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INDIRECT ELECTROCHEMICAL DYEING OF COTTON FABRICS WITH INDIGO VS. TRADITIONAL REDUCTION: A COMPARATIVE STUDY

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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 cellulosic fiber dyeing, holding a significant market share in textile coloration owing to its superior fastness properties against light, laundering, and chlorine bleaching—making it the primary dyestuff employed in denim fabric manufacturing.[1] However, the water insolubility of indigo poses a substantial technical challenge in dyeing processes, as its application necessitates preliminary reduction into its water-soluble form, known as leuco-indigo. This reduced species exhibits high affinity for diffusion into and binding with cellulosic matrix fibers, followed by post-dyeing re-oxidation via atmospheric oxygen to restore its original

insoluble parent structure, thereby trapping and fixing the color within the fiber network.[2] The reduction of indigo to leuco-indigo constitutes the key, rate-determining step in the dyeing cycle, where sodium dithionite ($Na_2S_2O_4$), commercially known as "hydrosulfite," is ubiquitously utilized as a reducing agent due to its cost-effectiveness, operational simplicity, and widespread commercial availability. Despite these merits, its application incurs severe environmental drawbacks; hazardous sulfurous by-products, such as toxic sulfates and sulfides, are generated during the reduction process, contributing significantly to water and air pollution while expanding the environmental burden of the textile processing industry.[3,4]

Within the paradigm of developing sustainable and eco-friendly technologies, numerous alternatives to sodium dithionite have been investigated, including α-hydroxyketone compounds, hydroxyalkyl sulfonate salts, and various reducing sugars.[3,5–8] Nevertheless, most of these alternatives are constrained by insufficient reductive capacity or elevated operational costs, which restricts their industrial-scale implementation. Consequently, there remains a compelling demand for the development of practical, efficient indigo reduction methodologies capable of minimizing conventional reductant consumption and meeting stringent environmental standards without compromising color yield or quality.[9] Electrochemical reduction has thus emerged as a highly promising alternative to conventional procedures relying on heavy stoichiometric loads of chemical reductants.[10,11] The primary advantage of this technique lies in supplying the electrons required for indigo reduction directly via electric current, yielding hydrogen gas as a clean by-product, thereby mitigating chemical pollutant generation.[12]

Electrochemical indigo reduction technologies have gained increasing traction in recent years, evolving along two principal pathways: direct electrochemical reduction and indirect electrochemical reduction. In the direct method, electron transfer occurs straight from the electrode surface to the dye molecules; however, the efficiency of this route remains inherently constrained by mass transfer limitations between the electrode surface and the suspended dye particles in the bulk solution, impeding scalable industrial application.[13] Conversely, indirect electrochemical reduction incorporates a redox mediator to shuttle electrons between the electrode and the dye species. The mediator is first reduced at the electrode surface and subsequently transfers electrons to the indigo molecules in the bulk phase. This mechanism substantially enhances reduction kinetics and overcomes mass-transfer barriers, establishing indirect electrochemical reduction as one of the most viable strategies for sustainable industrial dyeing operations.[14]

Numerous studies have evaluated various redox mediators in indirect electrochemical indigo reduction, most notably anthraquinone derivatives, alizarin,[15] and naphthoquinone compounds such as lawsone,[16] all of which demonstrate satisfactory reduction efficiency under strongly alkaline conditions and at elevated reduction potentials. Meanwhile, iron complexes have demonstrated remarkable efficacy as electrochemical mediators for indigo reduction. Among these, indigo reduction was successfully accomplished on a carbon fiber electrode utilizing an iron–triethanolamine complex (Fe–TEA),[17] while iron–gluconate complexes exhibited superior performance compared to binary complexes containing iron and calcium,[18] Furthermore, another study incorporated calcium gluconate into the iron–triethanolamine system to synthesize a higher-coordination mediator architecture for indigo reduction coupled with ultrasonic irradiation, which significantly accelerated the reduction rate,[19] Despite extensive research on iron complexes as mediators for electrochemical indigo reduction, there remains a critical research gap in evaluating the performance of the Fe–TEA complex on a stainless steel (SS) electrode, as well as investigating the impact of key operational parameters on dyeing quality and dye bath reusability.

