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Research Article

Innovative Salt-Free Reactive Dyeing of Cotton Using Cationization with *Vicia Faba* Bean Pod Waste

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Received: 13 February 2025; **Revised:** 9 April 2025; **Accepted:** 9 April 2025

Abstract: This study explores the cationization of cotton fabric using an extract from faba bean husk waste to enable salt-free reactive dyeing. By leveraging natural compounds in the husk, the process enhances dye uptake and fixation, eliminating the need for conventional salt additives. Optimized extraction conditions (7.5% HCl, 24-hour treatment, and 1 : 20 material-to-liquor ratio) achieved a 90% dye exhaustion rate and a fixation rate of 51.74%. The cationized fabric exhibited superior color strength (*K/S* value: 1.5291) compared to conventionally dyed fabric (1.3043). Colorfastness to washing, rubbing, and light was comparable to traditional methods, with minimal changes in mechanical properties. This approach demonstrates the potential of faba bean husk as a sustainable cationizing agent, promoting eco-friendly textile dyeing while utilizing agricultural byproducts. The study contributes to reducing environmental hazards and advancing salt-free dyeing technologies.

Keywords**:** salt-free dye, faba bean pods, cationization, reactive dye, fastness, exhaustion

1. Introduction

Cotton, the most widely used natural fiber in the textile industry, is prized for its softness, breathability, absorbency, and biodegradability.[1] Its compatibility with reactive dyes, which form covalent bonds with cellulose, makes it ideal for producing vibrant, durable colors with excellent fastness properties.[2] However, traditional reactive dyeing processes rely heavily on inorganic salts, such as sodium sulfate, to overcome the electrostatic repulsion between negatively charged dye molecules and cotton fibers. While salt enhances dye uptake, its excessive use (30-150 g/L) results in low dye fixation rates (30-50%) and generates highly saline wastewater, posing significant environmental challenges, including water pollution and soil salinization.[3] These issues have spurred research into sustainable, salt-free dyeing methods that minimize environmental impact while maintaining dyeing efficiency.[4]

Recent advancements in salt-free dyeing have focused on modifying cotton fibers to introduce cationic groups, which enhance the affinity for anionic reactive dyes without the need for salt.[5] Techniques such as cationization using synthetic ammonium salts, chitosan, or amino acid extracts have shown promise in improving dye exhaustion and fixation.[6] However, these methods often involve costly, time-consuming processes or raise concerns about skin irritation and environmental safety.[7] Innovative approaches, such as non-aqueous media dyeing and the use of agricultural byproducts, have emerged as sustainable alternatives. For instance, non-aqueous dyeing systems reduce water

DOI: https://doi.org/10.37256/sce.6220256558

consumption and eliminate salt, while natural cationizing agents derived from agricultural waste offer eco-friendly solutions.[8] Recent advancements in salt-free dyeing, such as non-aqueous media dyeing and cationization techniques, have shown promise in reducing environmental impact while improving dye fixation.[9]

The development of salt-free dyeing methods has gained significant attention in recent years, with researchers exploring various strategies to improve dye fixation and reduce environmental impact. One promising approach involves the chemical modification of cotton fibers to introduce cationic charges, which attract anionic dye molecules and enhance dye exhaustion.[10] This method eliminates the need for salt and improves dye fixation, resulting in more efficient and sustainable dyeing processes. Additionally, non-aqueous dyeing systems, such as supercritical carbon dioxide dyeing, have been investigated as alternatives to traditional water-based methods.[11] These systems not only eliminate the need for salt but also reduce water consumption and wastewater generation. However, the high cost and complexity of these technologies have limited their widespread adoption.[12] Reactive dyes are fixed on cotton by hydroxyl groups in cotton fibers and dye molecules, usually at a high pH (higher than 10.5). This process creates covalent connections between the dye molecules.[13] In the alkaline solution, hydroxide ions (OH^-) may also interact with some dye molecules, resulting in decreased dye fixing. As a result, dyeing chemists have become increasingly interested in processes that utilize high salt concentrations while achieving slower fixation of reactive dyes. Unfortunately, this practice has contributed to the production of heavily colored wastewater with complex chemical compositions, posing significant environmental challenges and harming ecosystems.[14]

Reactive dyeing usually requires a significant amount of inorganic salt, such as sodium sulfate, to improve dye adsorption. In this context, using natural cationizing agents derived from agricultural byproducts presents a cost-effective and environmentally friendly alternative. Faba bean husk, a readily available agricultural waste, contains natural compounds that can be utilized to cationize cotton fibers. This study investigates the potential of faba bean husk extract as a sustainable cationizing agent for cotton, enabling salt-free reactive dyeing. By optimizing extraction parameters and application methods, we aim to achieve high dye uptake, improved fixation rates, and excellent colorfastness. This approach not only addresses the environmental challenges associated with traditional dyeing methods but also contributes to the valorization of agricultural waste, promoting a more sustainable and circular textile industry.

2. Material and methods

2.1 *Materials*

For this study, 100% half-bleached plain-weave cotton fabric with a yarn count of 21 Ne was utilized. The fabric had an average weight of 145 g/m^2, with a density of 24 ends and 18 picks per inch. This specific fabric was chosen as the foundation for all experimental work due to its consistent properties and suitability for textile applications. Additionally, *Vicia faba* bean pods were sourced locally from Wolkite City to explore their potential as a natural cationizing agent. The selection of these pods was critical for investigating their application in the cationization process and subsequent salt-free reactive dyeing methods, aligning with the study's focus on sustainability and the utilization of agricultural byproducts. Faba bean pods were sun-dried for 48 hours under controlled conditions (27 ± 3 °C and 65% relative humidity) to ensure consistency. The dried pods were cracked open, and the husks were ground into a fine powder using a laboratory cutting mill.

