymethylation of cotton by reacting it with monochloroacetic acid under basic conditions (Figure 2). A detailed analysis

of parameters such as reaction time, temperature, and reagent concentration revealed that even small quantities of monochloroacetic acid, when properly applied, could significantly modify cotton properties. The authors demonstrated, through pilot-scale tests, that carboxymethylation of cotton fabrics could be successfully carried out using conventional textile machinery. The treated fabric exhibited a firmer texture with a slightly starched feel. Further investigations revealed that the treatment enhanced the tensile strength and elongation properties of the fabric, improved its dyeability, and increased its resistance to soiling and ease of stain removal. Moreover, the treated materials retained their modified characteristics even after one year of storage.

Figure 2 – Carboxylation scheme of cellulose using chloroacetic acid under basic conditions



Source: adapted from Daul, Reinhard and Reid, (1952)

Incorporating carboxyl groups into chemically modified cotton is justified by the need to enhance its interaction with functional molecules, such as methylene blue dye. While the naturally occurring hydroxyl groups in cotton offer some degree of interaction with polar molecules, introducing carboxyl groups significantly improves this interaction by enabling the formation of ionic and dipole–dipole bonds with positively charged species. In the case of methylene blue, a cationic dye, this modification substantially enhances adsorption capacity onto the modified cotton, which is crucial for the kinetic and thermodynamic study of its adsorption process.

This study investigates the kinetic and thermodynamic aspects of methylene blue adsorption onto chemically modified cotton, employing carboxylation as a strategy to enhance the interaction between the fabric and the dye. The research seeks to provide a deeper understanding of the adsorption mechanisms and the implications of chemical modifications on cotton properties, thereby contributing to the advancement of academic and scientific knowledge in the field of functional textile materials. Ultimately, the study aims not only to demonstrate the effectiveness of carboxylation in enhancing dye adsorption but also to open avenues for future research into applications such as antimicrobial fabrics and other functional uses across various sectors.

The adsorption of dyes onto textile fibers depends on several factors, including the chemical nature of the adsorbent material and the dye (Ahmed; El-Shishtawy, 2010; Yue *et al*., 2017). Methylene blue, used as a model dye in this study, is a widely studied cationic dye due to its well-characterized structural and chemical properties. Its molecular structure comprises aromatic rings connected by a sulfur atom, and the presence of nitrogen imparts a positive charge in aqueous solution (Ayad; El-Naser, 2010; Firmino *et al*., 2024; Gürses *et al*., 2006).

Methylene blue ($C_{16}H_{18}ClN_3S$) belongs to the phenothiazine class of dyes and exhibits high water solubility, making it a suitable model compound for adsorption studies involving polar substrates. In chemically modified cotton that contains carboxyl groups, these functionalities interact strongly with methylene blue molecules through ionic bonds and electrostatic attractions. The positively charged dye is attracted to the negatively charged carboxylate groups ($–COO^-$), thereby facilitating adsorption (Nakhli *et al*., 2020; Song *et al*., 2011). Recent investigations have confirmed the high adsorption potential of chemically modified materials for methylene blue removal. For example, ball-milled biochar demonstrated enhanced performance due to an increased surface area and greater exposure of active sites (Wang *et al*., 2023). Likewise, Liu *et al*. (2023) reported that alginate–biochar composites modified with KOH/$FeCl_3$ exhibited excellent adsorption capacity, underscoring the viability of hybrid natural-based materials for effluent treatment.

In addition to its use as a textile dye, phenothiazines such as methylene blue possess antimicrobial properties, demonstrating effectiveness against a variety of bacteria and fungi (Moreira *et al*., 2017; Perni *et al*., 2009; Silva *et al*., 2024). This property has prompted interest in its application in functional textiles, particularly those intended for medical use, where the incorporation of antimicrobial features can help prevent infections. Thus, the chemical modification of cotton to enhance methylene blue adsorption may also enable fabric functionalization with antimicrobial properties. Recent studies have shown that methylene blue can be utilized in disinfection treatments, as its bactericidal action is activated by exposure to visible light, leading to the generation of reactive oxygen species (ROS) (Lam *et al*., 2020). This functionality can be incorporated into modified fabrics, creating multifunctional textile materials with combined adsorption and antimicrobial capabilities. Although methylene blue is used solely as an adsorption model in this study, future research may explore the potential antimicrobial activity activated by ROS generation in modified cotton fabrics.

