

Cotton dyeing by indigo with the borohydride process: Effect of some experimental conditions on indigo reduction and dyeing quality

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Received 28 August 2006; received in revised form 27 December 2006; accepted 7 January 2007

Abstract

Classical process for dyeing by indigo uses generally the sodium dithionite as reducing agent. In this paper, a new technique of reduction of indigo by sodium borohydride in the presence of a catalyst and without the addition of alkali was developed. This reduction was carried out at a temperature range of 40–70 °C. In order to determine the leuco-indigo concentration in the bath, a potentiometric titration procedure has been established. The effect of some main reaction parameters was studied: the temperature and the amount of catalyser. This study indicated that maximum yield of indigo reduction took place at 55 °C with an amount of 1% of catalyser.

The dyeing study of a cotton fabric was carried out at the same temperature of the reduction reaction. A “6-dip–6-nip” technique was used to study the performance of this dyeing. The dyeing results were evaluated by measuring the colour yield (K/S) at 660 nm. The best results were obtained at a temperature of 40 °C and with an amount of 1% of catalyser.

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Keywords: Dyeing by indigo; Reduction of indigo by sodium borohydride; Evaluation of dyeing quality

1. Introduction

Indigo (C.I. Vat Blue 1) is a vat dye which was probably one of the oldest known colouring agent. It has been used to dye cellulosic textiles especially cotton. This blue dye is still employed extensively today for dyeing cotton yarn in the manufacture of denims and blue jeans.

Dyeing with indigo was an ancient art [1]. Since this dye is insoluble in water, it is necessary to reduce it to its leuco-soluble form using a suitable reducing agent with an alkali such as sodium hydroxide. When the preparation of leuco-indigo is achieved, the textile is dipped with the reduced dye. Then, the textile is exposed to air in order to oxidize the dye back to its insoluble form. These two steps (dipping/exposing) would be repeated many times to obtain the desired shade.

Until now in most industrial processes, vat dyes especially indigo are reduced by sodium dithionite $\text{Na}_2\text{S}_2\text{O}_4$. This procedure causes several problems especially problems relating to the wastewaters quality: some of the by-products formed

in the decomposition of sodium dithionite are sulphur compounds which can heavily contaminate the environment and the pH of wastewaters generated from this dyeing process is very high. Some other problems are relating to parameter controls of the reduction process and the storage of the reducing agent. Therefore, many attempts have been made to overcome these problems: so, various eco-friendly reducing agents were tested to replace the sodium dithionite for example thiourea dioxide [2], hydroxyketones [3,4], and even the use of electrochemical reduction with directly and indirectly processes are studied [5,6]. For technical and economic reasons, most of them seem to be not very satisfying.

Sodium borohydride is a well-known reducing agent and has been extensively employed in chemistry synthesis and in some hydrogen generation processes. The use of sodium borohydride in aqueous solution presents many advantages: facility of storage in alkaline solution, the by products formed in the decomposition of sodium borohydride are sodium borate and its hydrates. These compounds are completely non-toxic and have minimum effects on environment [7].

Only relatively few papers have appeared during recent years on the use of sodium borohydride in vat dyeing techniques. Most of these papers have investigated only some examples of

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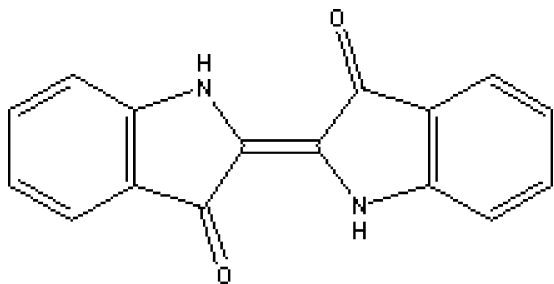


Fig. 1. Chemical structure of indigo.

vat dyes [8], without studying the indigo reduction by sodium borohydride. Previous attempts to reduce vat dyes with sodium borohydride have not been completely fulfilled, in spite of varying many reaction conditions: use of large excess of reagent, long reaction times and high temperatures [8,9]. These low performances may be explained by the highly conjugated carbonyl groups in vat dyes. So, it is difficult to reduce them because of the powerful resonance stabilization of the carbonyl groups [9,10] (Fig. 1).