Experimental

1. Instrumentation and Equipment

- **Analytical Balance:** Sartorius high-precision analytical balance (precision ±0.0001 g).
- **Thermometer:** Precision thermometer for continuous monitoring of reaction temperature.
- **Hotplate Magnetic Stirrer:** AREC hotplate magnetic stirrer.
- **Digital Multimeter:** DT9205 digital multimeter (operating range: 200 µA – 20 A).
- **DC Power Supply:** PROMAX DC power supply (voltage range: 0–12 V, current range: 0–3 A).
- **Glassware:** 100 mL beakers, volumetric flasks, and assorted laboratory glassware.
- **Syringe Filters:** Nylon syringe filters (pore size: 0.45 µm, diameter: 25 mm) for ultrafine filtration.
- **Electrodes:** Stainless steel (SS) rod electrodes.
- **Crockmeter:** SDL Atlas (SDLinternational) rubbing fastness tester (dry and wet crocking).
- **Light Fastness Tester:** SDL Atlas (SDLinternational) color fastness to light apparatus, equipped with a mercury-blended tungsten fluorescent (MBTF) lamp.
- **Washing Fastness Tester:** SDL Atlas (SDLinternational) Rotawash color fastness to washing device.
- **Spectrophotometer:** GretagMacbeth Color i5DV benchtop spectrophotometer (D65 standard illuminant, 10° standard observer angle).

2. Chemicals and Reagents

Chemical Name / Reagent	Manufacturer / Supplier	Purity / Grade
Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)	Titan Biotech Ltd.	99%
Triethanolamine (TEA)	Titan Biotech Ltd.	85%
Sodium hydroxide (NaOH)	Sigma-Aldrich	98.0–100.5%
Sodium sulfate (Na_2SO_4)	Sigma-Aldrich	99%
Indigo dye powder	Sigma-Aldrich	95%
Sodium dithionite ($Na_2S_2O_4$)	Commercial grade	—

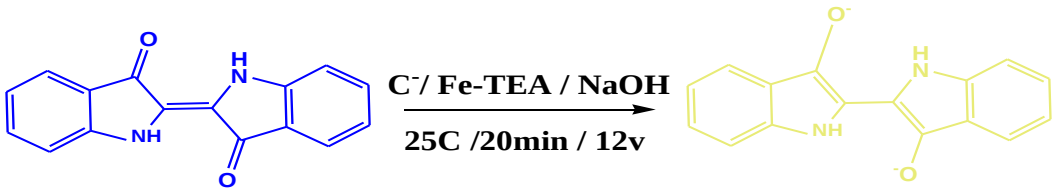
3. Preparation of Iron–Triethanolamine Complex (Fe–TEA)

The iron–triethanolamine complex (Fe–TEA, designated as L1) was synthesized at a molar ratio of Fe:TEA = 1:11 in an alkaline medium containing sodium hydroxide at a concentration of 13.4 g/L. Initially, the required amount of NaOH 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 beaker, 9.26 g of iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was dissolved in an appropriate volume of distilled water. This solution was then added dropwise to the alkaline NaOH–TEA mixture under vigorous and continuous stirring. Stirring was maintained for 20 min to ensure complete complexation and to prevent any potential precipitation of iron hydroxide. Subsequently, the resulting solution was transferred to a 1 L volumetric flask, diluted to the mark with distilled water, and stirred for an additional 90 min to yield a homogeneous, stable complex solution ready for subsequent use as a electron-mediating redox mediator in the indirect electrochemical reduction of indigo dye.[20] The complex was utilized immediately after preparation in its iron(II) oxidation state (Fe^{2+}) to directly initiate the electrochemical reduction cycle.

4. Electrochemical Cell Design and Dyeing Process

The indirect electrochemical reduction of indigo dye was carried out using a two-compartment divided electrochemical cell (catholyte and anolyte compartments, each with a volume capacity of 100 mL). The two compartments were interconnected via a salt bridge consisting of a plastic tube filled with a solution containing sodium hydroxide and Glauber's salt (sodium sulfate) to facilitate ionic transport and maintain electrical equilibrium between the cell halves. The cathode assembly comprised three stainless steel (SS) rod electrodes (diameter: 9 mm, immersed length: 2 cm per electrode), whereas a single stainless steel rod electrode of identical dimensions served as the anode. Continuous magnetic stirring was maintained in both compartments to ensure solution homogeneity and enhance mass transfer during the reaction.