The subsequent sections of this article present a detailed overview of the employed methodology (Section 2), including the functionalization and characterization of the cotton substrate, as well as the adsorption experiments conducted with methylene blue. Section 3 provides the results and discussion, encompassing kinetic and thermodynamic modeling, adsorption isotherms, and model fitting. Finally, Section 4 offers concluding remarks on the practical implications of cotton carboxylation for adsorption applications and outlines prospective research directions.

2 Methodology

This section outlines the procedures adopted for the chemical modification and characterization of the cotton substrate, as well as the kinetic and thermodynamic adsorption assays conducted with methylene blue. The experimental protocol is described in detail to ensure reproducibility and clarity, covering sample preparation, functionalization steps, experimental conditions, and data analysis models.

2.1 Characterization and functionalization of the adsorbent

The material used was 100% cotton fabric with a basis weight of 210 ± 5 $g.m^{-2}$. Initially, the fabric was pre-washed in a 1% (w/v) neutral detergent solution, thoroughly rinsed with water, and left to dry in a well-ventilated environment. After washing, it was air-dried at room temperature in the shade for 24 hours. Once fully dried, the material was cut into small rectangular pieces, each weighing 20 ± 0.5 g.

The functionalization procedure followed the method described by Daul, Reinhart, and Reid (1952). Cotton samples were immersed in a 15% (w/v) aqueous solution of monochloroacetic acid for 5 minutes. Subsequently, the samples were transferred to a 40% (w/v) sodium hydroxide aqueous solution maintained at approximately 70 °C for 45 seconds. After the reaction, the samples were treated with an acetic acid solution prepared in absolute ethanol, rinsed with ethanol, then washed with tap water until they reached a neutral pH, and finally air-dried in the shade.

2.2 Adsorption assays

Kinetic adsorption assays were performed using a methylene blue solution at a 15 $mg.L^{-1}$ concentration. Both untreated and carboxylated cotton samples were placed in tubes containing 10 mL of the solution and agitated in a thermostatic bath with controlled temperature. Fourteen independent experiments with contact times ranging from 5 to 70 minutes were conducted. Each time point was tested in triplicate, and adsorption results were expressed as the average difference in absorbance at 670 nm between the initial and final solutions. All absorbance readings were obtained using a previously established calibration curve constructed with standard methylene blue solutions, ensuring linearity between absorbance and concentration and enabling precise quantification across all assays.

A fixed solid-to-liquid ratio of 2 $g.L^{-1}$ (20 mg of fabric per 10 mL of dye solution) was maintained in all tests. The tubes were placed in a thermostatic water bath equipped with orbital shaking and precise temperature regulation (±0.5 °C), ensuring consistent experimental conditions

throughout the assays. The amount of dye adsorbed at a given time (q_t) was calculated using Equation 1.

$$q_t = \frac{(C_0 - C)V}{m} \quad (1)$$

where C_0 and C (mg.L^{-1}) denote the initial and final dye concentrations, respectively; V is the solution volume (L); and m is the mass of the adsorbent (g). This standard approach was employed for both kinetic and equilibrium analyses. The kinetic data were plotted as graphs of the adsorbed quantity (q_t, mg.g^{-1}) versus time (t, min) at temperatures of 25, 35, and 45 °C.

Adsorption isotherms were constructed using methylene blue solutions with initial concentrations ranging from 1 to 100 mg.L^{-1}. Twenty milligrams of both untreated and carboxylated cotton samples were introduced into tubes containing 10.0 mL of methylene blue solution, under constant stirring at controlled temperatures. The amount adsorbed was determined based on the difference in absorbance between the initial and final solutions. All experiments were performed in triplicate, and the reaction time was fixed at 90 minutes, according to the optimal time identified in the kinetic studies.

The kinetic and isotherm data were fitted using non-linear modeling. For kinetic modeling, the Pseudo-first-order, Pseudo-second-order, Elovich, and intraparticle diffusion models were applied. For isotherm modeling, the Freundlich, Langmuir, and SIPs models were used (Largitte; Pasquier, 2016; Saleh, 2022).

3 Results and discussion

This section presents and discusses the main findings regarding the adsorption behavior of methylene blue onto untreated and carboxylated cotton. The analysis is organized into three primary segments: (i) kinetic modeling of adsorption data, (ii) isothermal studies at different temperatures, and (iii) thermodynamic parameters associated with the adsorption process. The discussion emphasizes the effects of chemical modification on adsorption capacity, mechanisms, and model fitting accuracy.