In this work, we report a novel technique to reduce indigo by sodium borohydride in the presence of potassium nickel cyanide and without the addition of alkali.

2. Experimental

2.1. Chemicals used and materials

Indigo (BEZEMA AG, Switzerland) and Sodium Borohydride, Hydrifin[®] (Finnish Chemicals OY, Finland) were used for the reduction without further purification. Caustic Soda (Kaustik JSC, Russia), Setamol WS[®] (BASF AG, Germany) and potassium hexacyanoferrate (Riede-deHaen, Germany) were used for the titration of leuco-indigo.

Commercially bleached but unfinished cotton fabric with the following specifications was supplied from SITEX, Tunisia: plain weave; ends per inch, 33.02; picks per inch, 38.1; warp count, 10.5 Open End; weft count, 15 Open End; weight, 204 g/m².

Potassium nickel cyanide was synthesised as described in inorganic synthesis [11]. The potassium nickel cyanide obtained was purified as follow: It was washed in chloroform and filtered to remove residual potassium cyanide. Then, the obtained product was recrystallised in methanol.

2.2. Reduction of indigo by sodium borohydride

A solution of 0.34 g of indigo and 1% of potassium nickel cyanide was prepared by addition to 140 ml of water. This solution was stirred (750 rpm) and heated up to 55 °C. Then, 0.34 g of sodium borohydride (previously dissolved in 20 ml of distilled water) was added. After 5 min, the final volume was adjusted to 170 ml with distilled water. This indigo reduction was carried out at 55 °C and was performed under nitrogen atmosphere to prevent oxidation.

The potential and pH in solution were measured every 3, 5 or 10 min using respectively a Pt-electrode versus (Ag/AgCl, 3 mol/l KCl) reference electrode with a potentiometer (Metrohm pH-meter 744, Switzerland) and a pH meter (Knick pH-Meter 765 Calimatic, Germany). The end of reduction was noted when the potential in solution rose rapidly and then remained quasi stable.

In the reduction of indigo by sodium borohydride, the volume of the dyebath decreases. So, when the reduction of indigo was achieved, this loss was compensated by addition distilled water at the same temperature of reduction to 170 ml and the weight of the amount of added water was measured.

2.3. Titration of the leuco-indigo in the dyeing bath

A potentiometric titration procedure of the leuco-indigo obtained by reduction with sodium borohydride has been established: 50 ml of a standard solution was prepared containing 1.2 g/l of Setamol WS (a commercial dispersant) and 4 g/l of sodium hydroxide. A combined redox electrode (Bioblock Scientific 90417, Portugal) was immersed. This solution was stirred and covered with a thin layer of light oil to prevent oxidation. Then, 20 ml of leuco-indigo obtained was added. This mixture was titrated with a solution of 0.05 mol/l of potassium hexacyanoferrate.

2.4. Dyeing process

The reaction medium obtained after the reduction procedure was used as dyeing bath. The fabrics were dyed at a liquor ratio 60:1 (dyeing bath volume (ml):fabric weight (g)) at the same temperature of the reduction reaction. Dyeing with indigo was carried out using a '6-dip-6-nip' padding operation. Dipping of the fabric in dye liquor for 30 s followed by airing for 1 min completed '1-dip-1-nip' cycle. Then, the dyed samples were subject to a hand washing with hot water for 5 min at 70 °C followed by a cold rinsing and finally they were dried at the room temperature.

2.5. Dyeing quality evaluation

The dyeing quality was evaluated using a colour yield parameter (K/S). The determination of K/S values of the dyed samples was carried out on SpectroFlash SF300 spectrophotometer with dataMaster 2.3 software (Datacolor International, USA) at 660 nm.

3. Results and discussions

Among the main operating conditions influencing dyeing with sodium borohydride process, we can cite: the temperature and the catalyst amount. We studied the effect of these two operating conditions on different parameters controlling the dyeing quality: the oxydo-reduction potential and pH of the dyeing bath, the indigo reduction yield and the colour yield K/S.

