Study of The Influence of Sodium Hydroxide Addition in The Borohydride Dyeing Process

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In this paper, the reduction of indigo by sodium borohydride and the use of the reduced dye solution in the dyeing of cotton fabric were studied. The evaluation of the performance of the reduction reaction was carried out by the establishment of potentiometric titration procedure of the leuco-indigo concentration in the dyeing bath. The dyeing results were evaluated by measuring the colour yield (K/S) of the coloured samples at 660 nm. The influence of the amount of indigo and the addition of alkali on reduction performances and on the dyeing quality were discussed. In these studies, it appears that the maximum of the reduction yield and of the colour yield took place at 132.35 % of indigo. The addition of alkali slowed the rate of the reduction reaction of indigo by sodium borohydride. However, it enhanced the indigo reduction yield, the colour yield and notably sodium borohydride hydrolysis. The optimal amount of alkali was obtained for 5 % of sodium hydroxide.

Key Words: Indigo reduction reaction, Sodium borohydride, Cotton dyeing process, Alkali effect.

INTRODUCTION

Indigo (C.I. Vat Blue 1) is one of the oldest vat dyes used to colour cellulosic textiles and specially cotton yarn for blue jeans. This dye is insoluble in water. In order to apply it to a textile, it is necessary to reduce the indigo dye to its water-soluble leuco form using a suitable reducing agent in the presence of an alkali such as sodium hydroxide (Fig. 1). When the preparation of leuco-indigo is achieved, the textile is immersed in the reduced dye solution. Then, the textile is exposed to air in order to oxidize the dye back to its insoluble form. These two steps (immersion/exposure) would be repeated many times to obtain the desired shade of blue.

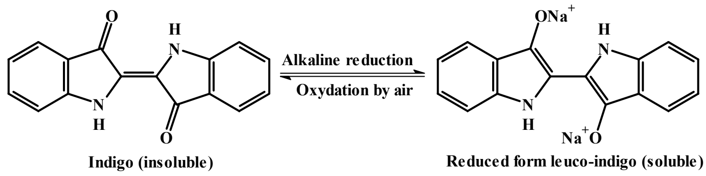

Fig. 1. The dyeing process by indigo

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Typically, vat dyes and especially indigo are reduced by sodium dithionite. Others reducing agents are also used for this purpose, such as salts of organic sulfinic acids, thiourea dioxide and hydroxyketones[1-4]. Generally, all these processes require the addition of large quantities of alkali in the dyeing bath for a number of reasons: (a) To activate the reduction procedure of the reducing agent. (b) To avoid precipitation of the reduced dye by transformation to its acid form. (c) To avoid the loss of the reducing agent through decomposition reactions by water or oxygen.

In case of some vat dyes, it is even necessary to use a strong alkaline solutions (pH = 12-14) for vatting and dyeing. This great amount of alkali consumed increases the cost of production, the charges of treatment of the dyeing effluent and limits the use of most vat dyes to cellulosic fibres.

Sodium borohydride is a well known reducing agent. This reagent is extensively employed in chemistry synthesis[5-7] and in some hydrogen generation processes[8-11]. Its use in aqueous solution presents several advantages[10]: (a) Facility of storage in alkaline solutions. (b) Safety in using it. (c) The by-products formed in the decomposition of sodium borohydride are sodium borate and its hydrates. These compounds are non toxics and have minimum effects on environment.

In the presence of a catalyzer, sodium borohydride can reduce indigo easily and in a complete absence of alkali. This process can offer a good yield of reduction with a good quality of dyeing. The ability of sodium borohydride to reduce indigo and vat dyes in absence of alkali can be explained by the reduction mechanism of this reducing agent which is different from the other reducing agents mechanism like sodium dithionite. As all hydrides, the reduction of indigo by sodium borohydride is carried out using H^- ions as a reducing agent. Whereas, the reduction of indigo by sodium dithionite is carried out using electrons as reducing agents. These electrons are obtained only by dissociation of sodium dithionite in alkaline medium.

In this work, we study first the effect of the amount of indigo on reduction yield and cotton dyeing quality. Then, since the amount of alkali usually presents an important factor in the indigo dyeing processes, we investigate the influence of the addition of sodium hydroxide in the borohydride process and determine its optimal amount which gives the best results of indigo reduction performances and dyeing quality.

