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INDIRECT ELECTROCHEMICAL DYEING OF INDIGO DYE USING IRON–TRIETHANOLAMINE COMPLEX ON STAINLESS STEEL ELECTRODE

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ABSTRACT

Indigo is one of the most significant vat dyes used in cotton fiber dyeing; however, its traditional reduction to the water-soluble leuco form relies heavily on reducing agents—primarily sodium dithionite—which pose severe environmental challenges due to the generation of toxic sulfurous by-products. This study evaluates the feasibility of indirect electrochemical reduction as an eco-friendly alternative for indigo dyeing using an iron–triethanolamine (Fe–TEA) complex as a redox mediator and a stainless steel (SS) electrode as the cathode. The electrochemical reduction was conducted in an alkaline medium, and the resulting leuco-indigo solution was applied to 100% woven bleached cotton fabrics via the dip-oxidation method. Key process variables were systematically investigated, including dye concentration (0.5%, 1%, and 2% owf), sodium hydroxide concentration in the dye bath (11, 13, 15, and 17 g/L), and dye bath recyclability over five consecutive dyeing cycles. For comparison, traditional indigo reduction was performed using sodium dithionite ($Na_2S_2O_4$) in an alkaline sodium hydroxide medium, followed by dip-oxidation dyeing under identical dye concentrations. Dyeing performance was rigorously evaluated through spectrophotometric reflectance measurements, color yield (K/S) determination, CIELAB color coordinates, and colorfastness tests to washing, light, and dry/wet rubbing. The results demonstrated that increasing the indigo concentration in both methods led to a significant increase in K/S values and a corresponding decrease in lightness (L*), indicating deeper color shades. The electrochemical method achieved superior color yield and shade depth compared to the traditional method at high dye concentrations, whereas both methods showed comparable performance at low concentrations. Regarding colorfastness, the electrochemical approach exhibited better fastness to light, washing, and rubbing at lower dye concentrations than the traditional method, while the traditional method displayed slightly higher fastness ratings at high dye concentrations. Increasing the NaOH concentration in the electrochemical dye bath enhanced color yield while maintaining excellent wash and light fastness, with only a minor decrease in rubbing fastness. Recyclability trials confirmed that the electrochemical dye bath could be reused for five consecutive cycles without compromising dyeing efficiency. Overall, indirect electrochemical reduction using the Fe–TEA complex and SS cathode presents a highly promising, sustainable alternative to conventional indigo dyeing, offering significant environmental benefits, bath recyclability, and robust colorimetric and fastness properties.

KEYWORDS: Indigo dye; Indirect electrochemical reduction; Iron–triethanolamine (Fe–TEA) complex; Stainless steel (SS) cathode; Sodium dithionite; Color yield (K/S); Dye bath recycling.

INTRODUCTION

Indigo dye is one of the most widely used colorants for dyeing cellulosic fibers, holding a substantial market share in textile dyes due to its exceptional fastness properties against light, laundering, and chlorine bleaching, which have made it the primary dye utilized in denim fabric manufacturing.[1] However, the water insolubility of indigo poses a technical challenge in dyeing processes, as its application necessitates initial reduction to its water-soluble reduced form, known as leuco-indigo. This leuco form possesses high affinity and permeability toward cellulosic fibers; following the

dyeing process, it is re-oxidized by atmospheric oxygen back to its original insoluble state, thereby fixing the color onto the fibers.[2] The reduction of indigo to leuco-indigo represents the key and most crucial step in the dyeing process, where sodium dithionite ($Na_2 S_2 O_4$), commercially known as hydrosulfite, is extensively employed as a reducing agent due to its low cost, ease of use, and commercial availability. Despite these advantages, its application leads to significant environmental issues, generating various sulfurous by-products during the reduction process—such as toxic sulfates and sulfides—which contribute to water and air pollution and exacerbate the environmental burden associated with the dyeing industry.[3,4]