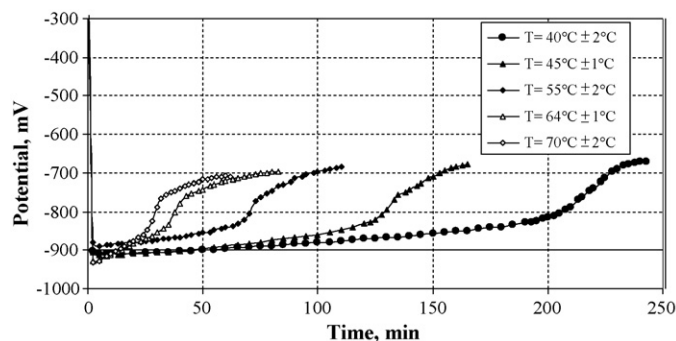


Fig. 2. Effect of temperature on the evolution of potential redox of the dyeing bath.

3.1. Effect of temperature

3.1.1. Effect of the temperature on the evolution of the oxydo-reduction potential and pH of the dyeing bath

The temperature of the reaction medium was varied in the range of 40–70 °C, and the evolution of redox potential of the medium was studied. The experimental results are shown in Fig. 2. From these results, the variation of reaction duration can be deduced when the temperature of the dyeing bath increases in the range of 40–70 °C. These results are reported in Fig. 3. Each experimental point is the mean of two experimental values.

In Fig. 2, it can be seen that all the curves representing the evolution of redox potential with temperature have the same shape whatever is the temperature of reduction. These curves are constituted with three parts: the first part represents a slow increasing of redox potential when the temperature increases. The second part is a rapid jump of redox potential. Then, in the third part, the potential remains quasi stable. The evolution of the medium potential represents the evolution of the reduction reaction and of the leuco-indigo formation. We suppose that the quasi stability of the redox potential indicates the end of the reaction of reduction, and the time of the beginning of this stability step is taken as the reduction reaction duration. This parameter versus temperature is reported in Fig. 3. In this figure, it can be observed that when the temperature increases, the reaction duration decreases. This can be explained by the rapid consumption of reducing agent when the temperature of the reduction reaction is increased.

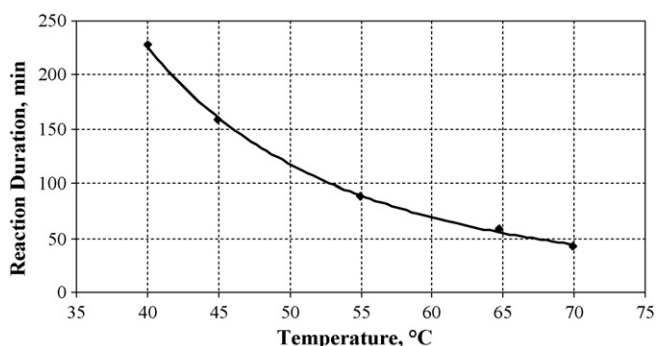


Fig. 3. Effect of temperature on the reaction duration.

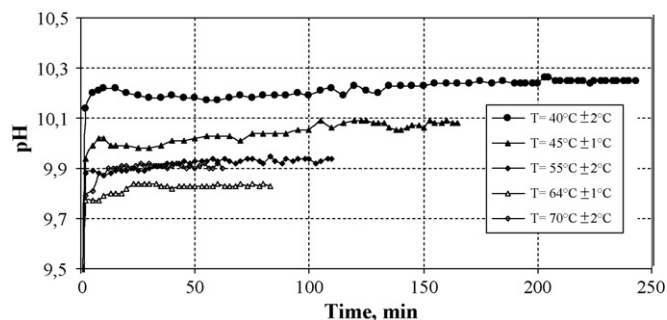


Fig. 4. Effect of temperature on the evolution of the reaction medium pH.