The catholyte solution consisted of the prepared Fe–TEA complex solution supplemented with the requisite quantity of indigo dye, while the anolyte compartment contained only the Fe–TEA complex solution without dye addition. Direct current (DC) was supplied to the cell via a regulated laboratory power supply, and the current intensity was monitored throughout the experiment using a digital multimeter. The progress of the reduction reaction was observed visually by the color transition of the solution from blue to yellow, signifying the formation of the soluble reduced form (leuco-indigo). Upon completion of the electrochemical reduction, the resulting leuco-indigo bath was immediately utilized to dye cotton fabrics using a sequential dip-oxidation method, followed by color strength and color fastness evaluations to assess overall dyeing performance.



Indigo **Leuco-Indigo**

5. Electrochemical Dyeing Experiments

All electrochemical dyeing processes were carried out under ambient atmospheric conditions (in the presence of atmospheric oxygen) without using an inert atmosphere shield or sparging with inert gases such as nitrogen or argon, thereby simulating practical industrial application conditions. To eliminate the effect of spontaneous aerobic oxidation and maintain the indigo dye stable in its soluble reduced form (leuco-indigo), a continuous direct electrical current (DC) supply was maintained across the cell throughout the dyeing duration, ensuring continuous electrochemical regeneration of the mediator within the dyebath.

5.1. Dyeing at Various Indigo Dye Concentrations

Dyeing operations were performed using 100% cotton fabric samples that were scoured, bleached, and pre-treated, each weighing 1 g. The liquor ratio (LR) was maintained at 1:40, utilizing 40 mL of dyeing solution per sample. To evaluate the effect of indigo concentration on the dyeing properties, three different 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.

The electrochemical reduction step was conducted at a constant cell potential of 12 V for 20 min, with current intensity fluctuating between 13 mA and 18 mA during the reduction process. Following complete electrochemical reduction and conversion of indigo into its water-soluble reduced state (leuco-indigo), dyeing was executed via a sequential dip-oxidation process at room temperature (20–25 °C). The process comprised five consecutive dip cycles (3 min per immersion phase) alternated with five aerial oxidation phases (2 min per exposure). Upon completion of the final cycle, the dyed samples were exposed to ambient air for 20 min to ensure complete re-oxidation and fixation of the dye within the cellulosic fibers. Subsequently, the fabrics were thoroughly rinsed with cold distilled water, neutralized in a 10% (v/v) acetic acid solution, and finally rinsed again with cold distilled water.

5.2. Dyeing at Various Sodium Hydroxide Concentrations

A series of dyeing experiments was conducted using four different 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 carried out at a constant potential of 12 V for 20 min until complete conversion of indigo into its soluble reduced form (leuco-indigo) was achieved. Current intensity ranged between 13 mA and 18 mA during the reduction phase.

Thereafter, a pre-treated 100% cotton fabric sample (1 g) was immersed into the dyebath and subjected to the sequential dip-oxidation dyeing procedure (five dip cycles of 3 min each, alternated with five aerial oxidation phases of 2 min each) at ambient temperature (20–25 °C). After dyeing, the samples were allowed to air-oxidize for 20 min to guarantee full re-oxidation and dye entrapment within the fiber matrix. The samples were subsequently washed with cold distilled water, neutralized using a 10% acetic acid solution, and given a final rinse with cold distilled water prior to colorimetric measurements and fastness testing.

5.3. Dyebath Recycling Experiments

Dyebath recycling trials were performed to evaluate the reusability of the redox mediator system [Fe–TEA] and the maintenance of dyeing efficiency over successive operational cycles. In the first cycle, 40 mL of catholyte solution containing the iron–triethanolamine complex was charged with 0.005 g of indigo dye at a liquor ratio of 1:40. Electrochemical reduction was executed at a constant potential of 12 V for 20 min until complete reduction to leuco-indigo was accomplished. A 1 g scoured/bleached 100% cotton sample was dyed following the five-cycle dip-oxidation process (3 min dipping / 2 min aeration per cycle) at 20–25 °C, followed by a 20 min final aeration phase, cold water rinsing, 10% acetic acid neutralization, and final rinsing with distilled water.