In line with the drive toward developing more sustainable and eco-friendly technologies, numerous alternatives to sodium dithionite have been proposed, including α-hydroxyketones, hydroxyalkyl sulfonate salts, certain carbohydrates, and other reducing agents.[3,5–8] Nevertheless, most of these alternatives suffer from limited reducing power or high cost, thereby restricting their large-scale industrial applicability. Consequently, there is a pressing need to develop practical and efficient methods for indigo reduction that can decrease the consumption of conventional reducing agents and satisfy environmental safety requirements without compromising dyeing quality.[9] Electrochemical reduction has thus emerged as a promising alternative to traditional methods reliant on large quantities of chemical reducing agents.[10,11] The primary advantage of this technology lies in supplying the electrons necessary for reduction directly via an electric current, generating hydrogen gas as a side product, which substantially mitigates the pollutants associated with conventional chemicals.[12]

In recent years, electrochemical indigo reduction techniques have attracted increasing research attention, giving rise to two fundamental approaches: direct electrochemical reduction and indirect electrochemical reduction. In the direct method, electrons are transferred directly from the electrode surface to the dye molecules; however, the efficiency of this process remains constrained by mass transfer limitations between the electrode surface and the dye particles in solution, hindering its industrial scalability.[13] Conversely, in the indirect method, a redox mediator is utilized to shuttle electrons between the electrode and the dye, wherein the mediator is first reduced at the electrode surface and subsequently transfers electrons to the indigo molecules. This approach enhances reduction efficiency and alleviates mass transfer constraints, making it one of the most promising techniques for sustainable industrial dyeing applications.[14]

Numerous studies have investigated various redox mediators for indirect electrochemical indigo reduction, most notably anthraquinone derivatives, alizarin,[15] and naphthoquinone compounds such as lawsone,[16] all of which demonstrated good reduction efficiency under highly alkaline conditions and at high negative reduction potentials. Meanwhile, iron complexes as electrochemical mediators have exhibited remarkable performance in indigo reduction. Among these, indigo reduction was successfully achieved on a carbon fiber electrode using an iron–triethanolamine complex (Fe–TEA),[17] while iron–gluconate complexes demonstrated higher efficiency compared to binary complexes containing iron and calcium,[18] Furthermore, another study incorporated calcium gluconate into the iron–triethanolamine system, obtaining a more complex mediator architecture for indigo reduction under ultrasonic irradiation, which accelerated the reduction process,[19] Despite the growing body of literature examining iron complexes as mediators in electrochemical indigo reduction, there remains a distinct need to evaluate the performance of the Fe–TEA mediator on a stainless steel (SS) electrode, investigate the influence of various operating parameters on dyeing quality, and assess the bath reusability for sustainable application.

2. Experimental

2.1. Equipment and Instrumentation

The equipment and analytical instrumentation utilized in this study are detailed below:

Equipment / Instrument	Manufacturer / Specifications	Operational Range / Details
Analytical Balance	Sartorius	Precision: ±0.0001 g
Thermometer	—	Reaction temperature monitoring
Hotplate Magnetic Stirrer	AREC	Controlled magnetic stirring and heating
Digital Multimeter (Avometer)	DT9205	Current range: 200 µA – 20 A
DC Power Supply	PROMAX	Voltage range: 0–12 V; Current range: 0–3 A
Glass Beakers	—	Capacity: 100 mL
Syringe Filters	—	Nylon, Diameter: 25 mm, Pore size: 0.45 µm
Electrodes	—	Stainless steel (SS) meshes/plates
Volumetric Flasks & Beakers	—	Assorted laboratory glassware
Crockmeter	SDI International	Dry and wet rubbing colorfastness testing
Light Colorfastness Tester	SDI International	Equipped with Mercury Blended Tungsten Fluorescent (MBTF) lamp source
Washing Fastness Tester (Rotawash)	SDI International	Washing colorfastness testing
Benchtop Spectrophotometer	GretagMacbeth (Color i5DV)	D65 illuminant, 10° standard observer angle (Color strength K/S evaluation)

2.2. Reagents and Chemicals

The chemical reagents and materials used in the experimental procedures are listed in Table 2.