2.1.1 *Chemicals and reagents*

Hydrochloric acid (99% purity) was used to extract of amino acids from faba bean pods. Additionally, a range of laboratory-grade chemicals and reagents were employed in this study to ensure the quality and reliability of the experimental results. These included Reactive Red HE3B (C.I. Reactive Red 16), sodium carbonate (99% purity), sodium chloride (99% purity), acetic acid (96% purity), wetting agents (99% purity), and sequestering agents (99% purity). All chemicals used were of analytical grade to ensure reliability and reproducibility.

2.2 Methods

2.2.1 Collection and preparation of *Vicia faba* bean pods

Faba bean pods were purchased from a local market and sun-dried to reduce moisture content. Once dried, the pods were cracked open using a grinder to separate the seeds from the husks, as illustrated in Figure 1. The husks were then further processed using a laboratory cutting mill to produce a fine powder. The powdered material was dissolved in varying concentrations of hydrochloric acid at room temperature, with different treatment durations, to optimize the extraction conditions for the intended application. After the extraction process, a diluted sodium hydroxide solution (0.1 g/l) was added to adjust the pH of the mixture to a range of 5.5 to 6.0. The solution was then filtered to remove any solid residues, yielding a clear liquid containing the extracted amino acids from the faba bean husks. This solution was collected and used for subsequent experiments.

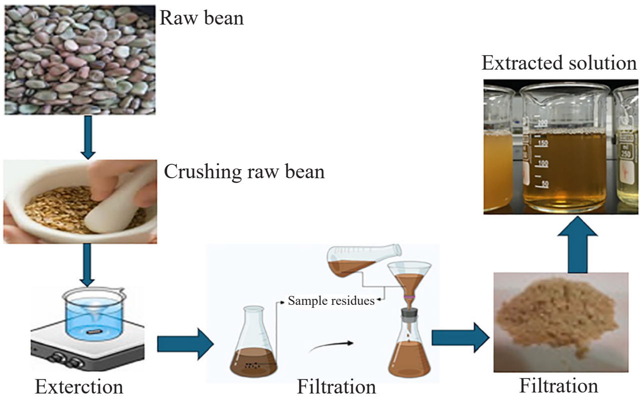

Figure 1. Collection, preparation, and extraction of faba bean pods

2.2.2 Extraction conditions

Extraction was carried out using 20 grams of *Vicia faba* powder, with three different concentrations levels of hydrochloric acid and treatment times at room temperature. To optimize the extraction parameters, two key factors were investigated: hydrochloric acid concentration (tested at 2.5%, 5%, and 7.5%) and treatment duration (tested at 8, 16, and 24 hours). A consistent material-to-liquor ratio of 1 : 20 was maintained across all experiments. The experimental design included two replicates for each condition, resulting in a total of eighteen trials, as outlined in Table 1. These trials were conducted following the design of the experiment software. The optimization process was validated by measuring the quantity of filtered protein obtained from each extraction trial, ensuring the reliability and accuracy of the results.

Table 1. Extraction conditions

Mass of powder (gram)	Treatment time (hr.)	HCl con. (%)	M.L.R	pH	Temperature (°C)
20	16-24	2.5-7.5	1 : 20	5-6	27

After determining the optimal extraction conditions, the percentage yield of amino acids from the waste faba bean pods was evaluated. The yield of the extract was calculated using the following equation.

$$\text{Yield (\%)} \ \frac{(W_1 - W_2)}{W_1} \tag{1}$$

Where W_1 represents the initial weight of the waste *Vicia faba* pod powder, and W_2 denotes the residual weight of the powder after the extraction process. This calculation provided a quantitative measure of the extraction efficiency, ensuring the reproducibility and reliability of the results.

2.2.3 *Cationization of cotton*

The amino acid solution derived from the faba bean extract was applied to half-bleached cotton fabric using a padding technique as shown in Figure 2. This process was conducted in a laboratory setting using a two-bowl padded mangle, ensuring complete saturation of the fabric through two dips and two nips. The treatment was optimized to achieve 100% wet pickup, allowing the fabric to absorb the maximum amount of the solution. The treated fabric was then squeezed at varying pressures of 1, 2, 3, 4, and 5 bar, depending on the pressure applied by the squeezing rollers. Following padding, the cotton fabric was dried for 1 to 5 minutes at temperatures ranging from 90 °C to 110 °C (in increments of 5 °C). Subsequently, the fabric was cured for 3 minutes at temperatures between 110 °C and 150 °C (in increments of 10 °C). This stepwise drying and curing process ensured optimal fixation of the amino acid solution onto the cotton fabric.

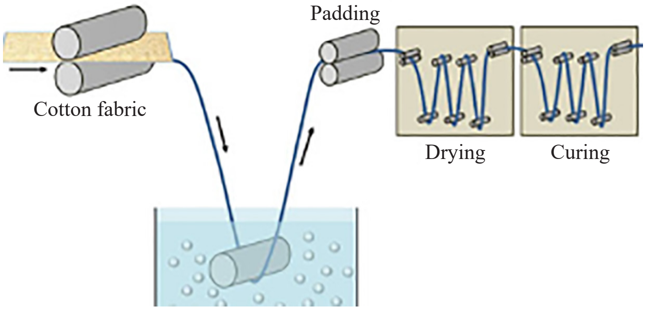

Figure 2. Pad-dry-cure process employed for cationizing cotton fabrics

2.2.4 *Dyeing treated fabric*

Both untreated and cationized cotton fabrics were dyed using a laboratory infrared dyeing machine, maintaining a material-to-liquor ratio of 1 : 20. A 2% shade was achieved using Reactive Red HE3B (C.I. Reactive Red-120), following standard dyeing protocols. Notably, the dye bath was prepared without the addition of salt, unless otherwise specified, to evaluate the effectiveness of the cationization process in promoting dye uptake in the absence of traditional salt-based methods. The fabric was treated for 30 minutes at 50 °C in a dye bath containing 2% (owf) acetic, acid, 5% (owf) sodium carbonate and 1% (owf) leveling auxiliary (Albegal B, Ciba). Subsequently, 2% (owf) Reactive Red HE3B was introduced into the bath. The temperature then increased to 90 °C at a gradient of 1.5 °C per minute and held at 90 °C for 45 minutes as shown in Figure 3. Following dyeing, the fabric was rinsed in a 1% (owf) ammonia solution (pH 8.4) at 80 °C for 15 minutes.