To recycle the dyebath, the residual leuco-indigo remaining in the bath was fully air-oxidized back into its insoluble form and separated by filtration using a 0.45 µm syringe filter to yield a clear filtrate containing the recycled mediator solution. A fresh dose of 0.005 g of indigo dye was then added to the filtrate, and volume loss due to sampling/evaporation was compensated by adding an appropriate amount of distilled water to preserve the initial liquor ratio (1:40). Electrochemical reduction and dyeing were subsequently repeated under identical operational parameters as the first cycle. This recycling sequence was repeated for five consecutive cycles. The quality of the dyed samples in each cycle was evaluated by color strength measurements and fastness testing to determine the stability and reusability of the mediator system during repeated dyeing operations.

6. Conventional Dyeing Experiments

Conventional chemical dyeing experiments were conducted at three indigo dye concentrations: 0.5%, 1%, and 2% o.w.f., corresponding to dye masses of 0.005 g, 0.01 g, and 0.02 g, respectively. The liquor ratio was fixed at 1:20, yielding a total dyebath volume of 20 mL per concentration. To prepare the dyebath, 0.24 g of sodium hydroxide (NaOH) was dissolved in a limited volume of distilled water at 60–70 °C under continuous stirring, and diluted to 20 mL to ensure complete dissolution of the alkali. The corresponding amount of indigo dye for each concentration was then added under vigorous stirring. To reduce the vat dye into its soluble form, sodium dithionite ($Na_2S_2O_4$) was added as a chemical reducing agent in amounts ranging from 1 to 3 g, and the reaction was allowed to proceed for several minutes until reduction was complete. Completion of vatting was indicated by the appearance of the characteristic bronzy surface sheen ("indigo flower") and a clear, yellow leuco-indigo solution.

Dyeing trials were applied to 100% cotton samples (1 g each) at room temperature (20–25 °C) under atmospheric conditions using the sequential dip-oxidation mechanism. The procedure comprised five consecutive cycles (3 min dipping followed by 2 min aerial oxidation per cycle). Upon completion, the samples were removed and exposed to air for 20 min to ensure full oxidation and precipitation of the insoluble dye within the fiber core.

The process concluded with cold distilled water rinsing, neutralization with 10% acetic acid, and a final rinse with cold distilled water to eliminate any unfixed chemical residues.

7. Colorimetric Measurements and Fastness Testing

Dyeing quality was evaluated by measuring CIELAB colorimetric coordinates using a spectrophotometer under standard illuminant D65 and a 10° standard observer angle. The following color parameters were used to characterize the dyed fabrics:

- **L* (Lightness):** Ranging from 0 for ideal black to 100 for perfect white.
- **a* (Red–Green axis):** Positive values indicate a red shift, whereas negative values denote a green shift.
- **b* (Yellow–Blue axis):** Positive values represent a yellow shift and negative values represent a blue shift.
- **C* (Chroma):** Reflects color saturation or purity; higher values indicate higher color vibrancy and saturation.
- **h° (Hue angle):** Defines the dominant hue position within the color space.
- **ΔE (Total color difference):** Calculated to assess the perceptibility of visual color variations between samples.
- **K/S (Kubelka–Munk color strength):** Calculated as a measure of color strength and dye uptake efficiency on the fibers, where higher values correspond to deeper color depth.[21]

Color fastness properties to washing, light, and rubbing (dry and wet) were also evaluated. Color fastness to washing was determined according to ISO 105-C06 (Test condition S1B) using a commercial standard detergent formulation containing alkylbenzene sulfonate (15%), sodium percarbonate (0.8%), sodium chloride (1%), sodium carbonate, and sodium sulfate (10%), along with emulsifiers, optical brighteners, and auxiliary additives. Color fastness to light and dry/wet rubbing fastness were evaluated according to standard testing specifications, and the comparative performance among different experimental sets was analyzed.

RESULTS, DISCUSSION

1. Effect of Indigo Dye Concentration

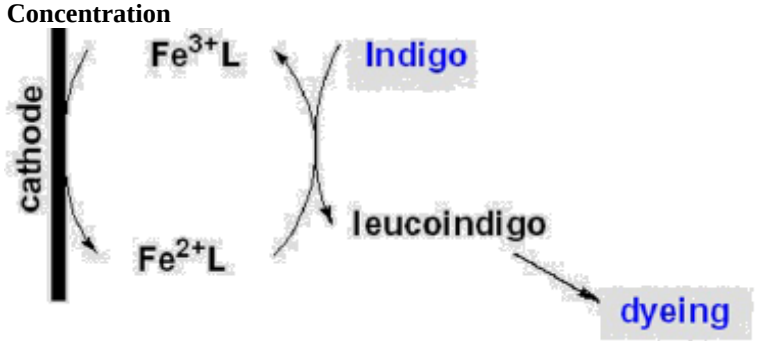


Figure 1: Schematic mechanism of the Fe–TEA complex as a mediator in indirect electrochemical indigo dyeing.