EXPERIMENTAL

Indigo (BEZEMA AG, Switzerland), sodium borohydride (Acros Organics, Germany) and sodium hydroxide (Kaustik JSC, Russia) were used for the reduction without further purification. 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/m^2.

Catalyst preparation: Potassium nickel cyanide $K_2[Ni(CN)_4]$ was synthesized using potassium cyanide and nickel sulphate as described in the literature[12]. 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 recrystallized in methanol.

Reduction of indigo by sodium borohydride: A solution containing indigo and 1 % (% in the weight of sodium borohydride) of potassium nickel cyanide was prepared by adding them to 130 mL of distilled water. This solution was stirred 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, 20 mL of distilled water (containing sodium hydroxide) was introduced. This indigo reduction was carried out at 55 °C and was performed under nitrogen atmosphere to prevent oxidation.

The redox potential and pH in reduction medium 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). It is supposed that the end of reduction was reached when the redox potential in the solution rose rapidly and then remained quasi stable.

Evaluation of the lost water by the hydrolysis reaction: In the reduction of indigo by sodium borohydride, the volume of water in the dyeing bath decreased. So, when the reduction of indigo was achieved, this loss was compensated by addition of measured distilled water at the same temperature of the reduction to the initial volume 170 mL (this weight of the amount of added water was measured).

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 as follows: a 50 mL of a standard solution was prepared containing 1.2 g/L of Setamol WS®, a commercial dispersant (naphthalene sulfonate condensed with formaldehyde) 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 the leuco-indigo obtained was added. The mixture was titrated with a solution of 0.05 mol/L of potassium hexacyanoferrate. The end of the titration was detected by a rapid increase of the redox potential solution. The determination of the equivalent point can indicate the amount of potassium hexacyanoferrate required to oxidise all the leuco-indigo molecules in the solution. This was used to calculate the leuco-indigo concentration and then the reduction yield.

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 indigo reduction. This dyeing 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 and were followed by a cold rinsing and finally, they were dried at the room temperature.

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). To calculate the colour yield (K/S) value, the reflectance of the dyed sample was measured at 660 nm and transferred to (K/S) according to the Kubleka-Munk function[13,14].

RESULTS AND DISCUSSION

In all experiments, the amount of sodium borohydride, the amount of catalyzer and the temperature of the reaction medium were kept constant. In these experimental conditions, the effect of two factors *i.e.*, the indigo amount and the addition of sodium hydroxide was investigated on different parameters controlling the dyeing bath performances (the oxo-reduction potential and pH of the dyeing bath, the indigo reduction yield) and also on the dyeing quality of the coloured fabrics (the colour yield K/S). It is important to note that the effect of the indigo amount was studied in absence of alkali.

Effect of the indigo amount

Effect of the indigo amount on the evolution of the oxo-reduction potential and pH of the dyeing bath: The amount of indigo was varied in the reaction medium from 50 to 300 % (% in the weight of sodium borohydride). The evolution of the redox potential of the medium was studied. The experimental results are shown in Fig. 2. In this figure, it can be seen that all the curves representing the evolution of the redox potential with time exhibit the same shape whatever is the amount of indigo in the reduction medium. These curves are constituted of 3 parts: the first part represents a slow increasing of redox potential when the amount of indigo increases. The second part is a rapid jump of redox potential. Then, in the third part, the redox potential remains quasi stable. The evolution of the medium redox potential represents the evolution of the reduction reaction and of the leuco-indigo formation. It is supposed that the quasi stability of the redox potential indicates the end of the reaction of reduction and the time of the beginning of this quasi stability step is taken as the reduction reaction duration. The variation of this parameter *versus* the amount of indigo is reported in Fig. 3. In this figure, it can be observed that when the amount of indigo increases from 50 to 300 % (% in the weight of $NaBH_4$), the reaction duration decreases progressively. This can be explained by the decrease of the rate of the hydrolysis reaction compared with the rate of the indigo reduction reaction:

The hydrolysis reaction has the following rate expression:

$$V_{hyd} = k_{hyd}\left[NaBH_4\right]$$

where, k_{hyd} is the constant rate of the hydrolysis reaction. Whereas, the indigo reduction reaction has the following rate expression:

$$V_{red} = k_{red}\left[Indigo\right]\cdot\left[NaBH_4\right]$$

where, k_{red} is the constant rate of the indigo reduction reaction. So, when the concentration of indigo increases in the medium, the rate of the indigo reduction increases too, but the rate of the hydrolysis reaction remains stable because the amount of $NaBH_4$ is kept constant in this study. Finally, for great quantities of indigo, the rate of the reduction becomes superior to the rate of hydrolysis reaction:

$$V_{red} > V_{hyd}$$

The effect of the amount of indigo 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 the different amounts of indigo. In Fig. 4, it is observed that all the curves are similar whatever the amount of indigo is. For each amount of indigo, it can be seen that the pH remains quite constant or varies slightly during the reduction reaction. Besides, it appears that increasing amount of indigo in the dyeing bath decreases pH of the reduction medium. The evolution of the mean value of this pH *versus* the indigo amount is shown in Fig. 5. This figure confirms the previous observation *i.e.*, when the amount of indigo increases, pH decreases. This decrease of pH of the reduction medium can be attributed also to the decrease of the rate of the hydrolysis reaction compared with the rate of the indigo reduction reaction. Brown *et al.*[15] reported that the hydrolysis reaction of sodium borohydride produces the strongly basic sodium metaborate ion:

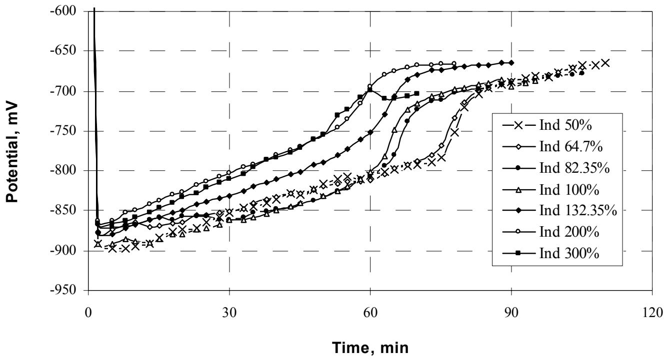

Fig. 2. Effect of the indigo amount on the evolution of redox potential of the dyeing bath

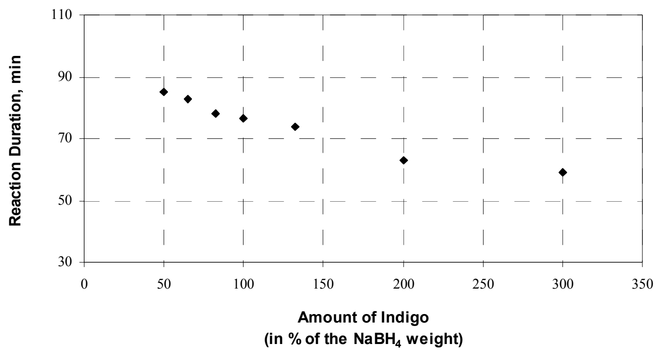

Fig. 3. Effect of the indigo amount on the reaction duration

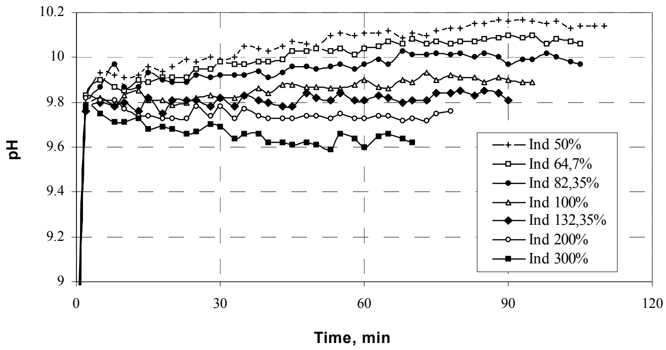

Fig. 4. Effect of the indigo amount on the evolution of the reaction medium pH

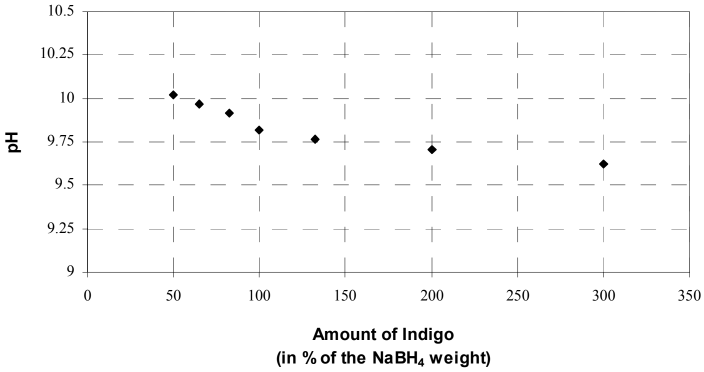

Fig. 5. Evolution of the mean value of the reduction medium pH *vs.* the indigo amount

$$NaBH_4 + 2\,H_2O \longrightarrow NaBO_2 + 4\,H_2\uparrow \qquad \Delta H^\circ = -188{,}6\ KJ.mol^{-1}$$

