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# Indirect Electrochemical Reduction of Indigo with Metal complex system of Fe( II )-DGS-Abal B

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**Abstract.** The indirect electrochemical reduction dyeing of cotton fabric with indigo are carried out in this work using the synergistic complexation system of Fe( II )-DGS-Abal B. The influences of concentration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$ , Abal B and NaOH on dyeing performances are discussed. The concentration of NaOH is found to be the main influence factors and the rate of dye reduction (Re) could be achieved to 90.88% in the optimized conditions. Compared to the traditional dyeing with  $\text{Na}_2\text{S}_2\text{O}_4$ , K/S value of the electrochemical dyeing of cotton fabric is increased by 6.14%, and the color fastness is basically the same as the traditional dyeing process.

## 1. Introduction

Indigo plays an important role in our today's dyeing industry due to the popularity of blue jeans [1]. However, it is insoluble in water and needs to be reduced to its water-soluble leuco form to accomplish the standardization of dyeing [2, 3]. In the current industrial dyeing processes, vat dyes are still reduced mainly by sodium dithionite. However, there are many problems in this method, such as a large amount of sodium dithionite, the complex dyeing process, which increases the burden of sewage treatment [4]. Therefore, many domestic and foreign scholars are trying to develop a green, environmentally friendly reduction system to replace the sodium dithionite, electrochemical techniques would be of wide prospects in the industrial applications because it minimizes the consumption of chemicals, reduces the cost of production, and diminishes the discharge of wastewater [5, 6-7]. Indirect electrochemical reduction dyeing is carried out by transferring electrons to indigo through a substance capable of obtaining and losing electrons. These media generally have multivalent states and have sufficient reducing properties such as hydroxyacetone and divalent iron salts [8, 9-10]. However, previous studies are generally focused on the formation of a complex system of specific ferric salts and ligands, while the study of ferrous salts directly as a medium associated are rare. The structure-activity relationship and mechanism of action between the rate of iron ion self-conversion and indigo reduction and its dyeing performance have not been studied.

The indirect electrochemical reduction dyeing of cotton fabric with indigo are carried out in this work using the synergistic complexation system of Fe( II )-DGS-Abal B. The influences of concentration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$ , Abal B and NaOH on dyeing performances are discussed. The parameters through optimizing method were explored.



## 2. Experimental

### 2.1. Chemicals and materials.

Ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium gluconate ( $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), potassium ferricyanide ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ), potassium chloride ( $\text{KCl}$ ) were obtained from Sinopharm Chemical Reagent Co, China. Indigo (98%) was supplied from the Aladdin Reagent Co., China. All solutions were prepared using  $\text{H}_2\text{O}$  with a resistivity of  $18.2 \text{ M } \Omega \text{ cm}$  obtained from Millipore Milli-Q system. Abal B (a complexing agent with high alkali resistance and electrical conductivity based on triethanolamine (TEA)) was supplied by Meishida Biochemical Co, Shijiazhuang of China. Cotton yarn of  $135 \text{ g/m}^2$  was obtained from Hebei Ningfang Co, China.

### 2.2. Cathodic Configuration.

The anode electrolyte were prepared by  $1.0 \text{ M NaOH}$  in  $250 \text{ mL}$  deionized water. The cathode electrolyte was prepared by  $8\text{--}12 \text{ g/L FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $6\text{--}10 \text{ g/L C}_6\text{H}_{11}\text{O}_7\text{Na}$ ,  $5\text{--}9 \text{ g/L Abal B}$ ,  $15\text{--}35 \text{ g/L NaOH}$  into  $200 \text{ mL}$  deionized water. The  $\text{NaOH}$ ,  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$ , Abal B are dissolve in water, then the pre-dissolved iron salt were added to the ligand solution, mixed and stirred evenly, and diluted to  $200 \text{ mL}$  to obtain the complex solution. The  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$ , Abal B were fully stirred until completely dissolved,  $\text{NaOH}$  was added in this solution to form mediator system of  $\text{Fe(II)-DGS-Abal B}$ , and  $2.5 \text{ g/L}$  indigo was added in the system to get the blue solution.