The indirect electrochemical reduction of indigo dye relies on using the iron–triethanolamine complex (Fe–TEA) as an electron mediator between the cathode surface and the dye molecules. Upon reduction at the cathode surface, the complex gains electrons that are subsequently transferred to indigo dye molecules, converting them into the water-soluble reduced form (leuco-indigo). After binding to cotton fibers, leuco-indigo re-oxidizes upon exposure to air, returning to its insoluble form within the fiber structure. This mechanism enhances electron transfer compared to direct reduction, thereby improving reduction efficiency and enabling better control over the dyeing process, as depicted in Figure 1.

To evaluate the effect of dye concentration on the quality of the resulting dyeing in both indirect electrochemical and conventional methods, spectrophotometric measurements were conducted at a minimum concentration of 0.5% and a maximum concentration of 2% within the studied concentration range. Reflectance measurements of samples dyed electrochemically showed that increasing the dye concentration from 0.5% to 2% (owf) resulted in clear changes in the colorimetric properties of the dyed fabrics. A significant increase in color strength (K/S), representing color intensity and dyeing efficiency, was observed (approximately a 5-fold increase) when the dye concentration was increased by 4-fold. In contrast, the K/S value for conventionally dyed samples increased by approximately 2-fold for the same 4-fold increase in dye concentration. This demonstrates the superiority of the electrochemical method over the conventional method in terms of dye reduction efficiency, bath exhaustion, and the amount of dye deposited and fixed onto cotton fibers.

This was accompanied by a sharp decrease in lightness (L*) for the electrochemical method and a minor decrease for the conventional method, indicating an increase in color darkness and depth at higher concentrations in both methods; however, electrochemically dyed fabrics exhibited significantly higher color depth than conventionally dyed ones. Color coordinate values (a* and b*) revealed a gradual shift in color tone, transitioning from pure blue at low concentrations to reddish-blue or violet at higher concentrations. Furthermore, total color difference values (ΔE)—calculated between samples from both methods

using the conventional method as a reference—support the visually observed difference in color strength and dyeing efficiency, indicating a clear, perceptible color distinction between the studied samples shown in Figures 2 and 3.

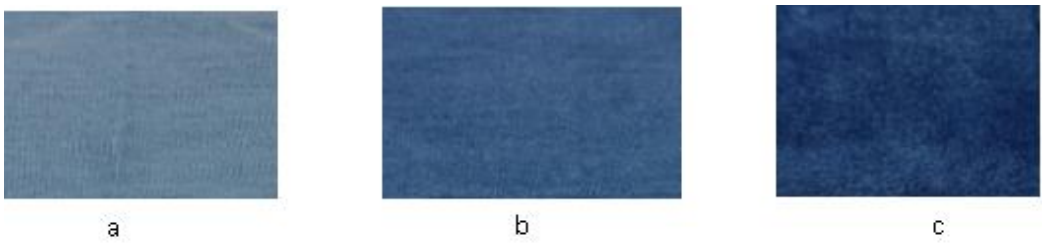


Figure 2: Effect of indigo concentration on the indirect electrochemical dyeing process using a stainless steel (SS) cathode in the presence of the Fe–TEA complex (a: 0.5% owf, b: 1% owf, c: 2% owf).



Figure 3: Indigo dyeing using sodium dithionite as a chemical reducing agent at various dye concentrations (x: 0.5% owf, y: 1% owf, z: 2% owf).

Regarding fastness properties, all samples displayed excellent washing fastness, indicating strong bonding between dye molecules and cotton fibers following oxidation, which prevents dye desorption or bleeding during washing. For light fastness, samples in both methods exhibited low fastness values across all concentrations; however, light fastness in the conventional method improved with increasing dye concentration, an effect not observed in the electrochemical method. Dry and wet rubbing fastness values ranged generally from good to excellent. However, rubbing fastness decreased at higher dye concentrations in the electrochemical method, whereas it improved at higher concentrations in the conventional method. The decrease in rubbing fastness for electrochemically dyed samples at higher concentrations is attributed to dye accumulation on the fiber surface, forming superficial aggregations that are not fully bound to the inner fiber matrix, making them susceptible to mechanical removal during friction. Therefore, it is recommended to introduce a soapy washing stage prior to the acid washing stage to remove unfixed surface dye and maintain high rubbing fastness at elevated concentrations. These results highlight a trade-off between achieving high color strength and maintaining mechanical fastness properties, making the selection of optimal dye concentration a critical factor for peak dyeing performance. Table 1 summarizes colorimetric and fastness properties at 0.5% and 2% indigo dye concentrations for both indirect electrochemical and conventional dyeing methods.