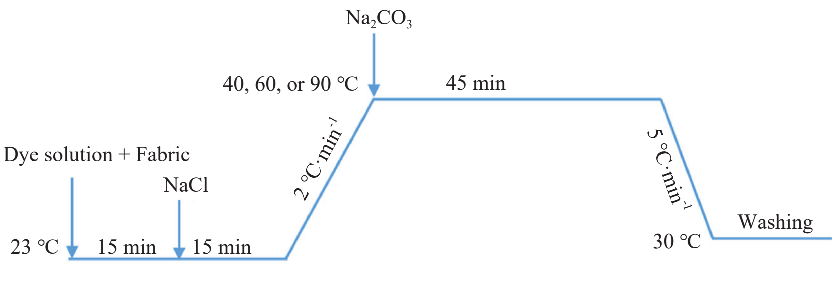

Figure 3. Process curve for dyeing cotton fabric with reactive dye

2.2.5 *Color strength measurement*

The color strength of the dyed fabrics was evaluated using a Color Eye 3,100 reflectance spectrophotometer under D 65 lighting with a 10° observer. Measurements were recorded in the Lab* color space. The color intensity (*K/S* values) of the cationized samples was determined under various conditions. Reflectance (*R*) values of the dyed fabric were measured at the maximum absorption wavelength (λ max) and processed using the computer color matching system's integrated software to calculate *K/S* values. The Kubelka-Munk equation, as shown below, was used to derive the *K/S* values.

$$\frac{K}{S} = \frac{\left(1 - R^2\right)}{2R} \tag{2}$$

where *R* represents the fraction of light reflected from the fabric, *K* quantifies the light absorbed by the dye, and *S* accounts for the light scattered by the fabric. This method provided a quantitative measure of the dye's color strength on the fabric.

2.2.6 *Determination of exhaustion percentages*

The optical density of the dye solution was measured before and after the dyeing process using a Ultraviolet-Visible Spectroscopy (UV/VIS) spectrometer, with measurements taken at the maximum absorption wavelength (λ max) of the dye. The percentage of dye bath exhaustion (% *E*) was then calculated using Equation (3), which provides insight into the fabric's efficiency in absorbing the dye during the dyeing process.

$$\% E = \frac{\left(A_0 - A_1\right)}{A_0} \tag{3}$$

where A_0 represents the absorbance of the dye at its maximum wavelength in the dye bath before dying, and A_1 denotes the absorbance of the residual dye in the bath after the dyeing process. This calculation allowed for the quantification of dye uptake by the fabric, ensuring an accurate assessment of the dyeing efficiency.

2.2.7 *Determination of fixation percentages*

The reflectance (*R*) values of the dyed fabric were measured across all wavelengths using the Color Eye 3,100 spectrophotometer. The maximum *K/S* value of the fabric was determined at a specific wavelength, both before and after the soaping process. The percentage of dye fixation (% *F*) was then calculated using Equation (4), which provides critical insight into the effectiveness of dye adherence to the fabric after dyeing and washing.

$$\% F = \frac{\left(\frac{K}{S}\right)_b}{\left(\frac{K}{S}\right)_a} \times 100 \tag{4}$$

where $(K/S)_b$ represents the color yield measured before soaping, and $(K/S)_a$ denotes the color yield measured after soaping. This calculation allowed for the evaluation of dye fixation efficiency, ensuring a comprehensive understanding of the dye's stability and permanence on the fabric.

2.2.8 *Fastness properties*

2.2.8.1 *Colorfastness to rubbing*

The colorfastness of the dyed samples to rubbing, both in wet and dry conditions, was evaluated using the AATCC

Test Method 8-2013. This standardized procedure measures the resistance of a fabric's color to abrasion caused by rubbing, simulating real-world wear and tear. The tests aimed to assess the durability of the dye and ensure that the color remained stable after washing and use. The results of this evaluation are critical for understanding the practical performance of the dyed polyester/cotton blend fabrics in everyday applications, providing valuable insights into their suitability for commercial use.

2.2.8.2 *Colorfastness to washing*

The colorfastness to washing of the dyed samples was evaluated following AATCC Test Method 61-1996, using a Launder-Ometer for the procedure. This test measures the resistance of the fabric's color to repeated laundering, simulating real-world washing conditions. The results were assessed using the Grey Scale for color change, which provides a standardized method for quantifying any color shifts that occur during the washing process. This evaluation is critical for determining the durability and longevity of the dye on the polyester/cotton blend fabrics, ensuring their ability to retain color and appearance after multiple wash cycles.

2.2.8.3 *Colorfastness to perspiration*

The colorfastness to perspiration of the dyed samples was evaluated using AATCC Standard Test Method 15-1997. This test simulates real-world conditions where the fabric may come into contact with sweat, assessing the resistance of the fabric's color to fading or bleeding when exposed to perspiration. This evaluation is critical to ensure that the dyed polyester/cotton blend fabrics maintain their color integrity and aesthetic appearance during wear, particularly in warm or humid environments. The results provide valuable insights into the durability and performance of the dyed fabrics under practical use conditions.

2.2.9 *Fourier transform infrared spectroscopy (FTIR) analysis*

The surface chemistry of both untreated (control) and treated cotton fabrics was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) with a Perkin Elmer FTIR instrument, following the ASTM 7575 test standard. Spectral data were collected in the frequency range of 4,000 to 400 cm^{-1} to ensure accuracy and reliability. Each sample underwent 20 scans to obtain consistent and representative spectra. A 500 ml laboratory beaker (Model No. P230, 115-volt) was used during the preparation and handling of samples. This analytical approach provided detailed insights into the chemical modifications and functional groups present on the fabric surfaces.