Chemical Name / Formula	Manufacturer / Supplier	Purity / Grade	CAS / Role
Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)	TITAN BIOTECH LTD	99%	Precursor for Fe–TEA complex
Triethanolamine (TEA)	TITAN BIOTECH LTD	85%	Ligand / Complexing agent
Sodium hydroxide (NaOH)	SIGMA-ALDRICH	98.0–100.5%	Alkaline medium / pH control
Sodium sulfate (Na_2SO_4)	SIGMA-ALDRICH	99%	Supporting electrolyte
Indigo dye powder	SIGMA-ALDRICH	95%	Vat dye

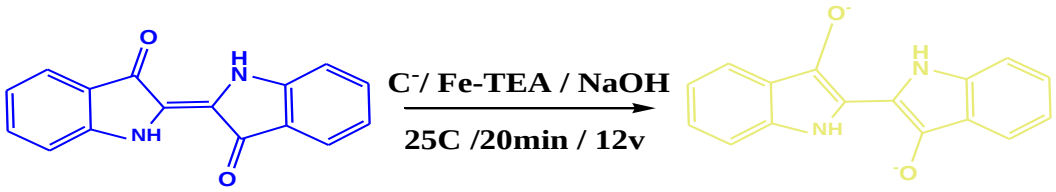
2.3. Preparation of Iron–Triethanolamine Complex (Fe–TEA)

The iron–triethanolamine complex (Fe–TEA, designated as 1 L) was synthesized at a molar ratio of Fe:TEA = 1:11 in an alkaline medium containing 13.4 g L^{-1} sodium hydroxide (NaOH). Initially, the required amount of sodium hydroxide was dissolved in 100 mL of distilled water, followed by the addition of 56.6 mL of triethanolamine (TEA) under continuous stirring until a homogeneous solution was obtained. In a separate vessel, 9.26 g of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was dissolved in an appropriate volume of distilled water. This solution was then added gradually to the NaOH–TEA mixture under continuous stirring, which was maintained for 20 min to ensure complete complexation and to prevent the precipitation of iron hydroxides. Subsequently, the resulting solution was transferred to a 1 L volumetric flask and diluted to the mark with distilled water. The stock solution was stirred for an additional 90 min to yield a stable, homogeneous complex, ready for use as a soluble electron mediator in the indirect electrochemical reduction of indigo dye.[20] The complex was used immediately after preparation in its ferrous oxidation state (Fe^{2+}) to initiate the electrochemical reduction cycle directly.

2.4. Electrochemical Cell Configuration and Design

Indirect electrochemical reduction of indigo was carried out in a two-compartment divided electrochemical cell comprising separate catholyte and anolyte chambers, each with a working capacity of 100 mL. The two chambers were interconnected via a salt bridge consisting of a flexible polymer tube filled with an aqueous solution of sodium hydroxide and Glauber's salt ($Na_2SO_4 \cdot 10H_2O$), ensuring ionic conductivity and maintaining electroneutrality between the half-cells. The cathode consisted of three stainless steel (SS) electrodes (rod geometry, 9 mm diameter, immersed length of 2 cm per electrode), while a single SS electrode of identical dimensions served as the anode. Continuous magnetic stirring was provided in both compartments to ensure homogeneous mixing and enhance mass transfer during the reaction.

The catholyte contained the prepared Fe–TEA complex solution along with the specified concentration of indigo dye, whereas the anolyte consisted solely of the Fe–TEA complex solution without dye addition. A constant direct current (DC) was supplied using a regulated laboratory DC power supply, with the current intensity monitored throughout the experiment using a digital multimeter. The progress of the reduction process was evaluated visually by monitoring the color change of the solution from insoluble blue indigo to soluble yellow leuco-indigo. Upon completion of the electrochemical reduction, the resulting leuco-indigo solution was utilized for cotton fabric dyeing via a conventional dip–oxidation (foulard) process. The dyed fabrics were subsequently evaluated for color strength (K/S) and color fastness properties.



Indigo **Leuco-Indigo**

2.5. Dyeing Experiments

All dyeing operations were performed under ambient atmosphere (in the presence of atmospheric oxygen) without employing an inert gas blanket or sparging with inert gases such as nitrogen or argon, thereby simulating practical industrial conditions. To eliminate the effect of auto-oxidative degradation and maintain indigo dye in its stable, solubilized reduced form (leuco-indigo), direct current (DC) supply to the electrochemical cell was continuously maintained throughout the dyeing process, ensuring continuous electrochemical regeneration of the mediator within the dyebath.