Kinetic studies indicated a better fit (R^2) to the pseudo-second-order (PSO) model, although similar fitting values were observed for the pseudo-first-order and Elovich models in certain cases. Adsorption experiments were carried out with a dye concentration of 15 mg. L^{-1}, using 20 mg of fabric in 10 mL of solution (2 g.L^{-1}), under constant agitation in a thermostatic water bath. The reaction tubes were monitored for 70 minutes, with data collected at 5-minute intervals. Orbital agitation ensured uniform contact between the adsorbent and the solution. These experimental conditions were consistently maintained for all tested temperatures (25, 35, and 45 °C). Model performance was evaluated using the determination coefficient (R^2), which served as the basis for comparing the fitting quality among different kinetic and isotherm models. No additional statistical analyses were conducted beyond this comparative assessment.

The superior fit to the PSO model suggests the occurrence of chemical interactions, as this model predicts bond formation between the adsorbate and the adsorbent. In systems using untreated fabric, a decrease in adsorption was observed with increasing temperature, a trend reversed following fabric carboxylation. Moreover, an increase in adsorption capacity (q_e) was observed after carboxylation, indicating enhanced interactions between the dye molecules and the modified fabric. Table 1 summarizes the kinetic modeling data for methylene blue adsorption onto untreated and carboxylated fabrics, while Figure 3 depicts the corresponding adsorption kinetics across the evaluated temperatures.

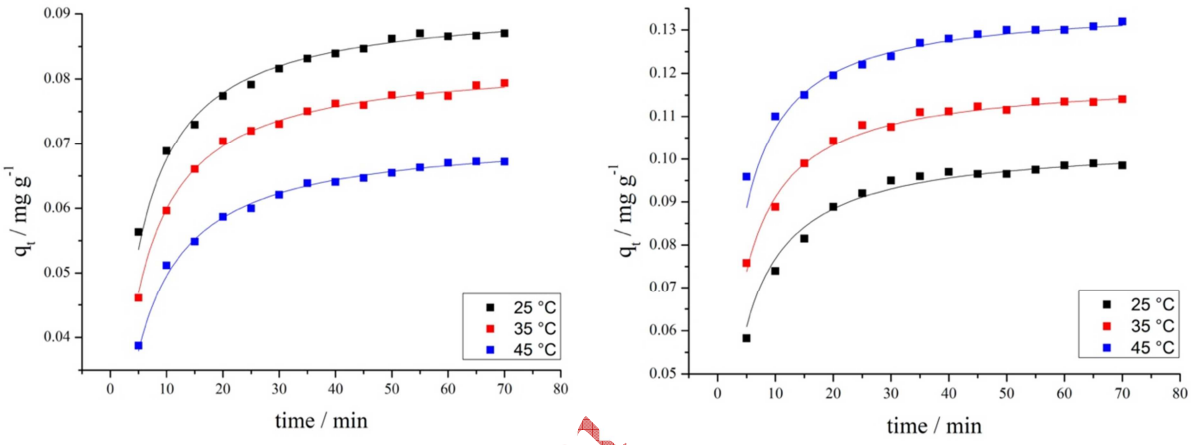
Table 1 – Kinetic parameters for methylene blue adsorption onto untreated cotton and carboxylated cotton at different temperatures

Model	Parameters	Temperature (°C)					
		Untreated			Carboxylated		
		25	35	45	25	35	45
Pseudo-first order	k_1 (min^{-1})	0.1726	0.1620	0.1472	0.1332	0.1900	0.2165
	q_e (mg.g^{-1})	0.0843	0.0765	0.0649	0.1006	0.1106	0.1267

	R^2	0.9698	0.9921	0.9718	0.9775	0.9798	0.9549
Pseudo-second order	k_2 ($g.mg^{-1}.min^{-1}$)	3.068	3.110	3.155	2.719	2.740	2.756
	q_e ($mg.g^{-1}$)	0.0917	0.0831	0.0715	0.1044	0.1191	0.1360
	R^2	0.9968	0.9923	0.9960	0.9985	0.9975	0.9894
Elovich	a ($mg^{-1}.min^{-1}$)	0.1250	0.284	0.113	0.1250	0.878	1.533
	b ($g.mg^{-1}$)	57.74	92.55	95.27	57.74	65.61	71.40
	R^2	0.9810	0.8333	0.9642	0.9810	0.9345	0.9812
Intraparticle diffusion	k_i ($mg.g^{-1}.min^{-0,5}$)	0.0083	0.0074	0.0066	0.0105	0.0105	0.0121
	Ci ($mg.g^{-1}$)	0.0292	0.0270	0.0204	0.0299	0.0412	0.0481
	R^2	0.7507	0.7016	0.7871	0.8073	0.7011	0.7077