2.2.10 *Testing of physical properties*

The physical properties of the dyed samples, including tensile strength and tear strength, were evaluated in accordance with established testing standards. Tensile strength was measured following ASTM D 5035-95, while tear strength was assessed using ASTM D 1424-09. These standardized methods ensure the accuracy, reliability, and comparability of the results, providing a comprehensive understanding of the mechanical performance of the fabric. This evaluation is essential for assessing the durability and suitability of the dyed fabrics for practical applications.

3. Results and discussion

3.1 *Optimization of extraction parameters*

Natural amino acids were extracted from faba bean husk powder using various extraction procedures. The extraction efficiency was influenced by key factors, including hydrochloric acid (HCl) concentration and treatment time. The percent yield was determined as the response variable, and the experimental design, consisting of 9 runs generated using Minitab software, is presented in Table 2. The extraction process was conducted at room temperature (27 ± 3 °C) to ensure effective solubilization of amino acids from the faba bean hulls. As shown in Table 2, the highest extraction efficiency of 90% was achieved during trial number 9. This result indicated that the optimal extraction conditions were a 7.5% hydrochloric acid concentration, a 24-hour treatment period, and a material-to-liquor ratio of 1 : 20. These conditions were found to maximize the yield of the amino acid solution. However, it is worth noting that using hydrochloric acid concentrations above 7.5% would significantly increase costs without proportionally improving extraction efficiency. These findings demonstrate that the optimized parameters provide the most effective and economical approach for extracting amino acids from faba bean husk powder.

Table 2. Optimization and extraction conditions

No. of experiment	Concentration of HCl (%)	Time (hr.)	MLR	Original weight (g)	Residual weight (g)	Yield (%)
1.	2.5	8	1 : 20	20	7.45	62.75
2.	2.5	16	1 : 20	20	5.62	63
3.	2.5	24	1 : 20	20	7.27	63.2
4.	5	8	1 : 20	20	7.82	65.24
5.	5	16	1 : 20	20	6.21	68.95
6.	5	24	1 : 20	20	8.43	75.5
7.	7.5	8	1 : 20	20	8.1	75
8.	7.5	16	1 : 20	20	*7.33*	82.5
9.	7.5	24	1 : 20	20	7.54	90

Among all the experiments conducted, Trial 9 demonstrated the highest extraction efficiency, outperforming the results of other trials. This superior yield makes Trial 9 the optimal choice for the extraction process. A higher extraction yield indicates greater process efficiency and suggests that the conditions employed in Trial 9 were particularly effective in maximizing the extraction of beneficial compounds, as illustrated in Figure 4. These findings highlight the effectiveness of the optimized parameters in enhancing the extraction of valuable components from the faba bean husk powder.

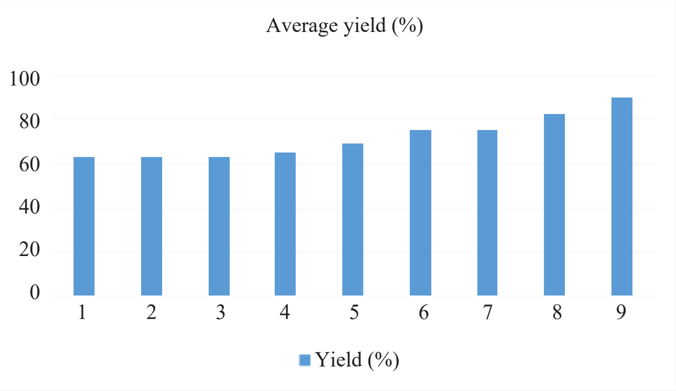

Figure 4. Extraction yield

An aqueous amino acid solution extracted from faba bean husk was used to cationize bleached cotton fabric through a two-bowl laboratory padding mangle at 100% wet pickup. Padding was performed under varying squeezing pressures to optimize the cationization conditions. This approach aimed to enhance the interaction between the cotton fibers and the amino acid solution, ensuring effective cationization. Following padding, the treated fabric was dried and cured under different conditions, with variables such as drying temperature, drying time, curing temperature, and curing duration systematically adjusted. The study focused on optimizing these parameters to improve the efficiency of the cationization process, ultimately enhancing the fabric's affinity for reactive dyes.

3.1.1 *Confirmation of cationization: FTIR analysis*

Fourier Transform Infrared (FTIR) spectroscopy was employed to analyse the cationized cotton samples and confirm the presence of amino acid extracts from faba beans. This technique successfully verified the cationization process by identifying specific functional groups associated with the faba bean extract on the cotton fabric. As illustrated in Figure 5, significant changes in the chemical composition of the cotton fabric were observed after cationization using the pad-dry-cure method, confirming the successful attachment of amino acids to the fabric.

A broad absorption band between 3,000 and 3,600 cm^{-1}, attributed to the stretching vibrations of O-H bonds involved in hydrogen bonding within the cellulose structure, was observed. Within this band, two distinct peaks at 3,296 cm^{-1} and 3,341 cm^{-1} were identified, corresponding to intramolecular and intermolecular hydrogen bonding, respectively. Additionally, peaks in the range of 2,854 to 2,920 cm^{-1} were attributed to the asymmetric vibrations of $-CH_2$ groups. Other notable absorption bands included a peak at 1,242 cm^{-1}, indicative of the symmetrical bending of $-CH_2$ groups, and a prominent band at 2,109 cm^{-1}, representing $-CH_2$ stretching. A novel and significant absorption band at 1,715 cm^{-1} was observed, indicating the presence of a quaternary nitrogen group ($-N^+-3R$), where '*R*' groups are substituted by amino groups. These absorption bands were nearly absent in the spectra of untreated (bleached) cotton, highlighting the chemical modifications induced by the cationization process. These findings provide clear evidence of the successful incorporation of amino acid extracts into the cotton fabric, confirming the effectiveness of the cationization treatment.[15]