2.5.1. Dyeing Using Different Indigo Dye Concentrations

Dyeing experiments were conducted using clean, bleached, pre-treated 100% cotton fabric samples weighing 1 g each, at a liquor ratio (LR) of 1:40 (40 mL of dye liquor per sample). To evaluate the influence of indigo dye concentration on dyeing performance, three distinct dye concentrations were investigated: 0.5%, 1%, and 2% on weight of fabric (o.w.f.), corresponding to dye masses of 0.005 g, 0.01 g, and 0.02 g of indigo, respectively. Electrochemical reduction was carried out at a constant potential of 12 V for 20 min, with current intensity fluctuating between 13 and 18 mA during the reduction phase. Upon complete electrochemical reduction and conversion of indigo to its soluble reduced form (leuco-indigo), dyeing was performed via successive dip-oxidation cycles at room temperature (20–25 °C). The procedure comprised five consecutive dipping cycles (3 min each) alternated with five air-oxidation cycles (2 min each). Following the final oxidation cycle, samples were exposed to ambient air for 20 min to ensure full dye oxidation and fixation onto the fibers. The dyed samples were subsequently rinsed with cold distilled water, washed with a 10% (v/v) acetic acid solution, and thoroughly rinsed again with cold distilled water.

2.5.2. Dyeing Using Different Sodium Hydroxide Concentrations

A series of experiments was conducted across four sodium hydroxide (NaOH) concentrations in the dyebath: 11, 13, 15, and 17 g/L. In all runs, 40 mL of catholyte solution containing the iron–triethanolamine complex [Fe–TEA] was utilized, supplemented with 0.005 g of indigo dye, maintaining a constant liquor ratio of 1:40. Electrochemical reduction was performed at a constant voltage of 12 V for 20 min until complete transformation of indigo into water-soluble leuco-indigo. Subsequently, a clean, bleached, pre-treated 100% cotton sample (1 g) was immersed in the dyebath. Dyeing proceeded via sequential dip-oxidation cycles consisting of five dipping steps (3 min each) interspersed with five air-oxidation steps (2 min each) at controlled ambient temperature (20–25 °C). Current intensity remained within 13–18 mA during reduction. Post-dyeing, samples were allowed to air-oxidize for 20 min to guarantee complete dye fixation and oxidation, followed by rinsing with cold distilled water, washing with 10% acetic acid, and a final rinse in cold distilled water prior to colorimetric and fastness testing.

2.5.3. Dyebath Recycling Experiment

Dyebath recycling experiments were conducted to assess the reusability of the [Fe–TEA] reducing complex and to evaluate the operational stability and efficiency of the dyeing system over consecutive operational cycles. In the initial cycle, 40 mL of catholyte solution containing the iron–triethanolamine complex was charged with 0.005 g of indigo at a liquor ratio of 1:40. Electrochemical reduction was executed at a constant potential of 12 V for 20 min to achieve full conversion to soluble leuco-indigo. A clean, bleached, pre-treated 100% cotton fabric sample (1 g) was dyed using five sequential dip-oxidation cycles (3 min dipping / 2 min air oxidation) at 20–25 °C. After dyeing, the sample was air-exposed for 20 min, rinsed with cold distilled water, washed with 10% acetic acid, and rinsed again with distilled water. To effect dyebath recycling, residual leuco-indigo in the exhausted bath was oxidized back to insoluble indigo, which was subsequently isolated by filtration through a 0.45 µm syringe filter to yield a clear filtrate containing the recycled mediator solution. A fresh charge of indigo dye (0.005 g) was added to the filtrate, and dyebath volume loss was replenished with distilled water to maintain a constant liquor ratio. Electrochemical reduction and dyeing were then repeated under identical conditions. This recycling sequence was iterated for five consecutive cycles. Dyeing quality for each cycle was systematically evaluated via color strength metrics and fastness tests to determine mediator stability and reusability in continuous dyeing operations.

2.6. Colorimetric Measurement and Fastness Testing

Dyeing quality was characterized by determining CIELAB chromaticity coordinates using a spectrophotometer under standard illuminant D65 and 10° standard observer angle. The following color parameters were employed for characterization:

- **L* (Lightness):** Denotes the lightness dimension, ranging from 0 (pure black) to 100 (pure white).
- **a* (Red–Green Axis):** Represents the red/green chromaticity coordinate, where positive values indicate reddish tones and negative values indicate greenish tones.
- **b* (Yellow–Blue Axis):** Represents the yellow/blue chromaticity coordinate, where positive values indicate yellowish tones and negative values indicate bluish tones.
- **C* (Chroma):** Defines color saturation or purity; higher values reflect greater color vividness and intensity.
- **h° (Hue Angle):** Expresses the dominant hue attribute within the color space.
- **ΔE (Total Color Difference):** Quantifies the overall chromatic distance between samples to assess visual perceptibility of color variation.
- **K/S (Kubelka–Munk Value):** Evaluates color strength and dye fixation efficiency on the fiber, calculated according to the Kubelka–Munk equation, where higher values correspond to greater color depth.[21]

Colorfastness properties—including fastness to washing, light, and dry/wet rubbing (crocking)—were rigorously evaluated. Washing fastness was tested according to ISO 105-C06 (S1B test condition). The commercial detergent formulation comprised linear alkylbenzene sulfonate (15%), sodium percarbonate (0.8%), sodium chloride (1%), sodium carbonate, and sodium sulfate (10%),

alongside emulsifiers, optical brighteners, and auxiliary agents. Lightfastness and dry/wet rubbing fastness were assessed in compliance with standard test methods, and comparative performance was systematically analyzed across all experimental conditions.

3. RESULTS AND DISCUSSION

3.1. Effect of Indigo Dye Concentration in Indirect Electrochemical Dyeing

The indirect electrochemical reduction of indigo relies on using the iron–triethanolamine complex (Fe–TEA) as a mediator (electron carrier) between the electrode surface and dye molecules. Upon reduction on the cathode surface, the complex acquires electrons that are subsequently transferred to indigo molecules, converting them into the soluble reduced form (leuco-indigo). After diffusing into and binding with the cotton fibers, this form is re-oxidized upon exposure to air, reverting to its insoluble state trapped within the fibrous matrix. This mechanism enhances electron transfer efficiency compared to direct reduction, increasing overall reduction efficiency and offering superior process control during dyeing, as illustrated in Figure 1.

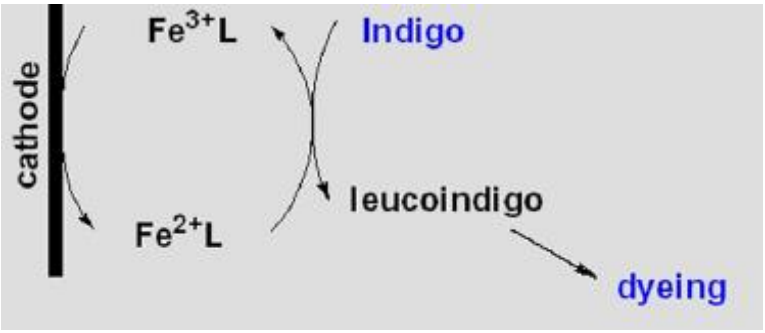


Figure 1: Mechanism of action of the Fe–TEA complex as a reduction mediator in indirect electrochemical indigo dyeing.

To evaluate the effect of dye concentration on the quality of the resulting dyeing, spectrophotometric measurements were conducted across the investigated concentration range, taking 0.5% as the minimum concentration and 2% as the maximum concentration (based on weight of fabric, % owf). Spectral reflectance measurements revealed that increasing the dye concentration from 0.5% to 2% led to pronounced changes in the colorimetric properties of the dyed fabrics. A significant increase in the color strength (K/S) value was observed, indicating higher color intensity and dyeing efficiency, which is attributed to the increased amount of dye deposited and fixed onto the cotton fibers. This was accompanied by a clear decrease in lightness (L*), demonstrating increased darkness and color depth at higher concentrations. Furthermore, the color coordinates (a*) and (b*) indicated a gradual evolution in color quality; the shade shifted from pure blue at lower concentration to a reddish-blue or violet hue at higher concentration. The total color difference value (ΔE = 27.95) supports this observation, confirming a substantial color variation easily perceptible to the naked eye between the studied samples shown in Figure 2.

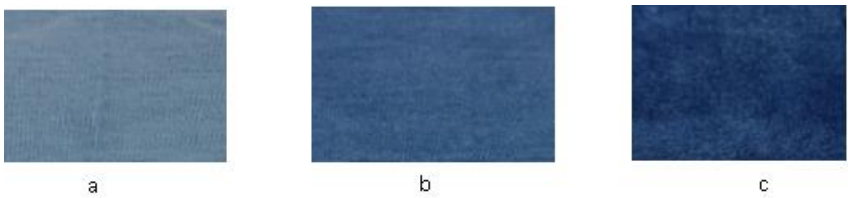


Figure 2: Effect of indigo dye concentration on indirect electrochemical dyeing using a stainless steel (SS) cathode in the presence of Fe–TEA complex (a: 0.5% owf, b: 1% owf, c: 2% owf).