So, when the indigo amount increases in the medium, the rate of hydrolysis reaction decreases. Therefore, pH of the reduction medium decreases due to the decrease of the metaborate concentration.

Effect of the amount of indigo on the reduction yield: The main reaction of the indigo reduction is accompanied by a competitive reaction which is the hydrolysis of sodium borohydride. These two reactions were estimated, respectively by calculating the reduction yield of the indigo and evaluating the loss of water from the dyeing bath (Fig. 6).

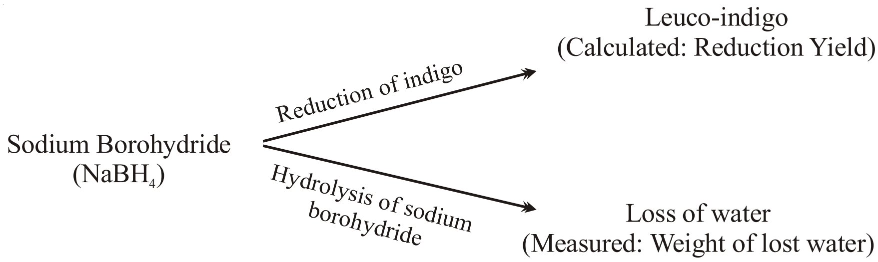

Fig. 6. The main competitive reactions in the reduction medium

Evaluation of the indigo reduction yield: The concentration of the leuco-indigo in the dyeing bath was evaluated by potentiometric titration with potassium hexacyanoferrate at the end of the reduction reaction. Fig. 7 shows a typical potentiometric titration curve. The determination of the equivalent point allows to calculate the concentration of the leuco-indigo in the dyeing bath and the yield of the indigo reduction. The results are reported in Fig. 8.

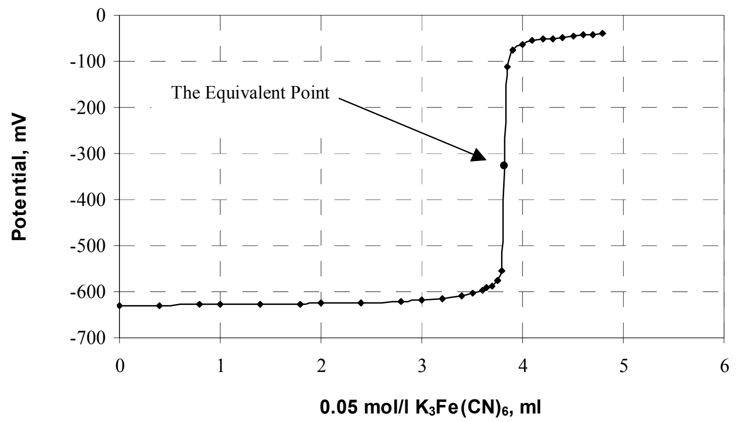

Fig. 7. Potential curve of the dyebath titrated with potassium hexacyanoferrate

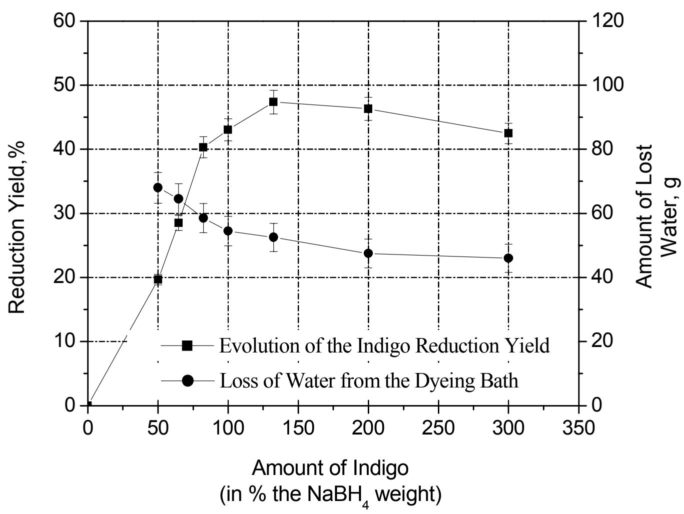

Fig. 8. Effects of the indigo amount on reduction yield and on the hydrolysis of sodium borohydride

Estimation of the hydrolysis reaction: Determination of the weight of the lost water from the dyeing bath during reduction reaction allows to estimate the extent of the hydrolysis reaction. The results are represented in Fig. 8.