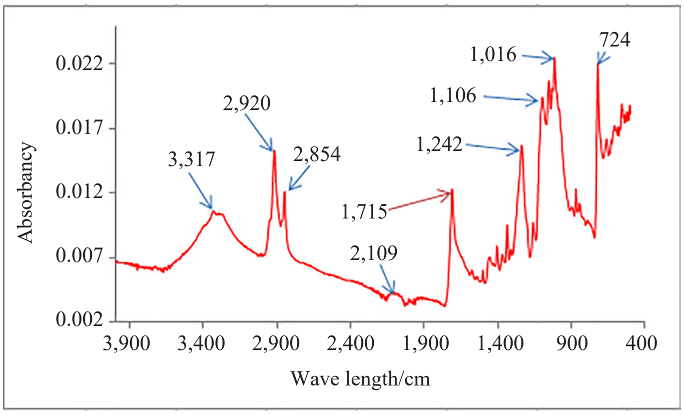

Figure 5. FTIR Analysis of cationized cotton

The FTIR spectrum of the cotton treated with faba bean extract exhibited stronger intensity, likely due to the formation of ester-COO-linkages. When faba bean amino acids were applied to cotton under heat and acidic conditions, ester linkages formed, facilitating the incorporation of free $-NH_2$ groups into the modified cotton. In acidic environments, these $-NH_2$ groups can convert to $-NH_3^+$, contributing to the cationization of the fabric. The spectral analysis confirmed that the amino groups effectively bonded to the primary alcohol groups of cellulose through ester linkages, enhancing the chemical interaction between the amino acids and the cotton fibers. This finding underscores the successful integration of the faba bean extract into the cotton structure, validating the efficacy of the cationization process.

3.2 *Dyeing of cationized cotton fabrics*

The extraction conditions (7.5% HCl, 24-hour treatment, and 1 : 20 material-to-liquor ratio) achieved a dye exhaustion rate of 90% and a fixation rate of 51.74%. This improvement is attributed to the strong ionic interactions between the cationic cotton and anionic dyes. To further enhance fixation rates, future studies could explore non-aqueous media dyeing, which has shown promise in reducing dye hydrolysis and improving color yield. In this study, the amino acid solution derived from faba bean extract was applied to cotton using the pad-dry-cure method to cationize the fabric. Pre-treating cotton with faba bean extract significantly enhanced the fixation of reactive dyes. The cationized fabric exhibited excellent dyeing uniformity, with minimal color variation ($\Delta E < 1.5$) across samples. This uniformity is due to the even distribution of cationic sites on the fabric surface, ensuring consistent dye uptake. These results demonstrate the effectiveness of faba bean husk as a natural cationizing agent for achieving high-quality, salt-free dyeing.

Table 3. Optimization of cationization conditions and their *K/S* values

No	Squeezing pressure (bar)	Drying temperature (°C)	Drying min (min)	Curing temp (°C)	Curing time (min)	Add-on (%)	*K/S* value
1.	1	90	1	130	1	36.2	1.3282
2.	1	95	2	130	2	38.5	1.4976
3.	1	100	3	130	3	40.2	1.5291
4.	2	90	1	140	1	38.2	1.3924
5.	2	95	2	140	2	38.6	1.5113
6.	2	100	3	140	3	37.2	1.4738
7.	3	90	1	150	1	38.4	1.4259
8.	3	95	2	150	2	34	1.3117
9.	3	100	3	150	3	38	1.4881

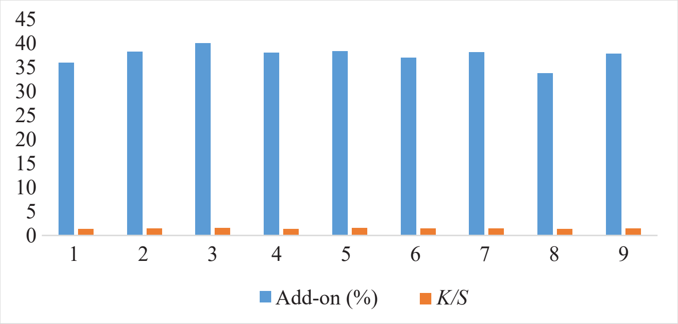

Figure 6. Optimization of cationization parameters

The sample treated with a squeezing pressure of 1 bar, dried for 3 minutes at 100 °C, and cured for 3 minutes at 130 °C exhibited a significantly higher *K/S* value, as detailed in Table 3 and illustrated in Figure 6. This sample was selected to highlight its superior dye-fixing performance compared to fabrics dyed using conventional methods. Under these optimized conditions, the highest *K/S* value of 1.5291 was achieved, with an add-on percentage of 40.2%. Additionally, the cationized fabric showed minimal scorching, demonstrating the effectiveness of the treatment in enhancing dye fixation while maintaining the fabric's structural integrity. The optimal cationization conditions for treating cotton fabric with the faba bean amino acid solution were determined to be a squeezing pressure of 1 bar, followed by drying at 100 °C for 3 minutes and curing at 130 °C for 3 minutes. These conditions resulted in a higher colour strength (*K/S* value) and a greater add-on percentage compared to other tested samples. This optimized process not only improved dye uptake and fixation but also ensured the preservation of the fabric's quality, making it a viable and efficient approach for sustainable textile dyeing.

As shown in Table 4, cationized cotton fabric exhibited significantly higher *K/S* values when dyed with HE Reactive Red dye under identical conditions and varying dyeing processes. The increase in *K/S* values for the fabric treated with the faba bean extract amino acid solution indicate enhanced dye absorption compared to untreated cotton. This improvement confirms that the cationization process significantly boosts color yield, demonstrating the effectiveness of the treatment in improving dye uptake and fixation on the fabric. These results highlight the potential of cationized cotton as a superior alternative for achieving vibrant and durable coloration in textile applications.

Table 4. *K/S* of different samples at 540 nm wavelength

Samples	Reflectance (%)	*K/S*
Untreated and salt free	34.11	0.6364
Conventional	22.92	1.3043
Cationized	20.62	1.5291

Cationized cotton fabric dyed with reactive dye using an acid bath dyeing method without salt demonstrated higher *K/S* values compared to traditionally dyed fabric that utilized salt. The enhanced dye uptake in the treated fabric is attributed to the introduction of a positive charge, which strengthens the attraction between the fabric and the negatively charged reactive dyes. This non-conventional dyeing method begins with an acid bath and concludes with an alkaline bath after fixing with alkali. By fostering a strong affinity between the anionic reactive dyes and the cationic sites on the modified cotton, this approach achieves exceptionally high exhaustion rates without the need for electrolytes in the dye bath.