The effect of temperature on the evolution of the pH of reduction medium was also studied. The results are reported in Fig. 4. This figure represents the variation of pH during the reaction evolution for different temperatures. Fig. 4 shows that all the curves are similar whatever is the temperature. The pH remains quite constant during the reduction reaction. Fig. 5 represents the evolution of the mean value of the pH of the reduction medium versus the temperature reaction. In this figure, it can be seen that the pH decreases when the temperature increases. The slight increasing of pH at 70 °C can be explained by the great evaporation of water observed at that temperature.

3.1.2. Effect of the temperature on the indigo reduction yield

The main reaction of indigo reduction is accompanied with a competitive reaction which is the hydrolysis of sodium borohydride (Fig. 6). The indigo reduction reaction is evaluated by the yield corresponding to leuco-indigo, and the hydrolysis reaction is evaluated by measuring the loss of water in the dyeing bath.

3.1.2.1. Evaluation of the yield of the indigo reduction. Fig. 7 shows a typical potential curve of solution titrated with potassium hexacyanoferrate. The determination of the equivalent point allows us to calculate the concentration of the leuco-indigo in the dyeing bath and the yield of reduction reaction.

3.1.2.2. Estimation of the hydrolysis reaction. The estimation of the hydrolysis reaction was measured by the weight of water lost during the reduction reaction.

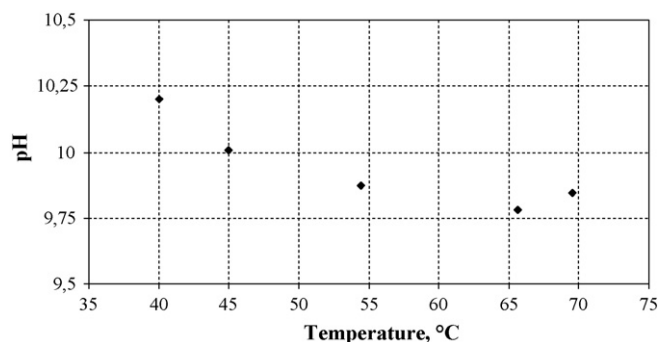


Fig. 5. Evolution of the mean value of the reduction medium pH vs. the temperature reaction.

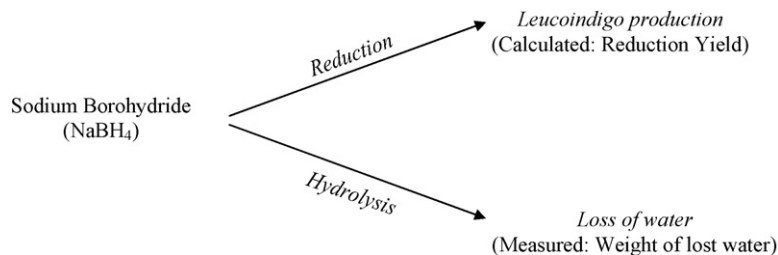


Fig. 6. The main competitive reactions in the reduction medium.

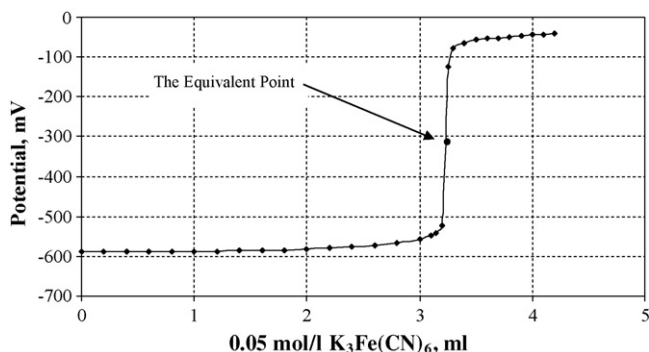


Fig. 7. The potential curve of dyebath titrated with potassium hexacyanoferrate.

The experimental results are reported in Fig. 8. Each point of the represented curves is the mean value of two experiments. The experimental deviation of the evaluation of the weight of water lost and the indigo reduction yield is also reported. In Fig. 8, it can be observed that increasing temperature between 40 and 45 °C has no significant influence on indigo reduction yield and hydrolysis reaction of sodium borohydride. However, at 55 °C the maximal reduction yield was obtained. With higher temperatures, the reduction yield decreases rapidly and the weight of water lost from dyeing bath becomes more and more important. It is clear that increasing temperature enhances evaporation and notably hydrolysis reaction of sodium borohydride as indicated in previous study [12,13].