### 2.3. Electrolysis Experiments.

A conventional two-compartment glass H-cell (TianJin Aida HengSheng technology Co, China), separated by a Nafion-321 membrane, was used for the electrolysis experiments to obtain the optimized electrolysis condition. The electrochemical reaction experiment was carried out in constant current mode with RXN-1503 dc stabilized voltage power supply (ZhaoXin electronics CO, China). The cathode and anode were manufactured from graphite electrode and stainless steel (TianJin Aida HengSheng technology Co, China). The volume of catholyte and annolyte were  $200 \text{ mL}$  and  $250 \text{ mL}$ . The working voltage is  $9 \text{ V}$ , energization time is  $30 \text{ min}$ , and the cathode electrode area is  $10 \text{ cm}^2$ . And the catholyte was stirred during the electrolysis process.

### 2.4. Potentionmetric Titration.

The rate of dye reduction ( $\text{Re}$ ) and ferrous iron conversion ( $\text{Xe}$ ) were calculated by potentionmetric titration using ZD-3A automatic Potential Titrator (ShangHai An'ting CO, China). A Pt electrode was used as the indicator electrode. And  $\text{Ag/AgCl}$  electrode was used as the reference electrode.  $50 \text{ mL}$  of cathode electrolyte was accurately absorbed, and paraffin was immediately injected on the surface of the solution and nitrogen was injected.  $0.05 \text{ mol/L K}_3[\text{Fe}(\text{CN})_6]$  was used as titrant for titration. Based on the data recorded in the test, the titration curve was drawn and the titration end point was determined using the first-order derivative method.  $\text{Re}$  and  $\text{Xe}$  were calculated according to the formula 1 and 2.

$$\text{Re} = 4C \times (V_2 - V_1) \times M / 2m \times 100 \% \quad (1)$$

$$\text{Xe} = (A - 4C \times V_1) / A \times 100 \% \quad (2)$$

Where,  $C$  is the concentration of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  standard solution ( $\text{mol} \cdot \text{L}^{-1}$ );  $V_2$  is the  $\text{K}_3[\text{Fe}(\text{CN})_6]$  standard solution volume ( $\text{mL}$ ) consumed by two successive titrations in the second sudden jump;  $V_1$  is the  $\text{K}_3[\text{Fe}(\text{CN})_6]$  standard solution volume ( $\text{mL}$ ) consumed by two titrations in the first sudden jump;  $M$  is the molecular mass of indigo ( $\text{g} \cdot \text{mol}^{-1}$ );  $m$  is the initial addition of indigo ( $\text{g}$ ).  $A$  is the initial amount of ferrous ion ( $\text{g}$ );  $C$  is the concentration of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  standard solution ( $\text{mol} \cdot \text{L}^{-1}$ ).

### 2.5. Dyeing procedure.

The dyeing experiments were carried out by the exhaustion method with the ratio of 1:20. Cotton fabric (5 g) was dyed with cathode electrolyte for 1 min. Then the fabric was oxidized in the air for 5 min and washed in distilled water until the water was neutral and air-dried.

### 2.6. Color measurement.

The colorimetric values of all dyed cotton fabrics were measured by a Color-i5 spectrophotometer (Data-color CO, USA) under D65 at 10°. The K/S values were calculated using the Kubelka-Munk equation as shown in formula (3):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (3)$$

Where R is the reflection of the dyed cotton fabric.

### 2.7. Color fastness.

The wash fastness of the dyed cotton fabrics was tested according to ISO 105 - A02: 1993, Dry and wet rubbing fastness was measured according to AATCC Test Method 8-2007.