Table 1: Effect of indigo concentration on colorimetric parameters and fastness properties of cotton fabrics dyed via indirect electrochemical and conventional methods.

Dyeing Method	Conc. (% owf)	L*	a*	b*	c*	h*	K/S	ΔE	Rubbing (Dry)	Rubbing (Wet)	Light	Wash (Staining)	Wash (Change)
Electrochemical	0.5%	64.23	-1.43	-22.38	22.42	266.35	1.49	5.12	5	5	2	4/5	5
	2.0%	36.38	0.86	-23.03	23.05	272.13	7.36	20.87	3	2/3	2	4/5	5
Conventional	0.5%	61.21	0.91	-25.80	25.82	272.03	1.73	-	4	3	1	4/5	5
	2.0%	56.34	1.42	-29.12	29.15	272.78	2.41	-	5	4/5	3	4/5	5

2. Effect of Sodium Hydroxide Concentration

The effect of sodium hydroxide (NaOH) concentration was evaluated across the studied range, taking measurements at a minimum concentration of 11 g/L and a maximum of 17 g/L, as presented in Table 2. Increasing the NaOH concentration in the dyebath led to a noticeable increase in color strength (K/S), reflecting enhanced color intensity and higher dyeing efficiency under highly alkaline conditions. This trend was further confirmed by lightness (L*) values, which decreased with increasing alkali concentration, indicating darker and deeper shades compared to samples dyed at lower alkali concentrations (Figure 4).



Figure 4: Effect of sodium hydroxide concentration on indirect electrochemical indigo dyeing using a stainless steel (SS) cathode and Fe–TEA complex (d: 11 g/L, e: 13 g/L, f: 15 g/L, g: 17 g/L NaOH).

Regarding chromatic coordinates, b* values remained relatively consistent across samples, preserving the characteristic blue hue of indigo. Conversely, a* values shifted further in the negative direction with higher NaOH concentrations, indicating a slight chromatic shift toward green. Chroma (c*) exhibited a minor decrease at elevated alkali concentrations. The total color difference (ΔE = 3.24) indicates a visually perceptible color distinction between samples, confirming the direct impact of NaOH concentration on the final visual appearance of dyed fabrics. Fastness evaluations showed excellent washing fastness, good light fastness, and good-to-excellent dry and wet rubbing fastness. All fastness parameters remained consistent across the studied alkali range, demonstrating that varying dyebath alkalinity within this domain does not significantly affect dye resistance to mechanical friction, washing, or photo-degradation.

Table 2: Effect of sodium hydroxide concentration on colorimetric properties and fastness performance of indirect electrochemically dyed cotton fabrics.

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

3. Dyebath Recyclability Study

Table 3 presents a comparison between the initial (1st cycle) and final (5th cycle) recycling stages. Reusing the dyebath across five consecutive cycles did not diminish dyeing efficiency; rather, a progressive increase in color strength was observed, evidenced by rising K/S values and declining lightness (L*) values from Cycle 1 to Cycle 5. Total color difference (ΔE = 13.54) further highlights pronounced visual color shifts between successive cycles, as shown in Figure 5.

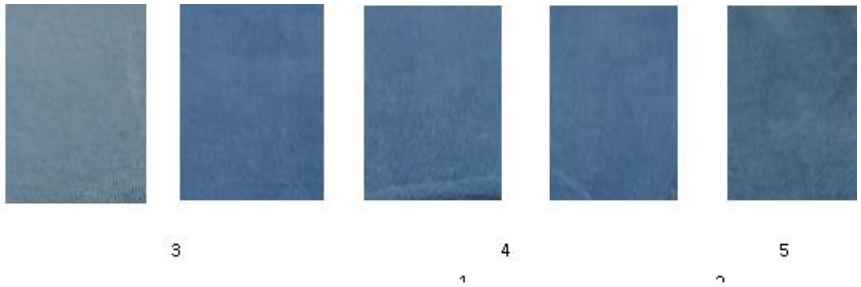


Figure 5: Effect of dyebath recycling on the visual appearance of cotton fabrics dyed with indigo via indirect electrochemical reduction using a stainless steel (SS) cathode and Fe–TEA complex (Numbers 1 to 5 denote recycling cycles 1 through 5, respectively).