Source: research data

Figure 3 – Adsorption kinectics of methylene blue onto untreated cotton (a) and carboxylated cotton (b) at different temperatures



Source: research data

The correlation coefficients (R^2) were generally similar, with the best fit consistently found for the Pseudo-Second Order model, reinforcing the hypothesis of chemical interaction involving bond formation between methylene blue and the cotton fabric. Based on the rate constants obtained from the Pseudo-Second Order model at different temperatures and the Arrhenius equation, activation energy values were calculated, achieving a high linear correlation (R^2 = 0.9926 for untreated fabric and R^2 = 0.9989 for carboxylated fabric). The calculated activation energy was 0.53 kJ/mol for the carboxylated fabric and 1.08 kJ/mol for the untreated fabric, suggesting that carboxylation lowers the activation energy required for adsorption.

Table 2 presents the thermodynamic parameters obtained through nonlinear regression modeling. The adsorption isotherms and the corresponding curves fitted through non-linear modeling are shown in Figure 4. The SIPs model best fits the experimental data, suggesting greater heterogeneity of adsorption sites at low concentrations and predominant monolayer formation at higher concentrations (Sivarajasekar; Baskar, 2014). Consistent with the kinetic experiments, the untreated fabric displayed reduced adsorption capacity with rising temperature, whereas the carboxylated fabric demonstrated the opposite behavior. The maximum adsorption capacity values derived from the SIPs model were closely aligned with those obtained from the kinetic data, indicating strong agreement between the experimental results.

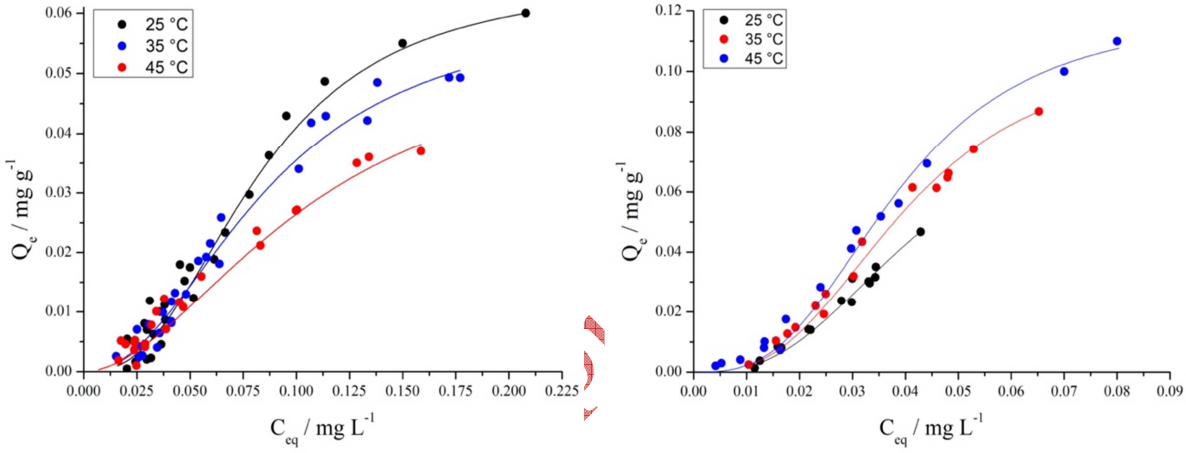
Table 2 – Thermodynamic modeling results for different adsorption isotherm models applied to methylene blue adsorption on fabrics

Model	**Parameters**	**Temperature (°C)**					
		Untreated			**Carboxylated**		
		25	**35**	**45**	**25**	**35**	**45**

Langmuir	K_L	0.2106	0.0923	0.0203	7.77E-4	5.70E-4	9.31E-4
	Q_{max} (mg.g^{-1})	1.6030	3.4275	12.660	11.390	21.82	14.88
	R^2	0.8885	0.9267	0.9600	0.8165	0.9095	0.9057
Freundlich	K_F	0.3732	0.3487	0.2891	13.65	3.756	2.002
	N	0.9523	0.9519	0.9504	0.5583	0.7432	0.8885
	R^2	0.8903	0.9285	0.9618	0.9704	0.9625	0.9663
SIPs	K_L	12.24	11.65	9.430	21.34	22.55	24.35
	Q_{max} (mg.g^{-1})	0.065	0.061	0.056	0.1036	0.1139	0.1368
	N	0.389	0.410	0.531	0.4005	0.4143	0.4463
	R^2	0.9706	0.9796	0.9769	0.9751	0.9883	0.9944