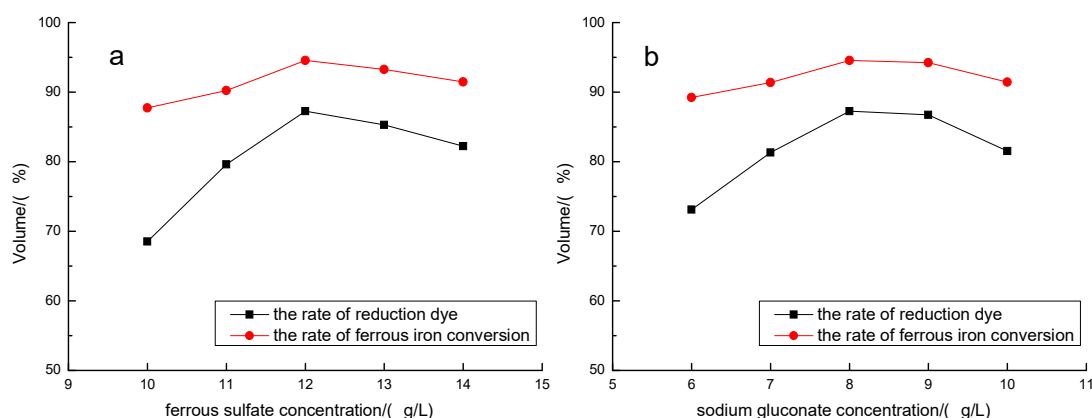
## 3. Results and Discussion

### 3.1. Optimization of electrolyte composition.

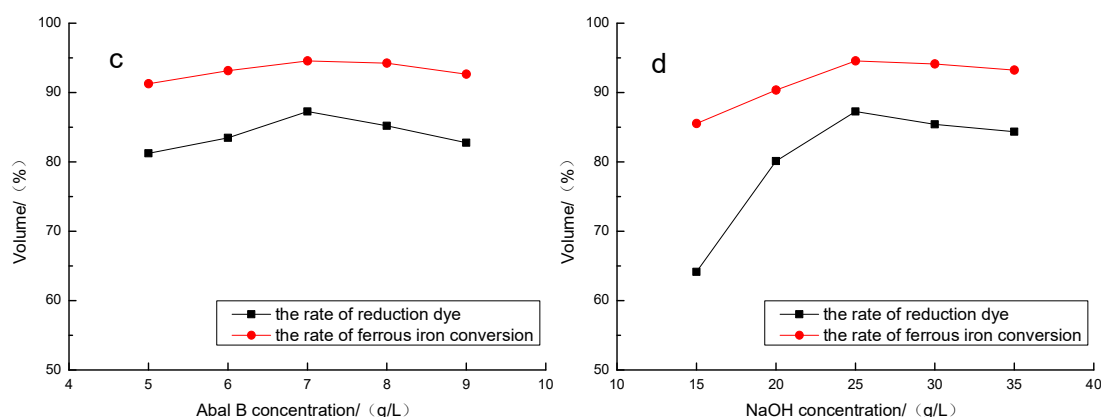
In the indirect electrochemical reduction dyeing of indigo, the synergistic complexation system of Fe<sup>3+</sup>/Fe<sup>2+</sup>-DGS-Abal B was used as a mediator to obtain electrons from cathode and reduce the indigo according to Eq.4 and 5.



The effect of concentration of FeSO<sub>4</sub>•7H<sub>2</sub>O, C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>Na, Abal B and NaOH on the reduction performance were investigated to obtain the optimal condition of electrolyte composition for the indirect electrochemical reduction of indigo. As shown in Fig. 1a, the Re and Xe all showed a trend of first increase and then decrease with the further increased concentration of FeSO<sub>4</sub>•7H<sub>2</sub>O, and the optimised reductive performance is achieved at the FeSO<sub>4</sub>•7H<sub>2</sub>O concentration of 12 g/L. The Re and Xe are increased with the increased concentration of FeSO<sub>4</sub>•7H<sub>2</sub>O due to the increased concentration of complex involved in the electron transfer. With the further increase of FeSO<sub>4</sub>•7H<sub>2</sub>O concentration, the precipitation was generated and the excessive ferrous ion and ferric iron ions could not be chelated due to the limited iron ion complexing ability of C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>Na and Abal B. Therefore, the concentration of FeSO<sub>4</sub>•7H<sub>2</sub>O was determined to be 12 g/L. It can be seen from Fig. 1b that the maximum Re and Xe are around 87.26% and 94.55% respectively with C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>Na concentration of 8 g/L. If the concentration of C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>Na continues to increase, it may induce adsorption on the surface of the electrode, which is not conducive to the iron ion complex with oxidation state to obtain electrons from the surface of the electrode. Therefore, the concentration of C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>Na is preferably 8 g/L.