3.1.3. Effect of the temperature on the colour yield

The obtained medium after the indigo reduction reaction is used as dyeing bath for cotton fabrics. Then, the dyeing quality

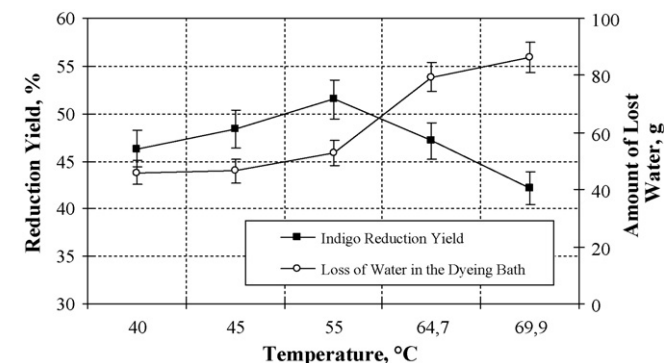


Fig. 8. Effects of temperature on indigo reduction yield and the hydrolysis of sodium borohydride.

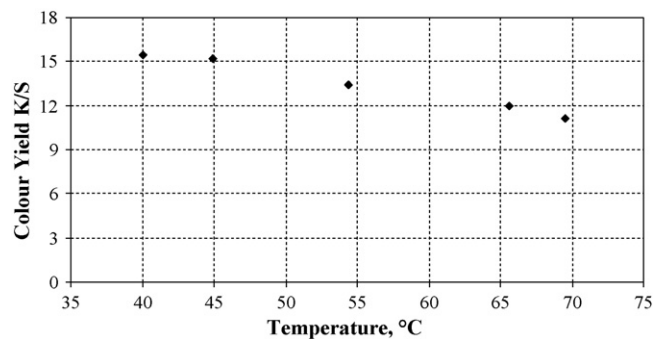


Fig. 9. Effect of temperature on the colour yield.

of the coloured samples was evaluated by measuring the colour yield K/S at 660 nm. The experimental results of the effect of the temperature on the colour yield are reported in Fig. 9. The values represented in this figure are the mean of two experiments. Fig. 9 shows that maximum colour yield occurs at 40 °C, whereas the maximum reduction yield is obtained at 55 °C as observed in Fig. 8. So, the colour yield is not directly linked to the concentration of the leuco-indigo in dyeing bath and the reduction yield. This can be explained with two main reasons:

First, it is well known that pH of dyebath affects considerably indigo dyeing and specially the retention of the dye by cotton fibre. When pH increases cotton fibres swell and become more accessible for dye. Therefore, colour yield rises rapidly. In Fig. 10 representing the evolution of colour yield versus the pH of the dyeing bath, it can be seen that increasing temperature from 40 to 70 °C, pH of dyebath before dyeing decreases and K/S decreases. Thus, it appears clearly that the colour of the dyed fabric is limited by the dyeing bath pH.

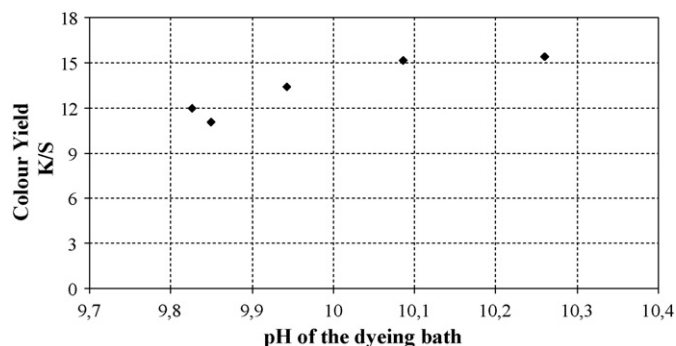


Fig. 10. Evolution of colour yield vs. the pH of the dyeing bath (variation of the temperature).