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 lost water and the indigo reduction yield were also given. Fig. 8 reveals that the curve representing the evolution of the reduction yield is constituted of two parts. The first one is an increasing curve going from 0 to 132.35 % of indigo. In this part, it can be observed a rapid increase of the reduction yield which attains 47.37 % for an amount of indigo equal to 132.35 % (percentage in the weight of sodium borohydride). In this range, it can be seen that the increase of the reduction yield is accompanied by an important loss of water. This result reveals that in this range, when the indigo amount rises in the medium, the indigo reduction reaction becomes more favourable than the hydrolysis reaction.

The second part of the curve representing the evolution of the reduction yield is situated after 132.35 % of indigo. In this part, the reduction yield decreases slowly when the amount of indigo exceeds 132.35 %. This part reveals also that the loss of water continues to decrease but not as rapid as previously. The decrease of the reduction yield in this range can be attributed to the amount of indigo which becomes in large excess to the amount of sodium borohydride required to produce an indigo reduction yield equal to 47.37 %. It is important to note that the indigo reduction yield was calculated from the ratio of the concentration of leuco-indigo (obtained with the potentiometric titration procedure) to the initial concentration of the indigo (introduced in the medium).

Effect of the amount of indigo on the dyeing quality: The obtained medium after the indigo reduction reaction was used as dyeing bath for cotton fabrics. Then, we evaluated the dyeing quality of the coloured samples by measuring the colour yield (K/S) at 660 nm. The experimental results of the influence of the amount of indigo on the colour yield are reported in Fig. 10. The values represented in this figure are the mean of two experiments. In this figure, it can be observed that the curve representing the evolution of the colour yield is constituted essentially of two parts. In first part, a rapid increase of the colour yield (K/S) is noted for the indigo amounts smaller than 132.35 %. This can be explained by the increase of the reduction yield (Fig. 8) and the concentration of leuco-indigo (Fig. 9) in this range. After 132.35 % of indigo, the colour yield (K/S) remained relatively constant in spite of the leuco-indigo increase in the medium (Fig. 9). It seems that cotton fibres were reached the absorption saturation of the leuco-indigo.

Effect of the addition of alkali

Effect of the amount of sodium hydroxide added on the evolution of the oxo-reduction potential: Sodium hydroxide used in this study. It was employed as auxiliary in this process because the reduction of indigo by sodium borohydride could occur in the absence of this reagent. The amount of sodium hydroxide was varied, in the reaction medium, from 0 to 20 % (% in the weight of sodium borohydride). The effect of this variation on the evolution of redox potential of the medium was investigated. The experimental results are shown in Fig. 11. In this figure, it can be

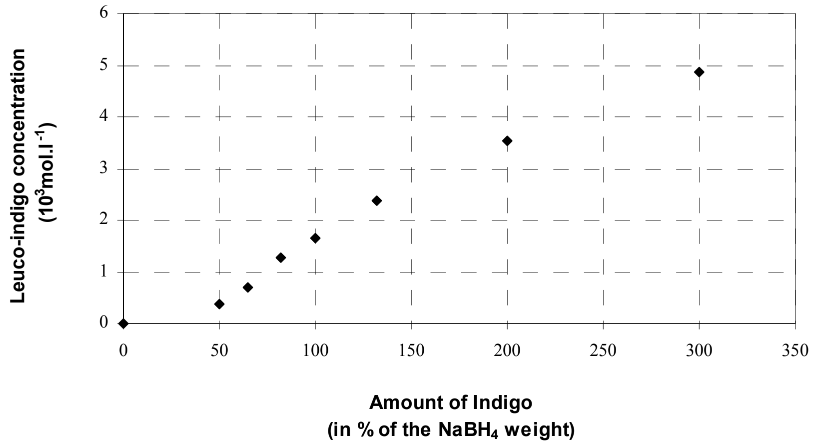

Fig. 9. Evolution of the leuco-indigo concentration *versus* the amount of indigo