**Fig. 1** Effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  concentration(a) and  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$  concentration(b) on the reduction of indigo (The cathodic liquid consisted of is 8 g/L  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$  + 7 g/L Abal B + 25 g/L NaOH(a), The cathodic liquid consisted of is 12 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  + 7 g/L Abal B + 25 g/L NaOH (b)).



**Fig. 2** Effect of Abal B concentration (c) and NaOH concentration (d) on the reduction of indigo (The cathodic liquid consisted of is 12 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  + 8 g/L  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$  + 25 g/L NaOH (c), The cathodic liquid consisted of is 12 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  + 8 g/L  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$  + 7 g/L Abal B (d)).

Fig. 2a presents that the Re and Xe are 87.26% and 94.55% respectively with Abal B concentration of 7 g/L. Abal B with good electrical conductivity is defined as ligand to form a complex mediator with  $\text{Fe}^{3+} / \text{Fe}^{2+}$ , which made the redox process stable and smooth. If the concentration of Abal B is low, the stable complex could not be formed as the excessive  $\text{Fe}^{3+} / \text{Fe}^{2+}$  changed to be  $\text{Fe}(\text{OH})_2 / \text{Fe}(\text{OH})_3$  precipitates under alkaline condition. The Re and Xe changed slightly with the further increased concentration of Abal B, causing the waste of drug. Thus, the concentration of Abal B was determined to be 7 g/L. From the Fig. 2b, we can see that different concentrated NaOH (15-35 g/L) was used for this operation. When the NaOH concentration increased from 15 to 25 g/L, the Re and Xe also increased; the maximum Re and Xe are around 87.26% and 94.55% respectively with NaOH concentration of 25 g/L. When the amount of NaOH raised from 25 g/L to above concentration the Re and Xe declined gradually. Because the complex formed was bound to be unstable which would influence conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in low concentration of NaOH. When the concentration of NaOH reached the high stage, the stability of complex environment was affected, thus resulting in a low Re and Xe. Therefore, the concentration of NaOH is preferably 25 g/L.

### 3.2. Indirect electrochemical dyeing performance.

According to the above experiments, indirect electrochemical dyeing of indigo and traditional dyeing with  $\text{Na}_2\text{S}_2\text{O}_4$  were carried out to determine the K/S value and color fastness as shown in Table 1.

**Table 1.** Comparison of dyeing performance of different dyeing processes

Process	K/S value	Dust fastness/grade	Rubbing fastness/grade	
			Dry	Wet
Traditional	11.73	5	4-5	3
Electrochemical	12.45	5	4-5	3

(The dye usage is 2.5 g/L for both dyeing processes.)

It can be seen from Table 1 that the dyeing performance of synergistic complexation system formed with  $\text{Fe(II)}$ -DGS-Abal B is superior than that of dyeing with  $\text{Na}_2\text{S}_2\text{O}_4$ . The K/S value of indirect electrochemical dyeing of indigo can be achieved to 12.45, which is increased by about 6.14% compared to that of  $\text{Na}_2\text{S}_2\text{O}_4$  dyeing with the same color fastness basically.

## 4. Conclusion

In our work, a new method was adopted on indirect electrochemical reduction dyeing with the synergistic complexation system of  $\text{Fe(II)}$ -DGS-Abal B as redox mediator. The result showed that the indigo could be reduced efficiently in the optimized parameters as the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was 12 g/L,  $\text{C}_6\text{H}_{11}\text{O}_7\text{Na}$  was 8 g/L, Abal B was 7 g/L, NaOH was 25 g/L. The reduction rate could be reached to 90.88% under the optimized electrochemical reduction dyeing process, and the K/S value of indirect electrochemical dyeing of indigo can be achieved to 12.45, which is increased by about 6.14% compared to that of  $\text{Na}_2\text{S}_2\text{O}_4$  dyeing with the same color fastness. The strategy presented here can be developed to replace a substantial part of electrochemical dyeing with  $\text{Na}_2\text{S}_2\text{O}_4$  in denim production.

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