This behavior is explained by residual trace amounts of indigo remaining in the dyebath following successive oxidation and filtration steps, leading to gradual dye accumulation in the dyeing medium and increased dye uptake/deposition on cotton fibers in subsequent cycles. Consequently, color depth and intensity increased with repeated dyebath reuse. Fastness assessments for washing as well as dry and wet rubbing yielded comparable results across all cycles, proving that fabrics retained strong resistance to mechanical friction and laundering despite repeated bath reuse. Interestingly, light fastness showed a progressive improvement, increasing from Grade 2 in Cycle 1 to Grade 4 in Cycle 5. This enhancement in light fastness is attributed to the slight buildup of dye concentration in the bath over recycling cycles, which increased internal fiber dye loading and rendered the dyed matrix more resilient to photodegradation upon prolonged light exposure. Overall, these findings demonstrate that the indirect electrochemical reduction system using the Fe–TEA complex possesses excellent recyclability, preserving dyebath efficiency over five consecutive cycles while keeping washing and rubbing fastness at highly acceptable levels and significantly enhancing light fastness.

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

Recycling Cycle	L*	a*	b*	c*	h*	K/S	ΔE	Rubbing (Dry)	Rubbing (Wet)	Light	Wash (Staining)	Wash (Change)
Cycle 1	64.99	-2.10	-21.32	21.42	264.37	1.38	-	5	5	2	4/5	5
Cycle 5	52.00	-1.40	-25.10	25.14	266.82	3.23	13.54	5	4/5	4	4/5	5

4. Comparison Between Indirect Electrochemical and Conventional Dyeing Methods

Comparing the results of indirect electrochemical dyeing with conventional chemical reduction demonstrates that sodium dithionite remains an effective reducing agent for indigo. However, the electrochemical method superiorly outperformed the conventional method in terms of color strength (K/S), reduction efficiency, and dyebath exhaustion across all dye concentrations. For instance, the K/S value in the electrochemical method increased from 1.49 at 0.5% dye concentration to 7.36 at 2% concentration, whereas the maximum K/S achieved in conventional dyeing was 2.41 (at 2% dye concentration). On the other hand, fastness properties were generally slightly higher in conventional dyeing. Nevertheless, indirect electrochemical dyeing represents a highly promising and sustainable alternative to sodium dithionite. Further optimization of operational parameters is recommended to fully realize its industrial applicability, leveraging the substitution of hazardous chemical reductants with an electrochemical electron source and enabling dyebath reusability.

CONCLUSIONS

This study confirms the feasibility of indirect electrochemical reduction of indigo dye using the iron–triethanolamine (Fe–TEA) mediator complex and a stainless steel (SS) cathode as a sustainable alternative to traditional sulfur-based reducing agents. Key conclusions include:

1. Increasing indigo dye concentration from 0.5% to 2% (owf) led to a pronounced enhancement in color strength (K/S) and a decrease in lightness (L*), yielding darker and deeper color shades. Washing and light fastness remained consistent, whereas rubbing fastness decreased due to surface dye accumulation on fibers.
2. The indirect electrochemical method surpassed the conventional method in reduction efficiency, bath exhaustion, and fiber dye uptake, achieving superior color strength and shade depth. However, overall fastness properties remained slightly superior in conventional dyeing.
3. Elevating alkalinity (NaOH concentration) increased color strength (K/S) without adversely affecting washing, rubbing, or light fastness properties.
4. Dyebath recycling experiments demonstrated excellent reusability over five consecutive cycles without loss of dyeing performance. Residual dye accumulation caused a progressive increase in K/S and marked improvement in light fastness (from Grade 2 to 4), while washing and rubbing fastness remained high.
5. Indirect electrochemical reduction is an eco-friendly, technically viable method that minimizes dependence on polluting chemical reductants and supports closed-loop dyebath reuse. Further parametric optimization will facilitate industrial scalability matching conventional productivity standards.

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