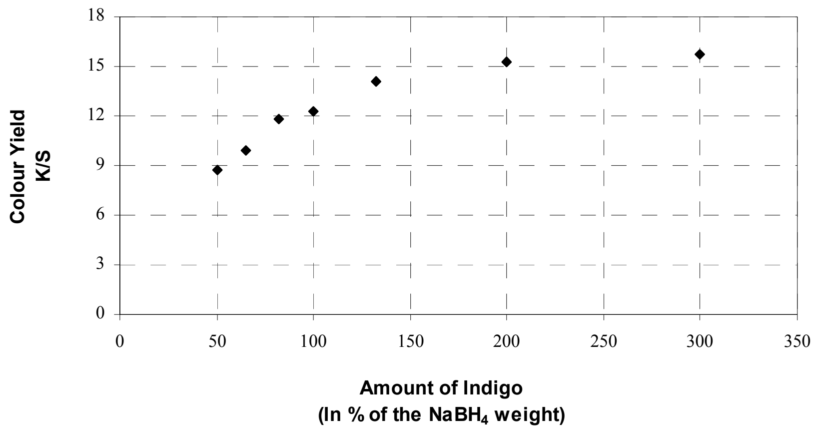

Fig. 10. Effect of the indigo amount on the colour yield

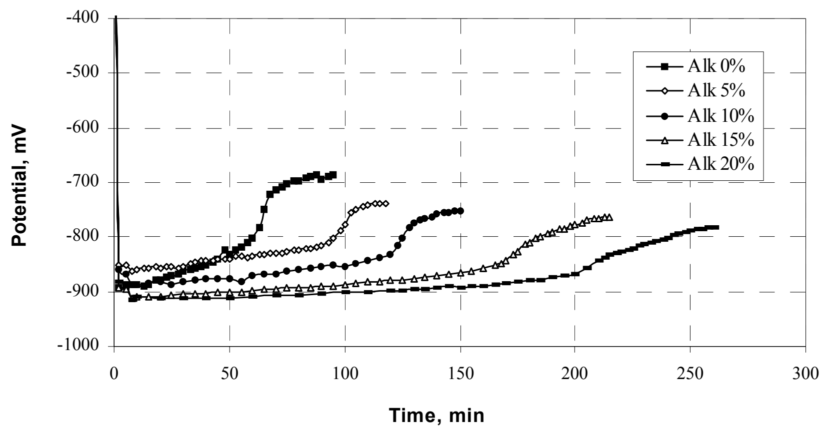

Fig. 11. Effect of the addition of alkali on the evolution of redox potential of the dyeing bath

observed that all the curves representing the evolution of redox potential with the amount of alkali have the same shape whatever is the amount of sodium hydroxide. All these curves are constituted with three parts. The first part represents a slow increasing of redox potential when the amount of sodium hydroxide 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 redox potential represents the evolution of the reduction reaction and of the leuco-indigo formation. It is supposed that the quasi stability of the redox potential indicates the end of the reduction reaction and the time of the beginning of this quasi stability step is taken as the reduction reaction duration. It can also be seen in Fig. 10 that when the amount of sodium hydroxide increases, the redox potential of reaction medium becomes more and more negative. This is in accordance with previous results[16].

Fig. 12 shows the effect of the variation of the sodium hydroxide amount on the reaction duration. Each experimental point is the mean of two experimental values. In this figure, it can be observed that when the amount of sodium hydroxide increases, the reaction duration increases linearly. So, it appears that the alkali addition decreases the rate of the indigo reduction by sodium borohydride.