Additionally, the increased dye uptake is facilitated by the generation of additional hydroxyl groups in the cationized (chemically modified) cotton, which expands the number of available attachment sites for the dye. These findings highlight the effectiveness of cotton fabric treated with an amino acid solution derived from faba bean extract in enabling salt-free reactive dyeing. The greater potential difference between the reactive dye anions and the amino groups on the faba bean-modified cotton enhances the attraction of Reactive Red HE3B (C.I. Reactive Red 120) to the cationic groups of the amino acid residues. This demonstrates the potential of cationized cotton as a sustainable and efficient alternative for achieving high-quality dyeing results without the environmental drawbacks of traditional salt-based methods.

3.2.1 *Effect of cationization on dye exhaustion and fixation*

3.2.1.1 *Effect on exhaustion (% E)*

The optical density of the dye solution was measured before and after the dyeing process using a UV/VIS spectrophotometer, specifically at the maximum wavelength of absorbance (λ max). The highest absorption was observed at 520 nm, which was subsequently used to calculate the percentage of dye exhaustion. This measurement provides insight into the efficiency of dye absorption by the fabric during the dyeing process. As shown in Table 5, the cationized fabric achieved a significantly higher dye exhaustion percentage, indicating more efficient dye utilization. This improvement also resulted in less pigmented effluent from the dye bath. Specifically, the dye exhaustion increased by 3.91% compared to conventional samples and by 60% compared to untreated, salt-free dyed samples. The enhanced dye uptake is attributed to the introduction of a positive charge in the modified fabric, which strengthens the interaction with the anionic reactive dyes. This demonstrates the effectiveness of cationization in improving dye absorption and reducing environmental impact by minimizing dye waste in the effluent. These results underscore the potential of cationized cotton as a sustainable alternative for achieving high efficiency dyeing processes.

Table 5. Percentage fixation of cationized cotton

Sample	Maximum absorbance before dyeing	Maximum absorbance after dyeing	Exhaustion percentage (E %)
Untreated and salt-free	5.69	3.69	35.42
Conventional	5.69	0.81	85.066
Cationized	5.69	0.65	89.74

In this study, the primary mechanism driving the dye-fiber attraction in the reactive dye and amino acid-modified cotton system is ionic interaction, particularly in the absence of salt. This interaction occurs between the protonated, electron-deficient amino groups of the amino acids, which are bonded to the cotton via ester linkages, and the negatively charged reactive dyes. The strong ionic attraction between these protonated amino groups and the anionic reactive dyes is responsible for the observed increase in dye exhaustion in the amino acid-treated cotton.[16] This enhanced interaction facilitates a more efficient transfer of dye molecules from the aqueous dye bath to the cationized cotton substrate, resulting in improved dye uptake. These findings highlight the effectiveness of amino acid-based cationization in promoting salt-free reactive dyeing while achieving high dye exhaustion rates.

3.2.1.2 *Effect on percentage fixation*

As shown in Table 6, cationized cotton achieved a higher dye fixation percentage compared to uncationized cotton dyed with salt. Specifically, the fixation percentage was approximately 32% higher than that of untreated cotton and 3.34% higher than that of uncationized cotton dyed with salt. This improvement in dye fixation can be attributed to the reduced likelihood of dye hydrolysis in the cationized fabric. The introduction of cationic groups on the cotton surface enhances the interaction between the fabric and the reactive dyes, leading to more efficient dye fixation and minimizing dye loss during the process. These results demonstrate the effectiveness of cationization in improving dye fixation and reducing environmental impact by minimizing dye waste.

Table 6. Percentage fixation of cationized cotton

Sample	Maximum *K/S* before soaping at 540 nm	Maximum *K/S* after soaping at 540 nm	Fixation percentage (F %)
Untreated and salt-free	1.6342	0.6364	38.942
Conventional	2.7712	1.3043	47.066
Cationized	2.9553	1.5291	51.74

The washing fastness ratings further confirm the improvement in dye fixation. The addition of alkali during the fixation process facilitates the reaction between the dye, the fibre, and the water in the system. Reactive dyes exhibit a higher affinity for the fibre compared to non-reactive dyes, leading to increased exhaustion rates and, ultimately, higher fixation levels. The reaction rate of reactive dyes plays a significant role in this process. The substantial improvement in dye fixation observed in cationized cotton demonstrates the success of the treatment. The enhanced esterification of amino acids into the cotton fabric significantly improved the fixation of reactive dyes by promoting a greater initial transfer of dye molecules. The initial absorption levels of reactive dyes on cotton treated with amino acids derived from faba bean extract were closely correlated with the final fixation rates. This correlation suggests that the presence of amino acids strengthens the adherence of dyes to the cotton fibres, resulting in superior dyeing outcomes.[17] These findings highlight the effectiveness of amino acid-based cationization in improving dye fixation and overall dyeing performance.

3.2.2 *Colorfastness properties for dyed cationized cotton fabric*

The color fastness to washing of the cationized fabric was evaluated and compared to traditionally dyed cotton fabric. The assessment focused on both color change and staining. The results indicate that the cationized fabric maintains its color integrity effectively after washing, demonstrating superior durability compared to conventional dyeing methods. These findings provide valuable insights into the enhanced performance of cationized cotton in retaining color and resisting staining, highlighting its potential as a more durable and sustainable alternative in textile applications.