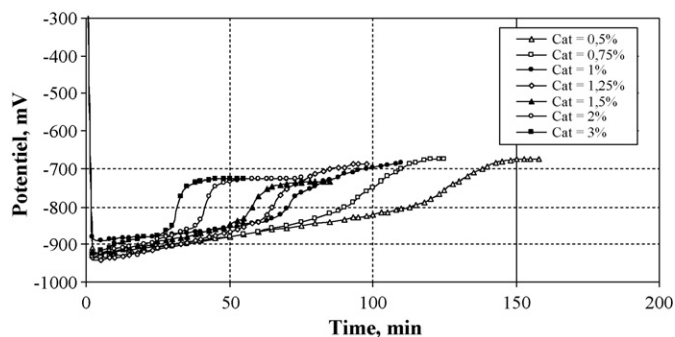


Fig. 11. Effect of catalyser amount on the evolution of potential redox of the dyeing bath.

Second, another factor which can highly affect the dye retention by cotton fibres is temperature. As known, indigo is a dye usually used in cold dyeing. This is due to the characteristic of this dye which has a maximum affinity to cotton fibres when the dyeing is carried out at a temperature between 20 and 40 °C. So, it is evident to obtain the maximum colour yield at 40 °C as observed in Fig. 9.

3.2. Effect of the amount of catalyser

3.2.1. Effect of the amount of catalyser on the evolution of the oxydo-reduction potential and pH of the dyeing bath

The used catalyser was potassium nickel cyanide. Its amount was varied in the reaction medium from 0.5 to 3% of the weight of indigo and the evolution of the redox potential of the medium was investigated. The experimental results are shown in Fig. 11. In this figure, it appears that all the curves representing the evolution of redox potential with the amount of catalyser have the same shape whatever is the amount of potassium nickel cyanide. All these curves are constituted with three parts: the first part represents a slow increasing of redox potential when the amount of catalyser increases. The second part is a rapid jump of redox potential. Finally, in the third part, the potential remains quasi stable.

The evolution of the medium potential represents the evolution of the reduction reaction and of the leuco-indigo formation. We suppose that the quasi stability of the redox potential indicates the end of the reaction of reduction, and the time of the beginning of this stability step is taken as the duration of reduction reaction. This parameter versus the catalyser amount is reported in Fig. 12. In this figure, it can be seen that when the amount of potassium nickel cyanide increases in the dyeing bath from 0.5 to 3% of the indigo weight, the reaction duration decreases. So, it can be said that as the temperature, potassium nickel cyanide increases the rate of sodium borohydride reactions.

The experimental results showing the effect of the variation of the catalyser amount on the evolution of pH of the reduction medium are reported in Fig. 13. It can be observed that all the curves are similar whatever is the amount of catalyser. The pH remains quite constant during the reduction reaction. It can be seen in this figure also that increasing the amount of potassium nickel cyanide has not a significant influence on pH of reduction

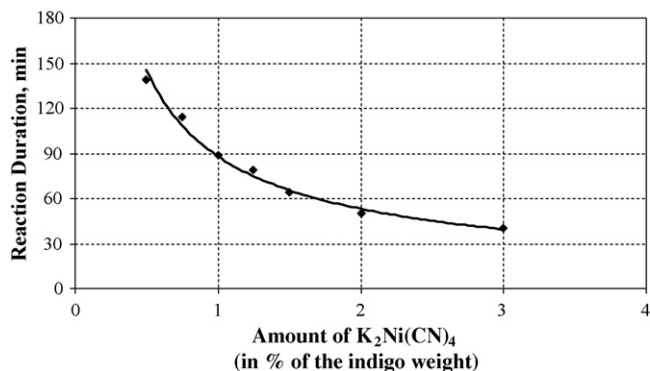


Fig. 12. Effect of catalyser amount on the reaction duration.