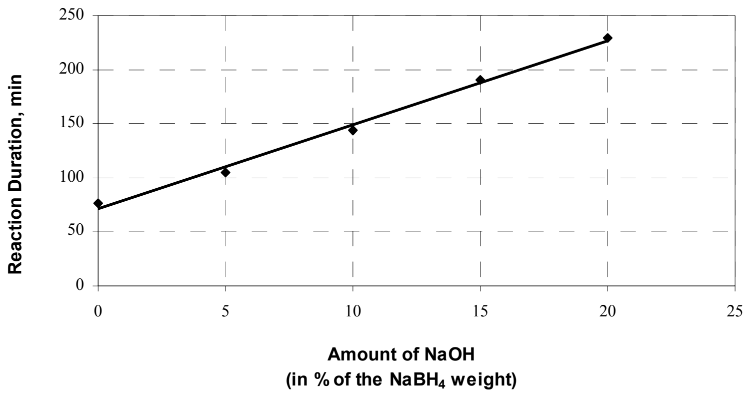

Fig. 12. Effect of the alkali addition on the reaction duration

Effect of the amount of sodium hydroxide added on reduction yield: The effects of the addition of sodium hydroxide on the indigo reduction yield and on the loss of water were also studied. 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. 13. 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 were also reported in this figure.

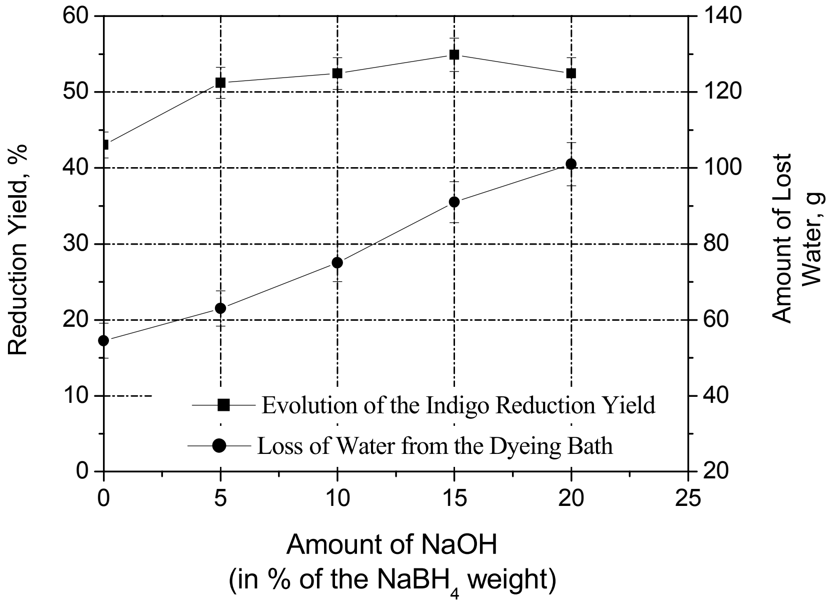

Fig. 13. Effects of the addition of alkali on the indigo reduction yield and on the hydrolysis of sodium borohydride

Fig. 13 shows that sodium hydroxide affects considerably the two main competitive reactions *i.e.*, the indigo reduction and the hydrolysis of sodium borohydride. First, it is important to note that if the sodium hydroxide is added before introducing sodium borohydride, this reducing agent fails to reduce indigo. It seems that probably the alkali blocks the action of sodium borohydride in this case.

In Fig. 13, it can also be seen that the addition of alkali in the indigo reduction by sodium borohydride enhances generally the reduction yield. The curve represents the evolution of the reduction yield in two parts. The first one is an increasing part going from 0 to 5 % of sodium hydroxide (% in the weight of sodium borohydride). In this range, the increase of the reduction yield is accompanied by an increase in the hydrolysis reaction. It appears here that, the addition of small quantities of sodium hydroxide enhances the two competitive reactions.

The second part begins after 5 % of sodium hydroxide and here it can be noticed a relative stability of the reduction yield. However, this quasi stability of reduction yield is accompanied by a remarkable increase of the hydrolysis reaction. Here, it can be observed that when the amount of sodium hydroxide exceeds 5 %, the consumption of water becomes very important. This great loss of water from the bath can be explained by the several forms of borates produced by the indigo reduction and the hydrolysis reaction[10,17,18]. These forms of borates are able to be hydrolyzed again and thus consuming an additional quantity of water from the medium.

Effect of the amount of the added sodium hydroxide on the dyeing quality: 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 representing the effect of the variation of the sodium hydroxide amount on the colour yield are reported in Fig. 14. The values represented in this figure are the mean of two experiments.