Source: research data

Figure 4 – Adsorption isotherms of methylene blue onto untreated cotton fabric (a) and carboxylated cotton fabric (b) at different temperatures



Source: research data

For untreated fabric, the adsorption constant (K) decreased with temperature, while the opposite trend was observed for carboxylated fabric, consistent with the kinetic data. A similar behavior was noted for the maximum adsorption capacity parameters, confirming that carboxylation enhances the fabric's adsorption capacity. Concerning the heterogeneity factor (n), minimal variation was detected, suggesting that temperature-induced surface changes were limited.

Using the isotherm data, plots of C_{eq}/Q_e versus Q_e were constructed, and extrapolation to the y-axis allowed for the determination of the equilibrium constant (K_{eq}) for each condition (Table 3). From these equilibrium constants, the Gibbs free energy change (ΔG) values were calculated for each temperature. In all cases, the adsorption process was spontaneous, as indicated by negative Gibbs energy values. Enthalpy (ΔH) and entropy (ΔS) changes were determined by linearizing the Gibbs equation (van't Hoff Equation 2):

$$\ln K_{eq} = \frac{\Delta H}{R} \times \frac{1}{T} - \frac{\Delta S}{R} \qquad (2)$$

where: R is the universal gas constant; T is the temperature; K_{eq} is the equilibrium constant; ΔH is the enthalpy change; and ΔS is the entropy change.

Table 3 – Thermodynamic parameters calculated from nonlinear modeling data using the SIPs model

Parameters	**Temperature (°C)**

	Untreated			Carboxylated		
	25	**35**	**45**	**25**	**35**	**45**
K_{eq}	8.95	6.43	5.59	15.60	16.49	17.78
ΔG (kJ.mol^{-1})	–5.43	–4.77	–4.55	–6.81	–7.18	–7.61
ΔH (kJ.mol^{-1})		–18.52			5.168	
ΔS (J.mol^{-1})		–44.15			40.15	
R^2		0.9880			0.9960	

Source: research data

The equilibrium constant (K_{eq}) results demonstrated excellent agreement with the experimental data, as evidenced by R^2 values close to 1. For untreated fabric, the spontaneity of the adsorption process was driven primarily by enthalpy changes, characterizing the process as exothermic. In contrast, for carboxylated fabric, entropy contributions were more significant, with the process being endothermic, thereby explaining the increase in adsorption capacity with temperature. It is hypothesized that the carboxylation reaction modifies the adsorption sites and increases system disorder following dye adsorption, demonstrating that carboxylation enhances the fabric's adsorption performance through surface modification.

The enhanced adsorption observed after carboxylation is likely attributed to the formation of specific interactions between methylene blue molecules and carboxyl groups introduced on the cotton surface. As a cationic dye, methylene blue can interact through ionic bonding with deprotonated carboxyl groups (–COO$^-$), as well as via electrostatic attraction and hydrogen bonding with polar sites within the cellulose matrix. These interactions are consistent with chemisorption-dominated systems and justify the superior fitting to the pseudo-second-order kinetic model observed in this study.

When compared with other natural adsorbents reported in the literature, carboxylated cotton demonstrated competitive or superior performance in methylene blue adsorption. Studies employing modified cellulose-based materials or biosorbents such as alginate–biochar composites and oxidized fibers have reported maximum adsorption capacities ranging from 0.05 to 0.12 mg.g^{-1} under similar experimental conditions (Liu *et al*., 2023; Wang *et al*., 2023). In the present work, the maximum q_e value obtained with carboxylated cotton reached 0.136 mg. g^{-1}, indicating enhanced efficiency of the chemically modified substrate. These results support the potential of carboxylated cotton as a cost-effective, scalable, and environmentally sustainable option for dye removal. Additionally, the favorable fitting to kinetic and isotherm models, along with advantageous thermodynamic parameters, underscores the scientific robustness of the experimental findings.

Nonetheless, it is important to acknowledge that the adsorption capacity values remain lower than those achieved with certain high-cost engineered adsorbents, such as graphene oxide-based composites or functionalized silica materials. However, the use of a renewable, abundant, and easily modifiable substrate such as cotton offers a promising balance between performance and sustainability.