Regarding color fastness properties, all samples exhibited excellent washing fastness, demonstrating robust binding between the dye molecules and cotton fibers following oxidation, which minimizes dye migration or desorption during washing. Light fastness showed low ratings across all concentrations, remaining constant as concentration increased from low to high levels. Conversely, rubbing fastness (both dry and wet) decreased at higher concentrations compared to lower concentrations. This decline is attributed to increased accumulation of dye on the fiber surface, forming superficial dye layers or aggregates that are not fully integrated into the internal fiber matrix, making them more susceptible to mechanical removal during friction. Therefore, it is recommended to introduce a soapy washing step prior to the acid washing stage to eliminate deposited unfixed surface dye, thereby maintaining high rubbing fastness at elevated concentrations. These results highlight a trade-off between achieving high color strength and preserving mechanical fastness properties,

making the selection of an optimal dye concentration a critical factor for achieving optimal dyeing performance. Table 1 summarizes all measured colorimetric parameters and fastness ratings at 0.5% and 2% indigo dye concentrations.

Table 1: Effect of indigo dye concentration on colorimetric properties and fastness ratings of indirectly electrochemically dyed cotton fabrics.

Sample Conc.	L*	a*	b*	C*	h*	K/S	ΔE	Rubbing (Dry)	Rubbing (Wet)	Light Fastness	Wash (Color Change)	Wash (Staining)
0.5%	64.23	-1.43	-22.38	22.42	266.35	1.49	-	5	5	2	5	4/5
2.0%	36.38	0.86	-23.03	23.05	272.13	7.36	27.95	3	2/3	2	5	4/5

3.2. Effect of Sodium Hydroxide (NaOH) Concentration in Indirect Electrochemical Dyeing

The influence of hydroxide concentration was investigated by taking measurements for samples at the highest hydroxide concentration (17 g/L) and the lowest concentration (11 g/L) within the investigated working range, as shown in the results presented in Table 2. Increasing the sodium hydroxide concentration in the dyebath resulted in a marked increase in color strength (K/S), indicating enhanced color intensity and dyeing efficiency under higher alkaline conditions. This trend was corroborated by lightness (L*) values, which decreased with increasing alkali concentration, demonstrating that shades became deeper and darker compared to samples dyed at lower alkali concentrations (Figure 3).



Figure 3: Effect of sodium hydroxide (NaOH) concentration on indirect electrochemical indigo dyeing using a stainless steel (SS) cathode in the presence of Fe–TEA complex (d: 11 g/L, e: 13 g/L, f: 15 g/L, g: 17 g/L NaOH).

Regarding chromatic coordinates, the (b*) values remained relatively stable across different samples, preserving the characteristic blue hue of indigo dye. In contrast, (a*) values exhibited an increased negative shift with rising NaOH concentration, indicating a slight color shift toward the greenish region of the color space. The chroma value (C*) showed a minor decrease at elevated alkali concentrations, while the total color difference (ΔE = 3.24) revealed a clear color variation easily distinguishable by the human eye, confirming the direct impact of NaOH concentration on the final visual appearance of the dyed fabrics. Concerning fastness properties, the samples demonstrated excellent washing fastness, good light fastness, and excellent-to-very good dry and wet rubbing fastness. All fastness ratings remained virtually identical across the evaluated alkali range, indicating that variations in bath alkalinity within this range do not noticeably affect the resistance of the dye to mechanical rubbing, washing, or light exposure.

Table 2: Effect of sodium hydroxide (NaOH) concentration on colorimetric properties and fastness ratings of indirectly electrochemically dyed cotton fabrics.