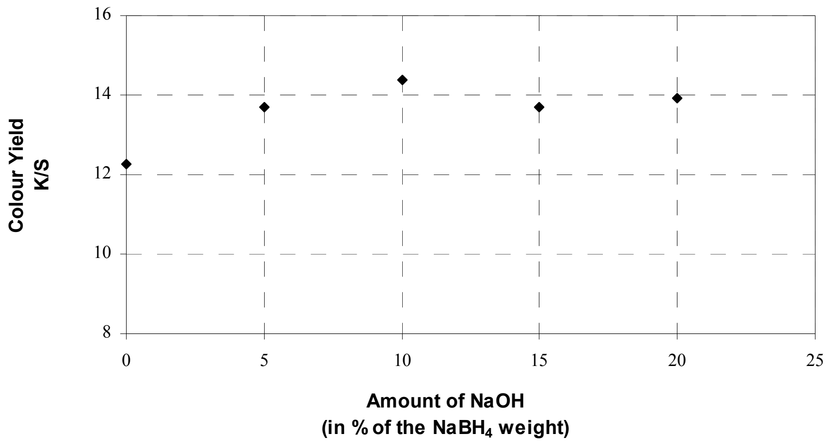

Fig. 14. Effect of the addition of alkali on the colour yield

Fig. 14 reveals that the addition of alkali in the dyeing bath generally causes an increase of the colour yield. However, after 5 % of sodium hydroxide, the colour yield remains relatively constant. This can probably be explained by the relative stability of the reduction yield obtained in this range of sodium hydroxide (Fig. 13).

Conclusion

This work describes an unconventional process of indigo reduction. This process consists in reducing indigo by sodium borohydride in the presence of a catalyzer. In this work, the influence of the indigo amount and the addition of sodium hydroxide were investigated.

In the absence of alkali in the medium, when the amount of indigo increased until 132.35 % (percentage in the weight of sodium borohydride), the reduction yield and the colour yield (K/S) rose rapidly. After 132.35 %, these parameters remained relatively constant. However, the sodium borohydride hydrolysis decreased whatever the amount of indigo introduced was. The optimal results took place at an amount of indigo equal to 132.35 % (% in the sodium borohydride weight).

The study of the effect of the alkali on the reduction performances and on the dyeing quality of this borohydride process revealed that the addition of sodium hydroxide until an amount of 5 % (percentage in the weight of sodium borohydride) enhanced the reduction yield, as well as the colour yield (K/S). For the sodium hydroxide amount up to 5 %, the reduction yield and the colour yield (K/S) remained quasi stable. Nevertheless, it appears also that the addition of the alkali in the medium slowed the indigo reduction rate by sodium borohydride and provoked the start of some hydrolysis reaction of the formed borates whatever the amount of alkali in the reduction medium was. The optimal results were obtained for 5 % of sodium hydroxide.

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REFERENCES

1. M. Weiss, *Am. Dyestuff Reporter*, **67**, 35 (1978).
2. E. Marte, *Textil Praxis Internat.*, **44**, 737 (1989).
3. U. Baumgarte, *Melliand Textilber.*, **68**, 189, 176 (1987).
4. H. Schluter, *Textilveredlung*, **25**, 218 (1990).
5. H.C. Brown, Boranes in Organics Chemistry, Cornell University Press, Ithaca (1972).
6. H.C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979).
7. M. Periasamy and M. Thirumalaikumar, *J. Organomet. Chem.*, **609**, 137 (2000).
8. C.A. Kaufman and B. Sen, *J. Chem. Soc., Dalton Trans.*, 307 (1985).
9. S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo and M. Binder, *Int. J. Hydrogen Energy*, **25**, 969 (2000).
10. D. Hua, Y. Hanxi, A. Xinping and C. Chuansin, *Int. J. Hydrogen Energy*, **28**, 1095 (2003).
11. J.H. Kim, H. Lee, S.C. Han, H.S. Kim, M.S. Song and J.Y. Lee, *Int. J. Hydrogen Energy*, **29**, 263 (2004).
12. W.C. Fermeliusn, Inorganic Synthesis, Rober E. Krieger Publishing Company, New York, Vol. 2, pp. 227-228 (1978).
13. J.N. Etters, *Am. Dyestuff Reporter*, **81**, 17 (1992).
14. J.N. Etters, *Am. Dyestuff Reporter*, **83**, 26 (1994).
15. H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra and E.K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).
16. G.P. Nair and R.C. Shah, *Textile Res. J.*, **40**, 303 (1970).
17. R.E. Davis, E. Bromels and C.L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962).
18. J.-H. Wee, K.-Y. Lee and S.H. Kim, *Fuel Proc. Tech.*, **87**, 811 (2006).

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