4 Conclusion

Based on the studies and experimental investigations conducted, it is concluded that cotton fabric modified through carboxylation exhibits enhanced adsorption properties due to changes in the material's surface. The kinetic data demonstrated good agreement with the thermodynamic data, confirming that the fabric's functionalization affects its adsorption capacity. The carboxylation reaction was found to reduce the activation energy of the fabric-dye system and increase the adsorption capacity. These results demonstrate that fabric carboxylation is an effective strategy to improve the interaction between cotton fabrics and molecules intended for functionalization, such as pigments or antimicrobial agents.

Based on these findings, future research may explore the application of carboxylated fabrics in various fields, including biomedical materials and environmental remediation. Investigations into the long-term stability and performance of the modified fabrics under real-world conditions would provide valuable insights. Furthermore, efforts to optimize the carboxylation process to enhance adsorption efficiency, as well as studies on the incorporation of additional functional groups, may broaden the scope of applications for these materials. Comparative analyses involving different dye types and antimicrobial agents may also elucidate interaction mechanisms, contributing to the development of advanced materials with tailored functionalities. In particular, future studies could assess the antimicrobial potential of functionalized cotton fabrics, especially given the known photoactivated bactericidal properties of methylene blue.

Despite the promising adsorption performance of carboxylated cotton, the chemical modification process presents challenges for large-scale implementation. The use of strong alkaline solutions and halogenated carboxylating agents may raise concerns related to operational safety and waste management, particularly in industrial settings. Therefore, future studies should consider greener or more sustainable modification strategies, such as enzymatic oxidation or the use of less toxic reagents, to improve scalability and environmental compatibility.

Additionally, although the present study focused on adsorption performance, the environmental impact of the carboxylation process itself warrants further evaluation. Life cycle assessments and analyses of the ecological footprint of the modification steps would contribute to validating the overall sustainability of the material for real-world wastewater treatment applications.

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Conflict of Interest

The authors declare no conflict of interest.

Author contributions

SANTOS JUNIOR, E. C.; BERLARMINO, G. C.: data collection, analysis and/or interpretation; manuscript drafting and writing. **SILVA, A. C. P.:** manuscript drafting and writing; final review with critical and intellectual contribution. **SCACCHETTI, F. A. P.; TESSARO, A. L.; SAMULEWSKI, R. B.:** manuscript drafting and writing; final review with critical and intellectual contribution; overall supervision and project coordination. All authors participated in the writing, discussion, reading, and approval of the final version of the article.

References

AHMED, N. S. E; EL-SHISHTAWY, R. M. The use of new technologies in coloration of textile fibers. **Journal of Materials Science**, v. 45, p. 1143-1153, 2010. DOI: https://doi.org/10.1007/s10853-009-4111-6.

AYAD, M. M.; EL-NASR, A. A. Adsorption of cationic dye (methylene blue) from water using polyaniline nanotubes base. **The Journal of Physical Chemistry C**, v. 114, n. 34, p. 14377-14383, 2010. DOI: https://doi.org/10.1021/jp103780w.

BASHAR, M. M.; KHAN, M. A. An overview on surface modification of cotton fiber for apparel use. **Journal of Polymers and the Environment**, v. 21, p. 181-190, 2013. DOI: https://doi.org/10.1007/s10924-012-0476-8

CORTESE, B.; CASCHERA, D.; PADELETTI, G.; INGO, G. M.; GIGLI, G. A brief review of surface-functionalized cotton fabrics. **Surface Innovations**, v. 1, n. 3, p. 140-156, 2013. DOI: https://doi.org/10.1680/si.13.00008.

DARIA, M.; KRZYSZTOF, L.; JAKUB, M. Characteristics of biodegradable textiles used in environmental engineering: a comprehensive review. **Journal of Cleaner Production**, v. 268, 122129, 2020. DOI: https://doi.org/10.1016/j.jclepro.2020.122129.

DAUL, G. C.; REINHARDT, R. M.; REID, J. D. Studies on the partial carboxymethylation of cotton. **Textile Research Journal**, v. 22, n. 12, p. 787-792, 1952. DOI: https://doi.org/10.1177/004051755202201204.

FIRMINO, H. B.; VOLANTE, E. K. T. S.; SILVA, A. C. P.; SCACCHETTI, F. A. P.; LIS, M. J.; MARTÍ, M.; SAXENA, S.; TESSARO, A. L.; BEZERRA, F. M. β-cyclodextrin-modified cotton fabric for medical and hospital applications with photodynamic antibacterial activity using methylene blue. **Coatings**, v. 14, n. 9, 1100, 2024. DOI: https://doi.org/10.3390/coatings14091100.