NaOH Conc.	L*	a*	b*	C*	h*	K/S	ΔE	Rubbing (Dry)	Rubbing (Wet)	Light Fastness	Wash (Color Change)	Wash (Staining)
11 g/L	61.24	-1.91	-22.33	22.41	265.11	1.73	-	5	5	3	5	4/5
17 g/L	58.12	-2.75	-22.01	22.18	262.88	2.41	3.24	4/5	4	3	5	4/5

3.3. Reusability and Recyclability of the Dyebath

Table 3 compares the results between the first recycling cycle (initial baseline) and the fifth cycle (final step). Reusing the dyebath across five consecutive cycles did not result in a decline in dyeing efficiency; on the contrary, a progressive increase in color strength was observed, reflected in higher K/S values and lower lightness (L*) values from Cycle 1 to Cycle 5. The total color difference (ΔE = 13.54) supports this finding, indicating distinct color changes visually discernible between samples from successive cycles, as illustrated in Figure 4.



Figure 4: Effect of dyebath recycling on the visual appearance of indigo-dyed cotton fabrics via indirect electrochemical dyeing using a stainless steel (SS) cathode in the presence of Fe–TEA complex (Numbers 1 to 5. represent dyeing cycles 1 through 5, respectively).

This behavior can be explained by residual amounts of indigo remaining in the dyebath following successive oxidation and filtration steps, leading to a gradual accumulation of dye within the medium and subsequent increase in dye uptake on cotton fibers in subsequent cycles. Consequently, shade depth and intensity increased with continued bath reuse. Regarding fastness properties, washing fastness and dry/wet rubbing fastness values remained consistently high across all cycles, proving that the samples retained their resistance to mechanical friction and washing despite repeated bath reuse. Interestingly, light fastness showed a progressive enhancement, increasing from rating 2 in Cycle 1 to rating 4 in Cycle 5. This improvement in light fastness is directly linked to the residual dye accumulation in the bath, which slightly elevated dye concentration in the fiber interior over successive cycles, providing higher resistance to photodegradation upon prolonged light exposure. These findings demonstrate that the indirect electrochemical reduction system using Fe–TEA complex possesses excellent recyclability, maintaining high dyeing efficiency across five consecutive cycles with robust washing and rubbing fastness, while light fastness markedly improved.

Table 3: Effect of dyebath recycling on colorimetric properties and fastness ratings of indirectly electrochemically dyed cotton fabrics.

Cycle No.	L*	a*	b*	C*	h*	K/S	ΔE	Rubbing (Dry)	Rubbing (Wet)	Light Fastness	Wash (Color Change)	Wash (Staining)
Cycle 1	64.99	-2.10	-21.32	21.42	264.37	1.38	-	5	5	2	5	4/5
Cycle 5	52.00	-1.40	-25.10	25.14	266.82	3.23	13.54	5	4/5	4	5	4/5

3.4. Comparison with Literature

Comparing the present findings with published literature reveals that sodium dithionite remains an effective reducing agent for indigo, with studies reporting good color strength and fastness properties on cotton fabrics. For instance, a previous study reported K/S values up to 7.41 using sodium dithionite.[22] In comparison, the present study demonstrates that indirect electrochemical reduction via Fe–TEA can yield high color strength, with K/S values rising from 1.49 at 0.5% indigo to 7.36 at 2% indigo concentration. However, these figures should not be interpreted as a direct head-to-head performance comparison due to variations in reduction and dyeing conditions across studies. The key advantage of the proposed system lies in replacing chemical reducing agents with an eco-friendly electrochemical electron source combined with excellent dyebath reusability.

4. CONCLUSIONS

- The results demonstrate the feasibility of indirect electrochemical reduction of indigo dye using iron–triethanolamine complex (Fe–TEA) and a stainless steel (SS) cathode as a promising alternative to conventional sulfur-based reducing agents.
- Increasing indigo dye concentration from 0.5% to 2% owf led to a significant increase in color strength (K/S) and a reduction in lightness (L*), yielding darker and deeper shades. Washing and light fastness remained consistent across concentrations, whereas rubbing fastness decreased due to surface dye accumulation.
- Higher sodium hydroxide concentration enhanced color strength while maintaining excellent washing, rubbing, and light fastness properties.
- Dyebath recycling experiments confirmed excellent reusability over five consecutive cycles without efficiency loss. A progressive increase in color strength and light fastness was observed due to residual dye accumulation, while washing and rubbing fastness remained high.
- Indirect electrochemical reduction represents a sustainable, environmentally friendly, and commercially viable technology that eliminates hazardous chemical reductants while enabling multi-cycle dyebath reuse.

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