3.2.2.1 *Wash fastness*

As shown in Table 7, the cationized cotton fabric exhibited no discoloration, demonstrating wash fastness comparable to conventionally dyed cotton fabric. Both dyeing methods achieved excellent ratings based on the standard grayscale assessment. This performance is attributed to the strong ionic bonds formed between the fibre and dye, which are nearly as effective as the covalent bonds typically formed during dye-fibre interactions. These results confirm the efficacy of dye fixation achieved through pretreatment with the amino acid solution derived from faba bean extract, enabling successful salt-free dyeing. The modified dyeing process, which begins with an acidic dye bath pH and transitions to an alkaline fixation pH, does not adversely affect reactive dye fixation on cationized cotton. This approach effectively preserves the dye fixation process, ensuring high-quality and durable coloration outcomes.

Table 7. Wash fastness properties of conventional and cationized cotton fabric

Fastness	Untreated and salt-free	Conventional	Cationized
Wash fastness			
Change in color	4/5	4/5	4/5
Staining on white	5	4/5	4/5
Lightfastness	6	6	5
Dry rubbing fastness			
Change in color	4/5	4/5	4/5
Staining on white	4/5	4/5	4/5
Wet rubbing fastness			
Change in color	4	4/5	4
Staining on white	4	4/5	4
Alkaline perspiration fastness			
Change in color	4/5	4/5	4/5
Staining on white	4/5	4/5	4/5

3.2.2.2 *Rubbing fastness*

Colour fastness against rubbing is a critical test for evaluating the quality of dyed materials, as it measures the transfer of colour from the fabric surface to other surfaces during rubbing. The rubbing fastness of the cationized fabric was compared to that of conventionally dyed cotton fabrics. All samples received excellent ratings for dry rubbing fastness, with no significant differences observed. This performance is due to the strong ionic interactions between the anionic dye molecules and the cationic surface of the cotton. For wet rubbing fastness, the cationized samples achieved acceptable ratings, though slightly lower than those of conventionally dyed samples. This minor discrepancy may result from hydrogen bonds formed between hydrolysed dyes and the amino acids on the cotton surface derived from the faba bean extract.

3.2.2.3 *Perspiration fastness*

The colour fastness to sweat of the cationized fabric was also evaluated and compared to conventionally dyed cotton fabric. Both fabric types showed comparable colour change ratings in acidic and alkaline environments. The staining characteristics of the cationized and uncationized fabrics were nearly identical, with no staining observed on the polyester fabric in any of the tests. These results indicate that both cationized and uncationized fabrics dyed with HE-reactive dye exhibit excellent sweat fastness.

3.2.2.4 *Light fastness*

Light fastness, which measures the ability of dyed fabrics to retain colour under daylight exposure, was evaluated for both untreated fabrics dyed with salt and cationized fabric dyed without salt. The untreated fabric demonstrated outstanding light fastness, with ratings of 4 or higher, which are generally considered acceptable. However, the cationized cotton fabric showed a one-step lower light fastness rating compared to the untreated fabric. This slight reduction may be attributed to the presence of aliphatic molecules between the dye and fibre, which could disrupt the dye's stable electronic state. When exposed to light, this disruption may cause electrons to transition to higher energy levels, leading to dye degradation. Despite this minor decrease, the cationized fabric maintained relatively high light fastness, likely due to the improved dye penetration enabled by the cationization process.[18] Overall, these findings highlight the effectiveness of cationized cotton in achieving excellent wash, rubbing, and sweat fastness, with only a marginal reduction in light fastness. The results underscore the potential of cationized cotton as a sustainable and high-performance alternative for textile dyeing.

3.2.3 *Effect of cationization on physical properties*

The economic viability of treated or cationized fabrics depends not only on their dyeing efficacy and color fastness but also on their physical properties. Prior to physical testing, all fabric samples were conditioned for 48 hours at 27 °C (± 2 °C) and 65% (± 5%) relative humidity. The results of these physical property evaluations are detailed in Table 8.

Table 8. Effect of cationization on physical properties

Properties	Conventional			Cationized cotton		
	Weft way	Warp way	Overall	Weft way	Warp way	Overall
Tensile strength (N)	91	215	153	88	212	150
Tear strength (N)	41.34	42.66	42	41.02	42.01	41.51
Bending length (cm)	2.00	2.22	2.11	2.02	2.25	2.135

3.2.3.1 *Tensile strength*

The cationized samples exhibited only a minor decrease in tensile strength compared to conventionally dyed fabrics. This slight reduction may be attributed to the thermal degradation of cotton during the curing process. Despite this, the overall tensile strength remained largely intact, indicating that the cationization process does not significantly compromise the fabric's mechanical durability.[19]

3.2.3.2 *Tear strength*

Tear strength, which measures the fabric's ability to initiate, maintain, or propagate a tear, showed no significant difference between cationized and conventionally dyed fabrics. This stability can be explained by the minimal impact of cationic reactants on the intermolecular hydrogen bonds within the cotton structure. The cationization process primarily involves cross-linking without disrupting these bonds, preserving the fabric's tear resistance.[20] The findings support the hypothesis that cationization predominantly occurs at the methyl hydroxyl groups of cotton cellulose, specifically at carbon number six (C6), without significantly affecting the hydrogen bonds between molecules. As a result, the structural integrity of the fabric is largely maintained after modification with the protein solution. This ensures that the cationized fabric retains its physical properties, making it a viable option for practical applications.

In summary, the cationization process has a negligible impact on the physical properties of cotton fabric, with only minor reductions in tensile strength and no significant changes in tear strength. These results underscore the potential of cationized cotton as a durable and economically feasible alternative for textile applications.

4. Conclusion

This study successfully demonstrated the use of faba bean husk waste as a sustainable cationizing agent for salt-free reactive dyeing of cotton. Optimized conditions (7.5% HCl, 24-hour treatment, and 1 : 20 material-to-liquor ratio) achieved a 90% dye exhaustion rate and a fixation rate of 51.74%, with superior color strength (*K/S* value: 1.5291). The cationized fabric exhibited excellent colorfastness and mechanical properties, comparable to conventionally dyed cotton. This approach not only reduces environmental hazards but also offers economic benefits by minimizing water and chemical usage. Future research will explore non-aqueous media dyeing and advanced characterization techniques to further improve dye fixation and uniformity. This work contributes to the development of sustainable textile processing methods, aligning with global efforts to reduce the environmental impact of the textile industry.