GÜRSES, A.; DOĞAR, Ç.; YALCIN, M.; AÇIKYILDIZ, M.; BAYRAK, R.; KARACA, S. The adsorption kinetics of the cationic dye, methylene blue, onto clay. **Journal of Hazardous Materials**, v. 131, n. 1-3, p. 217-228, 2006. DOI: https://doi.org/10.1016/j.jhazmat.2005.09.036.

HENRIKSSON, G.; LENNHOLM, H. Cellulose and carbohydrate chemistry.In: EK, ,M.; GELLERSTEDT, G.; HENRIKSSON, G. (org.). **Wood chemistry and wood biotechnology.** Berlin: De Gruyter, p. 71-100, 2009. DOI: https://doi.org/10.1515/9783110213409.71.

JOSEPH, P.; TRETSIAKOVA-MCNALLY, S. Chemical modification of natural and synthetic textile fibres to improve flame retardancy. In: **Handbook of fire resistant textiles**. Woodhead Publishing, p. 37-67, 2013. DOI: https://doi.org/10.1533/9780857098931.1.37.

ORNAGHI JÚNIOR, H. L.; NEVES, R. M.; MONTICELI, F. M.; DALL AGNOL, L. Smart fabric textiles: recent advances and challenges. **Textiles**, v. 2, n. 4, p. 582-605, 2022. DOI: https://doi.org/10.3390/textiles2040034.

KWON, C. H.; KO, Y.; SHIN, D.; KWON, M.; PARK, J.; BAE, W. K.; LEE, S. W.; CHO, J. High-power hybrid biofuel cells using layer-by-layer assembled glucose oxidase-coated metallic cotton fibers. **Nature Communications**, v. 9, n. 1, 4479, 2018. DOI: https://doi.org/10.1038/s41467-018-06994-5.

LAM, P.-L.; WONG, R. S.-M.; LAM, K.-H.; HUNG, L.-K.; WONG, M.-M.; YUNG, L.-H.; HO, Y.-W.; WANG, W.-Y.; HAU, D. K.-P.; GAMBARI, R.; CHUI, C.-H. The role of reactive oxygen species in the biological activity of antimicrobial agents: an updated mini review. **Chemico-Biological Interactions**, v. 320, 109023, 2020. DOI: https://doi.org/10.1016/j.cbi.2020.109023.

LARGITTE, L.; PASQUIER, R. J. C. E. R. A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. **Chemical Engineering Research and Design**, v. 109, p. 495-504, 2016. DOI: https://doi.org/10.1016/j.cherd.2016.02.006.

LIU, H.; ZHU, J.; LI, Q.; LI, L.; HUANG, Y.; WANG, Y.; FAN, G.; ZHANG, L. Adsorption performance of methylene blue by KOH/$FeCl_3$ modified biochar/alginate composite beads derived from agricultural waste. **Molecules,** v. 28, n. 6, 2507, 2023. DOI: https://doi.org/10.3390/molecules28062507.

MEDRONHO, B.; ROMANO, A.; MIGUEL, M. G.; STIGSSON, L.; LINDMAN, B. Rationalizing cellulose (in) solubility: reviewing basic physicochemical aspects and role of hydrophobic interactions. **Cellulose**, v. 19, p. 581-587, 2012. DOI: https://doi.org/10.1007/s10570-011-9644-6.

MOREIRA, L. M.; LYON, J. P.; LIMA, A.; CODOGNOTO, L.; SEVERINO, D.; BAPTISTA, M. S.; TESSARO, A. L.; GEROLA, A. P.; HIOKA, N.; RODRIGUES, M. R.; BONACIN, J. A.; SANTOS, S. C.; ROMANI, A. P.; OLIVEIRA, H. P. M. The methylene blue self-aggregation in water/organic solvent mixtures: relationship between solvatochromic properties and singlet oxygen production. **Orbital: The Electronic Journal of Chemistry**, v. 9, n. 4, p. 279-289, 2017. DOI: http://dx.doi.org/10.17807/orbital.v9i4.996.

NAKHLI, A.; BERGAOUI, M.; TOUMI, K.-H.; KHALFAOUI, M.; BENGUERBA, Y.; BALSAMO, M.; SOETAREDJO, F. E.; ISMANDJI, S.; ERNST, B.; ERTO, A. Molecular insights through computational modeling of methylene blue adsorption onto low-cost adsorbents derived from natural materials: a multi-model's approach. **Computers & Chemical Engineering**, v. 140, 106965, 2020. DOI: https://doi.org/10.1016/j.compchemeng.2020.106965.