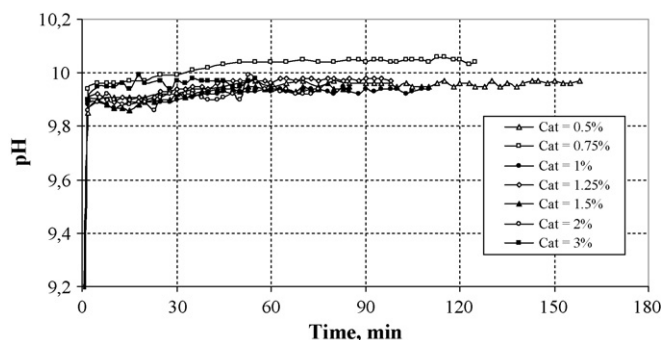


Fig. 13. Effect of catalyser amount on the evolution of the reaction medium pH.

reaction. Fig. 14 represents the evolution of the mean value of the pH of the reduction medium versus the temperature reaction. It appears in this figure that the pH is relatively constant when the amount of catalyser increases in the reaction medium.

3.2.2. Effects of the amount of catalyser on indigo reduction yield

The effect of the variation of the catalyser amount on the reduction yield and the intensity of sodium borohydride hydrolysis reaction were also investigated. The evaluation of the indigo reduction yield and the estimation of the sodium borohydride hydrolysis were carried out as described previously. The experimental results of these two studies are reported in Fig. 15. Each point of the presented curves is the mean value of two

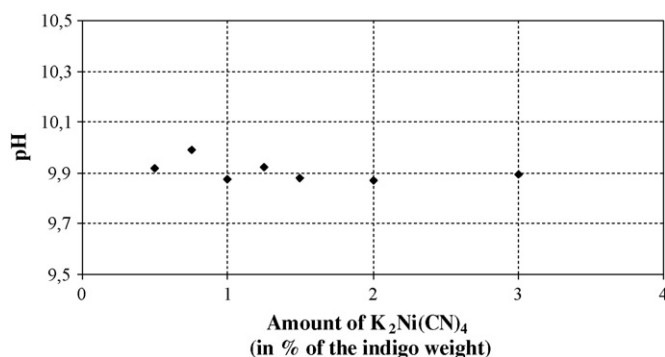


Fig. 14. Evolution of the mean value of the reduction medium pH vs. the catalyser amount.

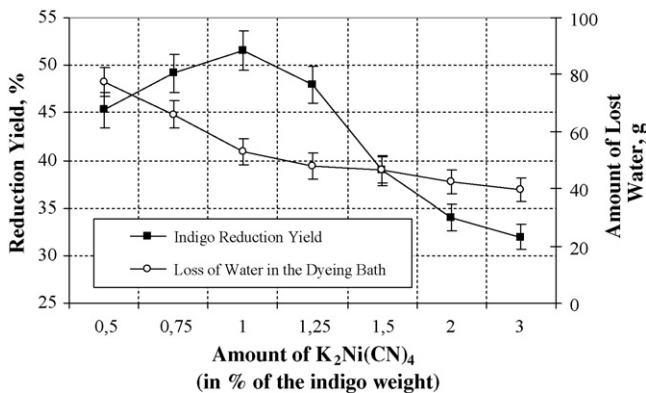


Fig. 15. Effects of catalyser amount on the indigo reduction yield and the hydrolysis of sodium borohydride.

experiments. The experimental deviation of the evaluation of the weight of water lost and the indigo reduction yield is indicated.

Fig. 15 shows that potassium nickel cyanide affects the two main competitive reactions: the indigo reduction and the hydrolysis of sodium borohydride. At first, it is important to note that in the absence of catalyser, sodium borohydride fails to reduce indigo. This is in accordance with results of previous studies which studied the reduction of other vat dyes [8]. As explained in some papers [9,10]: it appears that the carbonyl groups in vat dyes structures have a low reactivity. This can be attributed to the high stability of vat dyes structures due to the high conjugation of these carbonyl groups. So, under these conditions it can be only observed the competitive reaction of hydrolysis of sodium borohydride.

In Fig. 15, it can be seen that the curve representing the evolution of the reduction yield is constituted essentially with two parts. The first is an increasing part going from 0.5 to 1% of catalyser amount. In this part, it can be noted a rapid increasing of the yield reduction which attains 51.5% for an amount of 1% of potassium nickel cyanide. It can be also observed that in this part the loss of water decreases rapidly when the amount of catalyser increases.