Authors' contribution

All the authors of this study made contributions to different parts of the endeavor, such as data entry, information gathering, and documentation. Each author has approved the final draft of the manuscript for publication.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from all authors upon reasonable request.

Acknowledgment

The authors would like to express their gratitude to the Ethiopian Institute of Textile and Fashion Technology (EiTEX) and Wolkite University for their support and resources that contributed to the success of this research.

Ethical declarations

Ethics approval and consent to participate: This study did not include human participants, human data, human tissue, or animal subjects. Therefore, no additional consent for publication is necessary beyond the approval of each author.

Consent for publications

All authors have consented to this study's publication, including the main manuscript and supporting information.

Conflicts of interest

The authors declare that they have no known financial conflicts of interest or personal relationships that could have influenced the work presented in this paper.

References

[1] Ali, N. F.; El-Thalouth, J. I. A.; Hebeish, A. A. Green strategy for development of antimicrobial printed textile fabrics. *Res. J. Text. Apparel* **2012,** *16*(1), 77-85.

[2] Correia, J.; Rainert, K. T.; Oliveira, F. R.; De Cássia Siqueira Curto Valle, R.; Valle, J. A. Cationization of cotton fiber: An integrated view of cationic agents, processes variables, properties, market and future prospects. *Cellulose* **2020,** *27*, 8527-8550.

[3] De Vries, T. S.; Davies, D. R.; Miller, M. C.; Cynecki, W. A. Kinetics of the cationization of cotton. *Ind. Eng. Chem. Res.* **2014,** *53*(23), 9686-9694.

[4] Zhang, T.; Zhang, S.; Qian, W.; He, J. X. Reactive dyeing of cationized cotton fabric: The effect of cationization level. *ACS Sustainable Chem. Eng.* **2021,** *9*(36), 12355-12364.

[5] Bhuiyan, M. A. R.; Rahman, M. M.; Shaid, A.; Bashar, M. M.; Khan, M. A. Scope of reusing and recycling the textile wastewater after treatment with gamma radiation. *J. Cleaner Prod.* **2016,** *112*, 3063-3071.

[6] Arivithamani, N.; Dev, V. R. G. Sustainable bulk scale cationization of cotton hosiery fabrics for salt-free reactive dyeing process. *J. Cleaner Prod.* **2017,** *149*, 1188-1199.

[7] Tegegne, W.; Tesfaye, T.; Zeleke, Y.; Ketema, G. One-bath one-dye class dyeing of polyester/cotton blend fabric with disperse dye after esterification of cotton fabric. *Discov. Mater.* **2022,** *2*, 14.

[8] Singha, K.; Maity, S.; Singha, M.; Paul, P.; Gon D. P. Effects of fiber diameter distribution of nonwoven fabrics on its properties. *Int. J. Text. Sci.* **2012,** *1*(1), 7-14.

[9] Pei, L.; Sun, S.; Yi, J.; Shen J. F.; An Y. Y.; Sun, G.; Wang, J. P. Environmental modification of cellulose fibers for reducing dye diffusion rate by anionic polyacrylamide. *Polymer* **2024,** *315*, 127814.

[10] Pruś, S.; Kulpiński, P.; Matyjas-Zgondek, E.; Wojciechowski, K. Eco-friendly dyeing of cationised cotton with reactive dyes: Mechanism of bonding reactive dyes with CHPTAC cationised cellulose. *Cellulose* **2022,** *29*(7), 4167-4182.

[11] Tegegne, W.; Haile, A. Effect of papain enzyme surface modification on hydrophilic and comfort properties of polyester/cotton blend fabric. *Discov. Mater.* **2024,** *4*(1), 2.

[12] Zeleke, Y.; Feleke, T.; Molla, W. T.; Atinaf, Y. Design and development of false ceiling board composite material using pineapple leaf fibre reinforcement in unsaturated polyester matrix. *Int. J. Sustain. Eng.* **2022,** *15*(1), 144-152.

[13] Chattopadhyay, D. P.; Chavan, R. B.; Sharma, J. K. Salt-free reactive dyeing of cotton. *Int. J. Cloth. Sci. Technol.* **2007,** *19*(2), 99-108.

[14] Tegegne, W.; Haile, A.; Feleke, T. One-bath one-step dyeing of polyester/cotton blend fabrics through lipase enzyme surface modification. *J. Nat. Fibers* **2024,** *21*(1), 2399661.

[15] Tegegne, W.; Haile, A. Improving hydrophilicity and comfort characteristics of polyester/cotton blend fabric through lipase enzyme treatment. *Clean Technol. Environ. Policy* **2025,** *27*(1), 3-16.

[16] Khan, M. M. R.; Islam, M. M.; Khalil, E. Investigation on effluent characteristics of organic cotton fabric dyeing

with eco-friendly remazol reactive dyes. *Am. J. Eng. Res.* **2014,** *3*(12), 62-68.

[17] Nallathambi, A.; Rengaswami, G. D. V. Industrial scale salt-free reactive dyeing of cationized cotton fabric with different reactive dye chemistry. *Carbohydr. Polym.* **2017,** *174*, 137-145.

[18] Asaduzzaman, M. M.; Hossain, F.; Li, X.; Miah, M. R.; Onto, Z.; Quan, H. A study on the effects of pre-treatment in dyeing properties of cotton fabric and impact on the environment. *J. Text. Sci. Eng.* **2016,** *6*(5), 1000274.

[19] Fang, L.; Zhang, X. D.; Ma, J. H.; Sun, D. S.; Zhang B. T.; Luan J. Eco-friendly cationic modification of cotton fabrics for improving utilization of reactive dyes. *RSC Adv.* **2015,** *5*(57), 45654-45661.

[20] Mao, X. D.; Zhong, Y.; Xu, H.; Zhang, L. P.; Sui, X. F.; Mao, Z. P. A novel low add-on technology of dyeing cotton fabric with reactive dyestuff. *Text. Res. J.* **2018,** *88*(12), 1345-1355.