PEREPELKIN, K. E. Principles and methods of modification of fibres and fibre materials. A review. **Fibre Chemistry**, v. 37, n. 2, p. 123-140, 2005. DOI: https://doi.org/10.1007/s10692-005-0069-6.

PERNI, S.; PICCIRILLO, C.; PRATTEN, J.; PROKOPOVICH, P.; CHRZANOWSKI, W.; PARKIN, I. P.; WILSON, M. The antimicrobial properties of light-activated polymers containing methylene blue and gold nanoparticles. **Biomaterials**, v. 30, n. 1, p. 89-93, 2009. DOI: https://doi.org/10.1016/j.biomaterials.2008.09.020.

SALEH, T. A. Kinetic models and thermodynamics of adsorption processes: classification. In: SALEH, T. A. (org.). **Surface science of adsorbents and nanoadsorbents**. Elsevier, 2022. p. 65-97. DOI: https://doi.org/10.1016/B978-0-12-849876-7.00003-8.

SARKAR, M.; UPADHYAY, A.; PANDEY, D.; SARKAR, C.; SAHA, S. Cellulose-based biodegradable polymers: synthesis, properties, and their applications. In: SAHA, S.; SARKAR, C. (org.). **Biodegradable polymers and their emerging applications**. Singapore: Springer Nature Singapore, 2023. p. 89-114. DOI: https://doi.org/10.1007/978-981-99-3307-5_5.

SILVA, A. C. Q.; SILVESTRE, A. J. D.; FREIRE, C. S. R.; VILELA, C. Modification of textiles for functional applications. In: MONDAL, I. H. (ed.). **Fundamentals of natural fibres and textiles**. Woodhead Publishing, 2021. p. 303-365. DOI: https://doi.org/10.1016/B978-0-12-821483-1.00010-3.

SILVA, A. C. P.; ARRUDA, L. M.; MOREIRA, I. P.; SCACCHETTI, F. A. P.; OLIVEIRA, H. P. M.; SAMULEWSKI, R. B.; FANGUEIRO, R.; TESSARO, A. L. Functionalization of fibrous substrates with mesoporous silica nanoparticles as a strategy to obtain photodynamic antibacterial textiles. **Dyes and Pigments**, v. 230, 112342, 2024. DOI: https://doi.org/10.1016/j.dyepig.2024.112342.

SIVARAJASEKAR, N.; BASKAR, R. Adsorption of basic red 9 onto activated carbon derived from immature cotton seeds: isotherm studies and error analysis. **Desalination and Water Treatment**, v. 52, n. 40-42, p. 7743-7765, 2014. DOI: https://doi.org/10.1080/19443994.2013.834518.

SONG, J.; ZOU, W.; BIAN, Y.; SU, F.; HAN, R. Adsorption characteristics of methylene blue by peanut husk in batch and column modes. **Desalination**, v. 265, n. 1-3, p. 119-125, 2011. DOI: https://doi.org/10.1016/j.desal.2010.07.041.

THAPLIYAL, D.; VERMA, S.; SEN, P.; KUMAR, R.; THAKUR, A.; TIWARI, A. K.; SINGH, D.; VERROS, G. D.; ARYA, R. K. Natural fibers composites: origin, importance, consumption pattern, and challenges. **Journal of Composites Science**, v. 7, n. 12, 506, 2023. DOI: https://doi.org/10.3390/jcs7120506.

TOSHIKJ, E.; TARBUK, A.; GRGIĆ, K.; MANGOVSKA, B.; JORDANOV, I. Influence of different oxidizing systems on cellulose oxidation level: introduced groups versus degradation model. **Cellulose**, v. 26, p. 777-794, 2019. DOI: https://doi.org/10.1007/s10570-018-2133-4.

WANG, M.; TAN, Y.; YANG, H.; ZHAN, L.; SUN, G.; LUO, L. On the adsorption characteristics and mechanism of methylene blue by ball mill modified biochar. **Scientific Reports**, v. 13, 21174, 2023. DOI: https://doi.org/10.1038/s41598-023-48373-1.

YUE, X.; JIANG, F.; ZHANG, D.; LIN, H.; CHEN, Y. Preparation of adsorbent based on cotton fiber for removal of dyes. **Fibers and Polymers**, v. 18, p. 2102-2110, 2017. DOI: https://doi.org/10.1007/s12221-017-1211-9.