The second part of the curve begins at 1% of catalyser amount. This part shows a rapid decreasing of the reduction yield. Besides, this weight of water loss continues to decrease in this part but not as rapid as previously. These falls in the reduction yield and the loss of water can be explained by the appearance of a third competitive reaction between sodium borohydride and potassium nickel cyanide which becomes more and more important when the amount of catalyser increases in the dyeing bath [14].

3.2.3. Effect of the amount of catalyser on the colour yield

The obtained medium after the indigo reduction reaction is used as dyeing bath for cotton fabrics. The evaluation of the dyeing quality of the coloured samples was carried out using the colour yield parameter K/S. The experimental results of the effect of the variation of the catalyser amount on the colour yield are reported in Fig. 16. The values represented in this figure are

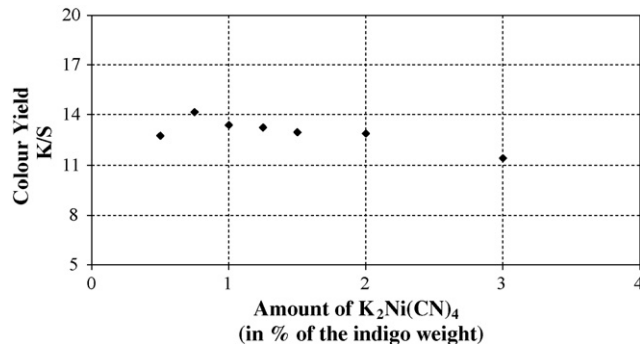


Fig. 16. Effect of catalyser amount on the colour yield.

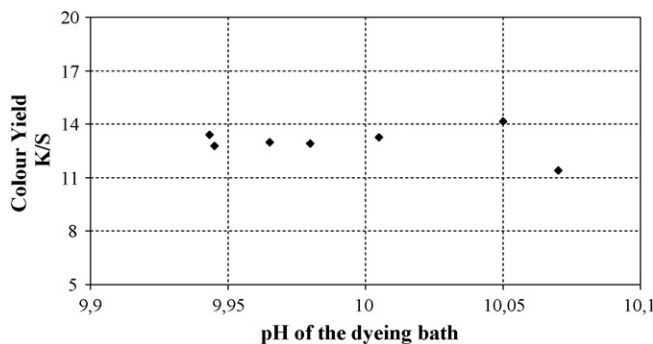


Fig. 17. Evolution of colour yield vs. the pH of the dyeing bath (variation of catalyser amount).

the mean of two experiments. This figure shows that the K/S values present a maximum colour yield for an amount of 0.75% of catalyser. With higher amounts the colour yield decreases until 11.37 for an amount of 3% of catalyser. The effect of the pH of the dyeing bath on the colour yield was reported in Fig. 17. It appears in this figure that the colour yield varies slightly with the pH of the dyeing bath. In spite of this, it can be observed for a pH of 10.05 a maximum of K/S equal to 14.18.

4. Conclusion

In this work, the experimental conditions of a new process of indigo reduction were adjusted. This process used sodium borohydride as reducing agent in the presence of potassium nickel cyanide as catalyser. The effect of the two main operating conditions the temperature and the catalyser amount on the oxydo-reduction potential, the pH of the dyeing bath, the indigo reduction yield and the colour yield were studied. It was observed that the maximum yield of indigo reduction took place at 55 °C with an amount of 1% of catalyser.

The study of the dyeing process of cotton fabrics showed that the colour yield depended essentially on the temperature of the reduction reaction, the catalyser amount and the pH of the dyeing bath. The dyeing performance corresponding to a K/S value equal to 15.43 was obtained at a temperature of 40 °C and with an amount of 1% of catalyser.

The obtained results show that the borohydride dyeing process is feasible with easy operating conditions and it yields satisfactory dyeing quality.

Acknowledgments

The authors are particularly grateful to Mr. Chikhrouhou Abdelaziz G.P.D. of SITEX (Société Industrielle des Textiles) and all the technical and administrative staff of this company for their assistance and valuable contribution.

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